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Insertion, Reduction, and Carbon–Carbon Coupling Induced by Monomeric Aluminum Hydride Compounds Bearing Substituted Pyrrolyl Ligands

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Abstract: A monomeric aluminum hydride complex bearing substituted pyrrolyl ligands, AlH[$C_4H_3N(CH_2NMe_2)$-2]$_2$ (**1**), was synthesized and structurally characterized. To further confirm the presence of Al–H bonds, the compound AlD[$C_4H_3N(CH_2NMe_2)$-2]$_2$ ([D]**1**) was synthesized by reacting $LiAlD_4$ with [$C_4H_4N(CH_2NMe_2)$-2]. Compound **1** and [D]**1** react with phenyl isothiocyanate yielding Al[$C_4H_3N(CH_2NMe_2)$-2]$_2$[η^3-SCHNPh] (**2**) and Al[$C_4H_3N(CH_2NMe_2)$-2]$_2$[η^3-SCDNPh] ([D]**2**) by insertion. The reactions of **1** with 9-fluorenone and benzophenone generated the unusual aluminum alkoxide complexes **3** and **4**, respectively, through intramolecular proton abstraction and C–C coupling. A mechanistic study shows that 9-fluorenone coordinates to [D]**1** and releases one equivalent of HD followed by C–C coupling and hydride transfer to yield the final product. Reduction of benzil with **1** affords aluminum enediolate complex **5** in moderate yield. Mechanistic studies also showed that the benzil was inserted into the aluminum hydride bond of [D]**1** through hydroalumination followed by proton transfer to generate the final product [D]**5**. All new complexes have been characterized by ^1H and ^{13}C NMR spectroscopy and X-ray crystallography.

Keywords: aluminum hydride · C–C coupling · insertion · pyrrole

Introduction

Highly reactive metal hydrides play an important role in catalytic reactions.[1] The kinetically reactive metal hydrides undergo a wide variety of reactions with organic carbonyl fragments, such as 1) addition or reduction,[2] 2) displacement or substitution,[3] and 3) proton abstraction.[4] Hydride addition may simply be treated as a nucleophilic attack of H^- where the hydride attacks the electron-deficient unsaturated carbonyl to generate a metal alkoxide fragment. In addition, the hydride functions may act as strong bases and abstract acidic protons from the substrates. Among these metal hydrides, aluminum hydrides[5] are well-known and widely used due to their high reactivity and relatively low cost. Most of the structurally characterized aluminum hydride compounds are dimers[6] or oligomers[7] and only a few structures of monomeric compounds are known.[8] The use of bulky or multidentate ligands as ancillary ligands is often a good strategy for obtaining monomeric aluminum hydride compounds.[9] In addition, the reactions of aluminum hydride complexes with ketones yield aluminum alkoxide complexes through hydride insertion.[10] Here we report the syntheses of new monomeric aluminum hydride complexes by a simple method and their reactions with phenyl isothiocyanate, 9-fluorenone, benzophenone, and benzil. The reactions of aluminum hydride with 9-fluorenone and benzophenone result in an intramolecular elimination of dihydrogen and a C–C coupling of the 9-fluorenone and the pyrrolyl rings. The reaction types involved here are combinations of addition and proton abstractions.

Results and Discussion

The reaction of $LiAlH_4$ with [$C_4H_4N(CH_2NMe_2)$-2][11] in diethyl ether at 0 °C generated AlH[$C_4H_3N(CH_2NMe_2)$-2]$_2$ (**1**) in 80 % yield (Scheme 1). Compound **1** was the only product isolated, even when the ratio of $LiAlH_4$/[$C_4H_4N(CH_2NMe_2)$-2] was varied from 1.0 to 2.0. The methylene protons of **1** gave rise to a singlet at $\delta = 3.87$ ppm in the room tempera-

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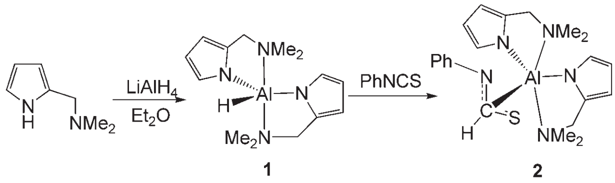


Scheme 1.

ture ^1H NMR spectrum. The Al–H hydride resonance was not observed, even at −60 °C (in $CDCl_3$ with a 200 MHz NMR spectrometer). However, the solid state IR spectrum of **1** in KBr supports the existence of Al–H bonds, as evidenced by the absorption at 1780 cm^{-1}, which is consistent with the reports in the literature.[12] To further confirm the existence of Al–H bonds, compound $AlD[C_4H_3N(CH_2NMe_2)\text{-}2]_2$ ([D]**1**) was synthesized by reacting $LiAlD_4$ and $[C_4H_4N(CH_2NMe_2)\text{-}2]$. Compound [D]**1** produced the same ^1H NMR spectrum as that of **1**. Moreover, the solid-state IR spectrum of [D]**1** does not exhibit the Al–H stretching frequency at $\tilde{\nu} = 1780\ cm^{-1}$. Calculations predict that the Al–D stretching frequency of [D]**1** should appear at $\tilde{\nu} = 1259\ cm^{-1}$.[13] However, this region of the IR spectrum was obstructed by the CH twisting and wagging frequencies.

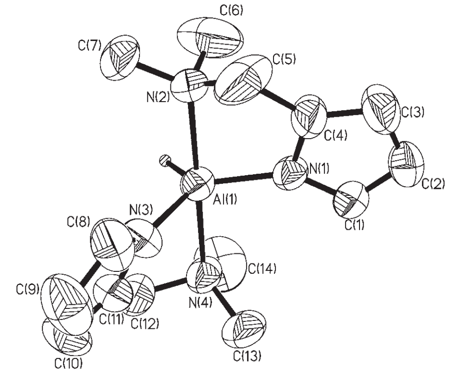


Figure 1. Molecular structure of **1**, the thermal ellipsoids were drawn at 50 % probability.

Crystals suitable for X-ray structural analysis were obtained from a saturated toluene solution of compound **1** (Figure 1). Summary of crystallographic data and selected bond lengths and angles for compounds **1**, **3**, **4**, and **5** are listed in Tables 1 and 2. Compound **1** can be best described as having a trigonal bipyramidal configuration with the two nitrogen atoms of the dimethylamino groups occupying axial positions with an angle for N(2)-Al-N(4) of 178.0(2)°. Compound **1** is not stable in $CDCl_3$; decomposition in $CDCl_3$ at 70 °C occurs within three days, as monitored by NMR spectroscopy. $AlCl[C_4H_3N(CH_2NMe_2)\text{-}2]_2$ and $Al[C_4H_3N(CH_2NMe_2)\text{-}2]_3$ were observed as products by ^1H NMR spectroscopy.[14]

Insertion reactions of isocyanates or isothiocyanates into M–X bonds (X = alkyl, halide, alkoxide, and hydride) have been reported in the literature.[15] However, only a few examples related to the insertion of isocyanate into Al–X bonds were reported.[16] The reaction of **1** with one equivalent of phenyl isothiocyanate in methylene chloride at room temperature results in the insertion of isothiocyanate into the Al–H bond forming a η^3-aluminum isothiocyanate compound $Al[C_4H_3N(CH_2NMe_2)\text{-}2]_2[\eta^3\text{-}SCHNPh]$ (**2**)[17] in 86 %

Table 1. Summary of crystallographic data for compounds **1**, **3**, **4**, and **5**.

	1	**3**$\cdot CH_2Cl_2$	**4**	**5**
formula	$C_{14}H_{23}AlN_4$	$C_{41}H_{39}AlCl_2N_4O_2$	$C_{40}H_{41}AlN_4O_2$	$C_{28}H_{33}AlN_4O_2$
fw	274.34	717.64	636.75	484.56
T [K]	293(2)	150(2)	150(2)	150(2)
crystal system	tetragonal	monoclinic	monoclinic	monoclinic
space group	$P4_32_12$	$P2_1/n$	$C2/c$	$P2_1/c$
a [Å]	9.2317(8)	17.9148(8)	33.8691(9)	19.8716(14)
b [Å]	9.2317(8)	9.8207(4)	11.1037(3)	10.5652(7)
c [Å]	36.837(5)	20.7697(9)	19.7754(5)	12.5833(9)
β [°]	90	92.855(3)	110.7280(10)	97.979(3)
volume [$Å^3$]/Z	3139.4(5)/8	3649.6(3)/4	6955.6(3)/8	2616.3(3)/4
density (calcd) [$Mg\,m^{-3}$]	1.161	1.306	1.216	1.230
absorption coefficient [mm^{-1}]	0.123	0.244	0.099	0.109
F(000)	1184	1504	2704	1032
crystal size [mm]	0.45 × 0.43 × 0.08	0.43 × 0.10 × 0.08	0.57 × 0.26 × 0.24	0.32 × 0.32 × 0.12
θ range [°]	2.21 to 27.54	1.47 to 29.04	1.29 to 29.07	1.03 to 29.11
collected reflections	19885	33341	65406	28120
independent reflections	3595 ($R_{int} = 0.0872$)	9704 ($R_{int} = 0.0899$)	9261 ($R_{int} = 0.0354$)	6980 ($R_{int} = 0.0296$)
max. and min. trans	0.9486 and 0.6211	0.9808 and 0.9024	0.9767 and 0.9459	0.9870 and 0.9659
data/parameters	3595/182	9704/455	9261/428	6980/324
goodness-of-fit on F^2	1.004	0.979	1.046	1.088
final R indices [$I > 2\sigma(I)$], R_1[a]	0.0612	0.0666	0.0390	0.0396
final R indices [$I > 2\sigma(I)$], wR_2[b]	0.1121	0.1485	0.0942	0.1122
R indices (all data), R_1[a]	0.1933	0.1689	0.0608	0.0620
R indices (all data), wR_2[b]	0.1252	0.1851	0.1041	0.1258
largest diff. peak and hole [$eÅ^{-3}$]	0.578 and −0.435	0.888 and −0.899	0.252 and −0.252	0.271 and −0.274

[a] $R_1 = \Sigma|F_0| - |F_c|/\Sigma|F_0|$. [b] $wR_2 = [\Sigma[\omega(F_o^2 - F_c^2)^2]/\Sigma[\omega(F_o^2)^2]]^{1/2}$.

Table 2. Selected bond lengths [Å] and bond angles [°] for compounds **1**, **3**, **4**, and **5**.

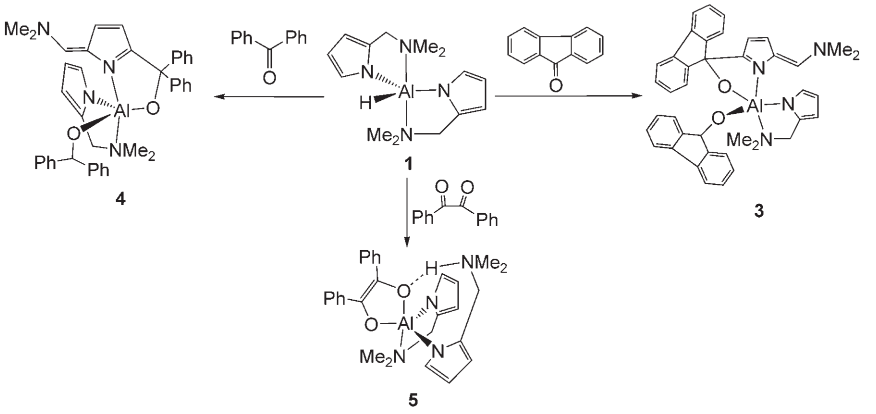
1			
Al(1)-N(3)	1.863(4)	Al(1)-N(1)	1.878(3)
Al(1)-N(2)	2.121(3)	Al(1)-N(4)	2.169(4)
N(3)-Al(1)-N(1)	119.1(2)	N(2)-Al(1)-N(4)	178.2(2)
N(3)-Al(1)-N(21)	99.2(2)	N(1)-Al(1)-N(2)	82.8(2)
N(3)-Al(1)-N(4)	81.4(2)	N(1)-Al(1)-N(4)	98.5(2)
3			
Al(1)-O(1)	1.743(2)	Al(1)-O(2)	1.772(2)
Al(1)-N(1)	1.892(2)	Al(1)-N(3)	2.005(2)
Al(1)-N(2)	2.143(2)	C(1)-C(2)	1.370(4)
C(1)-N(1)	1.374(4)	C(2)-C(3)	1.415(4)
C(3)-C(4)	1.368(4)	C(4)-N(1)	1.376(3)
C(4)-C(5)	1.499(4)	C(5)-N(2)	1.493(3)
C(10)-N(4)	1.318(3)	C(10)-C(11)	1.390(4)
C(11)-N(3)	1.401(3)	C(11)-C(12)	1.428(4)
C(12)-C(13)	1.369(4)	C(13)-C(14)	1.403(4)
C(14)-N(3)	1.328(3)		
O(1)-Al(1)-O(2)	123.3(1)	O(1)-Al(1)-N(1)	110.8(1)
O(2)-Al(1)-N(1)	125.2(1)	O(2)-Al(1)-N(3)	84.1(1)
N(1)-Al(1)-N(2)	80.3(1)	N(3)-Al(1)-N(2)	168.5(1)
4			
Al(1)-O(2)	1.750(1)	Al(1)-O(1)	1.764(1)
Al(1)-N(1)	1.892(1)	Al(1)-N(3)	1.998(1)
Al(1)-N(2)	2.126(1)	N(1)-C(7)	1.379(2)
N(1)-C(4)	1.380(2)	N(2)-C(3)	1.486(2)
N(3)-C(14)	1.331(2)	N(3)-C(11)	1.403(2)
N(4)-C(10)	1.316(2)	C(3)-C(4)	1.497(2)
C(4)-C(5)	1.369(2)	C(5)-C(6)	1.415(2)
C(6)-C(7)	1.376(2)	C(10)-C(11)	1.393(2)
C(11)-C(12)	1.424(2)	C(12)-C(13)	1.378(2)
C(13)-C(14)	1.419(2)	C(14)-C(15)	1.525(2)
O(2)-Al(1)-O(1)	125.0(1)	O(2)-Al(1)-N(1)	106.9(1)
O(1)-Al(1)-N(1)	127.1(1)	O(1)-Al(1)-N(3)	83.4(1)
N(1)-Al(1)-N(2)	81.3(1)	N(3)-Al(1)-N(2)	166.7(1)
5			
Al(1)-O(1)	1.780(1)	Al(1)-O(2)	1.852(1)
Al(1)-N(1)	1.892(1)	Al(1)-N(3)	1.903(1)
Al(1)-N(2)	2.174(1)	N(2)-C(5)	1.495(2)
N(4)-C(12)	1.516(2)	O(1)-C(15)	1.382(2)
O(2)-C(16)	1.379(2)	C(15)-C(16)	1.355(2)
O(1)-Al(1)-O(2)	87.6(1)	O(1)-Al(1)-N(1)	132.1(1)
O(1)-Al(1)-N(3)	114.9(1)	N(1)-Al(1)-N(3)	112.8(1)
O(2)-Al(1)-N(2)	167.3(1)	N(1)-Al(1)-N(2)	80.2(1)

yield. Compound **2** was characterized by ^{1}H and ^{13}C NMR spectroscopy. The proton and carbon resonances for the methine group of phenyl isothiocyanate appear at $\delta = 9.33$ and 181.5 ppm, respectively. The insertion was further proven to have occurred by the reaction of [D]**1** with phenyl isothiocyanate under the same conditions, yielding compound [D]**2**. The NMR spectral data of [D]**2** are almost the same as compound **2**. However, the resulting deuterated methine fragment of [D]**2** produces a triplet resonance at $\delta = 181.3$ ppm (J(C,D) = 28 Hz) in the ^{13}C{^{1}H} NMR spectra.[18]

Unlike the reaction of **1** with phenyl isothiocyanate, a novel aluminum aryloxide compound **3** was isolated while reacting **1** with one or two equivalents of 9-flurorenone (Scheme 2); however, the best yield (80%) for this reaction was found by using two equivalents of 9-fluornone. Compound **3** has been characterized by 1D and 2D NMR spectroscopies and X-ray structural analysis. The ^{13}C NMR spectrum of compound **3** is very complicated, and shows a total of 40 resonances for all the carbon atoms in the molecules. It is worth noting that one of the original 2-(dimethylaminomethyl)pyrrole fragments has converted to 2-(dimethylaminomethylene)-2H-pyrrole and coupled to the 9-carbon of 9-fluorenone.

Crystals of **3** suitable for X-ray structure determinations were obtained from a diethyl ether and methylene chloride mixture. The molecular structure of **3** (Figure 2) exhibits a distorted trigonal bipyramidal geometry in which the two nitrogen atoms of the dimethylamino group and the 2H-pyrrole fragment occupy axial positions with a N(3)-Al(1)-N(2) angle of 168.5(1)°. The σ-type aluminum pyrrole bond Al(1)-N(1) (1.892(2) Å) is shorter than the coordination bond of aluminum to the 2H-pyrrole (Al(1)-N(3) 2.005(2) Å). 9-fluorenone coupled with one pyrrole ligand through C–C coupling to form a new type of 9-(2-dimethylaminomethylene-2H-pyrrol-5-yl)-9H-fluoren-9-oato, forming a five-membered ring including the aluminum atoms.

Treatment of 9-fluorenone with **1** in $CDCl_3$ in an NMR tube lead to C–C coupling instead of direct carbonyl insertion into the Al−H bond. A plausible mechanism is shown in Scheme 3. 9-Fluorenone is first coordinated to [D]**1** forming an intermediate similar to a "transition metal ketyl"[19] and pushes the hydride fragment towards the methylene proton of the substituted pyrrolyl ligands. This leads to the elimination of HD followed by C–C coupling between the pyrrol-5-yl and 9-flouren-9-olate. The HD produced a triplet at $\delta = 4.67$ ppm in the ^{1}H NMR spectra with the diagnostic ^1J(H,D) coupling constant of 43 Hz.[20] A second equivalent



Scheme 2.

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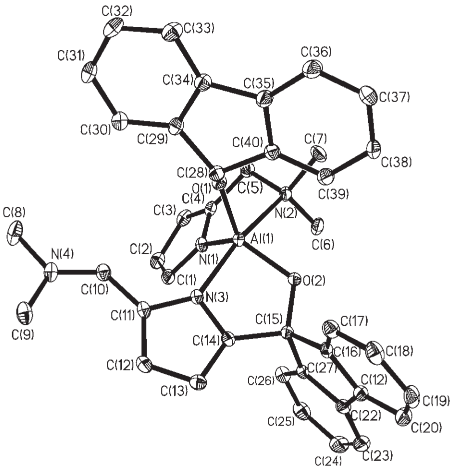
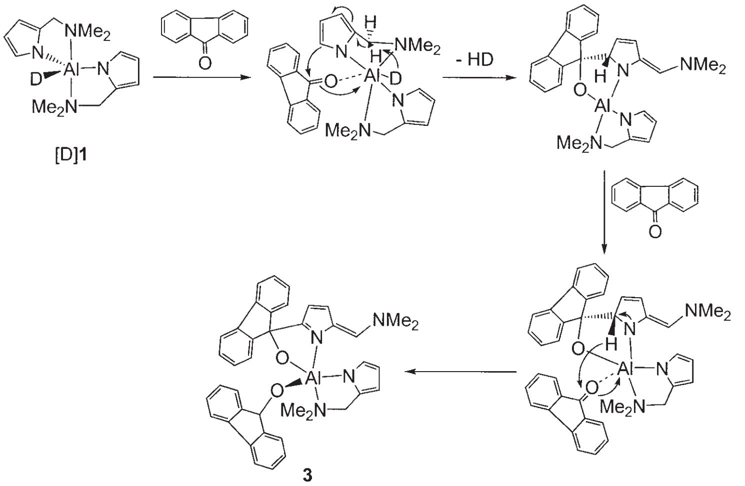


Figure 2. Molecular structure of **3**, the thermal ellipsoids were drawn at 30% probability.



3

Scheme 3.

of 9-fluorenone is coordinated to the aluminum center followed by a hydride transfer to yield the final product.

Similarly, the reaction of the aluminum hydride compound **1** with one equivalent of benzophenone in methylene chloride at room temperature affords the aluminum aryloxide compound **4** in 69% yield (Scheme 2). Compound **4** was characterized by 1D and 2D NMR spectroscopy and X-ray structural analyses. The ^{1}H NMR spectra of **4** exhibited complex resonances for the two pyrrolyl ligands, consistent with an asymmetrical coordination sphere about the aluminum center. One of the substituted pyrrolyl ligands remains in its original constitution with the methylene protons of CH_2NMe_2 appearing as two doublets at $\delta = 4.31$ and 3.43 ppm in the ^{1}H NMR spectrum. It is also worth noting that another substituted pyrrolyl ligand was coupled to benzophenone to yield a [1-(2-dimethylaminomethylene-2H-pyrrol-5-yl)-1,1-diphenylmethoxyl] fragment. The ^{1}H and ^{13}C NMR spectra of compound **4** show single resonances for the methine protons of the $=CHNMe_2$ ($\delta = 7.43$ and 152.5 ppm, respectively) and $CHOPh_2$ units ($\delta = 5.26$ and 76.0 ppm, respectively). While treating [D]**1** and benzophenone in $CDCl_3$ in an NMR tube, the formation of HD can be observed from the ^{1}H NMR spectra, which shows a triplet at $\delta = 4.61$ ppm with a ^1J(H,D) coupling constant of 42 Hz. The reaction mechanism is possibly the same as postulated for the reaction of **1** with 9-fluorenone (Scheme 3).

Crystals of compound **4** suitable for X-ray structural analyses were obtained from a toluene solution. The molecular structure of **4** (Figure 3) exhibits a distorted trigonal bipyramidal geometry of the Al atom with the nitrogen atoms of the dimethylamino group and the 2H-pyrrole fragment occupying axial positions with an angle of N(3)-Al(1)-N(2) 166.7(1)°. The σ-type aluminum pyrrole bond (Al(1)-N(1) 1.892(1) Å) is shorter than the dative bond between aluminum and 2H-pyrrole (Al(1)-N(3) 1.998(1) Å). The normal bidentate (2-dimethylaminomethyl)pyrrole chelates to the aluminum center forming a puckered five-membered ring. The benzophenone coupled with one pyrrole ligand through a C–C bond forms a new type of 1-(2-dimethylaminomethylene-2H-pyrrol-5-yl)-1,1-diphenylmethoxyl, which results in a five-membered ring involving the aluminum atom.

Treatment of **1** with two equivalents of benzil in a diethyl ether solution at 0 °C results in the enediolate aluminum compound **5**, $Al[C_4H_3N(CH_2NMe_2)\text{-}2][C_4H_3N(CH_2NHMe_2)\text{-}2][OCPhCPhO]$, in 71% yield (Scheme 2). Compound **5** was characterized by ^{1}H and ^{13}C NMR spectroscopy and X-ray structure determination. Compound **5** is thermally unstable

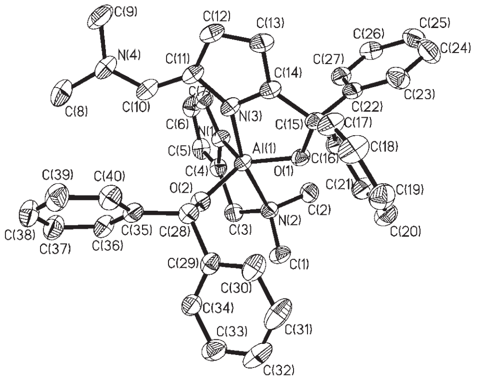


Figure 3. The molecular structure of compound **4**, the thermal elliopoids were drawn at 50% probability. All hydrogen atoms were omitted for clarity.

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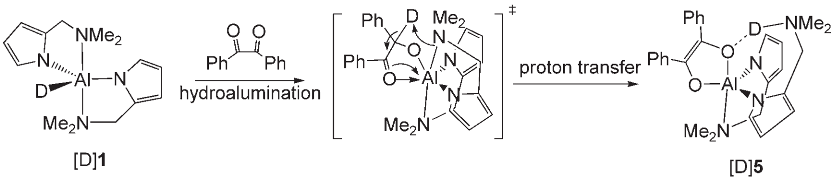
and can be stored for only two days in $CDCl_3$ at room temperature; this compound decomposes rapidly if the solution temperature rises above 40 °C. The ^{1}H NMR spectra of **5** revealed broad signals at 290 K; however, they sharpened when the temperature was dropped below 280 K, indicating the slow limit of compound fluxionality. A characteristic proton signal was observed at $\delta = 12.74$ ppm, indicating the presence of an acidic proton in the compound. Moreover, when [D]**1** was treated with benzil, an acidic deuterium was incorporated into compound [D]**5**. This can be verified by deuterium NMR spectra in which a broad deuterium signal was found at $\delta = 12.7$ ppm. In addition, the carbonyl groups of benzil were not observed in the ^{13}C NMR spectra and two new signals of an enediolate C=C double bond appeared at $\delta = 138.37$ and 135.14 ppm, showing that the two carbonyl groups of benzil were reduced by the aluminum hydride to yield an enediolate and acidic proton. A plausible reaction mechanism is shown in Scheme 4. The reductions of benzil to diphenylethylenediolate have been seen in the literature. The reducing agents used in these reactions contained low valent metals which became high valent metals when the benzil was converted to enediolate.[21] However, there are no reports of aluminum hydride being used as a reducing agent. We have successfully reduced benzil to enediolate by using aluminum hydride accompanied by the formation of an acidic proton.



Scheme 4.

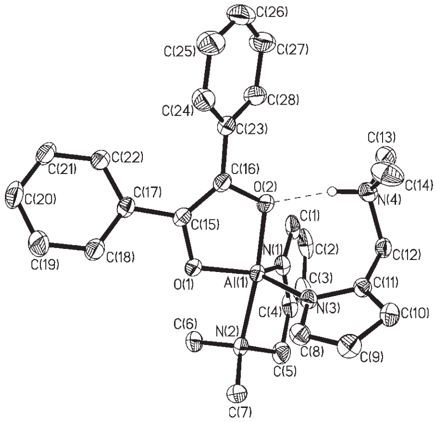


Figure 4. The molecular structure of compound **5**, the thermal ellipsoids were drawn at 50 % probability. All the hydrogen atoms except the dimethylammounium were omitted for clarity.

Crystals of compound **5** suitable for X-ray structural determination were obtained from a diethyl ether/methylene chloride solution. Compound **5** contains a five-coordinate aluminum center, with one enediolate, two pyrrolyl nitrogen atoms, and one dimethylamino nitrogen atom forming a distorted trigonal bipyramidal coordination geometry (Figure 4). One of the enediolate oxygen atoms and the dimethylamino nitrogen atoms occupy axial positions, with an angle of O(2)-Al(1)-N(2) at 167.3(1)°. As mentioned, there are several structurally characterized enediolate metal complexes;[22] however, we could not find any crystal structures of aluminum diphenylethyelenediolate complexes listed in the Cambridge Structure Database. The C=C bond length of the enediolate fragment (1.355(2) Å) is similar to that of the reported enediolate metal complexes. One of the dimethylamino fragments of the substituted pyrrolyl ligands was protonated, which prevents the nitrogen atom from being coordinated to the aluminum center. The acidic proton was weakly bonded to one of the two enediolate oxygen atoms through hydrogen bonding, with a bond length of 1.77 Å. The bite angles of the enediolate and the dimethylaminomethylpyrrolyl with the aluminum center were found to be 87.6(1) and 80.2(1)°.

Conclusion

New aluminum hydride compounds containing substituted pyrrolyl ligands have been synthesized by a simple method and can be produced in a large quantity. The pyrrolyl aluminum hydride reacting with small unsaturated organic molecules (PhNCS) results in an insertion of the isothiocyanate into the Al−H bonds. On the other hand, while 9-fluorenone and benzophenone were added to **1**, the bulky organic molecules have caused an unusual C–C coupling and result in the formation of new interesting organometallic compounds. Moreover, the monomeric aluminum hydride compound **1** reduces benzil under mild conditions to form an enediolate compound. Further studies of the reaction of **1** with a variety of unsaturated small and bulky organic molecules are currently in progress.

Experimental Section

General procedure: All reactions were performed under a dry nitrogen atmosphere by using standard Schlenk techniques or in a glove box. Toluene, diethyl ether, and THF were dried by refluxing over sodium benzophenone ketyl. CH_2Cl_2 was dried over P_2O_5. All solvents were distilled and stored in solvent reservoirs that contained 4 Å molecular sieves and were purged with nitrogen. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer. Chemical shifts for ^{1}H and ^{13}C spectra were recorded in ppm relative to the residual protons and ^{13}C of $CDCl_3$ ($\delta = 7.24$, 77.0 ppm) and C_6D_6 ($\delta = 7.15$, 128.0 ppm). Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyzer at the Instrument Center of the NCHU. $[C_4H_3NH(CH_2NMe_2)\text{-}2]$ was prepared according to a previously reported procedure.[11] $LiAlH_4$, 9-flurorenone, and phenyl isothiocyanate (Aldrich) were used as received.

$AlH[C_4H_3N(CH_2NMe_2)\text{-}2]_2$ (1): The contents of a 30 mL Schlenk flask charged with diethyl ether (10 mL) and $[C_4H_4N(CH_2NMe_2)\text{-}2]$ (6.0 g, 48.0 mmol) were added dropwise to a $LiAlH_4$ (1.84 g, 48.0 mmol) diethyl ether (10 mL) suspension with stirring at 0 °C. The mixture was allowed to warm to room temperature and was stirred for 2 h. The resulting suspension was filtered through Celite. The filtrate was dried under vacuum and the resulting solid was recrystallized from toluene to generate **1** (5.3 g) in 80 % yield. ^1H NMR (C_6D_6): $\delta = 2.00$ (s, 12 H; NMe_2), 3.42 (s, 4 H; CH_2N), 6.30, 6.56, 6.80 ppm (pyrrolyl protons); ^{13}C NMR (C_6D_6): $\delta = 44.6$ (q, J(C,H) = 138 Hz; NMe_2), 58.2 (t, J(C,H) = 139 Hz; CH$_2$N), 106.2 (d, J(C,H) = 171 Hz; pyrrole), 110.3 (d, J(C,H) = 169 Hz; pyrrole), 124.7 (d, J(C,H) = 177 Hz; pyrrole), 134.6 ppm (s; pyrrole); elemental analysis calcd for $C_{14}H_{23}N_4Al$: C 61.29, H 8.45, N 20.42; found: C 61.25, H 8.11, N 19.92.

$Al[SCHNPh][C_4H_3N(CH_2NMe_2)\text{-}2]_2$ (2): A solution of phenyl isothiocyanate (0.302 g, 2.19 mmol) in methylene chloride solution (20 mL) was added dropwise to a Schlenk flask containing **1** (0.60 g, 2.19 mmol) in methylene chloride (20 mL) precooled to 0 °C. The reaction was stirred at room temperature for 5 h and then the volatiles were removed under vacuum. A pale pink solid was crystallized from a heptane/methylene chloride solution to yield **2** (0.77 g) as orange/red crystals in 86 % yield. ^1H NMR ($CDCl_3$): $\delta = 2.50$ (s, 12 H; NMe_2), 3.82 (s, 4 H; CH_2N), 5.27 (s; CH_2Cl$_2$), 5.98 (m, 2 H; pyrrole CH), 6.10 (m, 2 H; pyrrole CH), 6.49 (m, 2 H; pyrrole CH), 6.77–6.80 (m, 2 H; phenyl CH), 7.13–7.24 (m, 3 H; phenyl CH), 9.33 ppm (s, 1 H; NCHS); ^{13}C NMR ($CDCl_3$): $\delta = 49.2$ (q, J(C,H) = 138 Hz; NMe_2), 53.4 (t, J(C,H) = 177 Hz; CH$_2$Cl$_2$), 61.7 (t, J(C,H) = 138 Hz; CH$_2$N), 103.5 (d, J(C,H) = 166 Hz; pyrrole CH), 108.8 (d, J(C,H) = 166 Hz; pyrrole CH), 120.5 (d, J(C,H) = 159 Hz; phenyl CH), 124.5 (d, J(C,H) = 179 Hz; pyrrole CH), 126.0 (d, J(C,H) = 161 Hz; phenyl CH), 129.3 (d, J(C,H) = 160 Hz; phenyl CH), 132.2 (s; pyrrole C_{ipso}), 144.5 (s; phenyl C_{ipso}), 181.5 ppm (d, J(C,H) = 179 Hz; NCHS); elemental analysis calcd for $C_{21}H_{28}N_5SAl{\cdot}0.3\,CH_2Cl_2$: C 58.81, H 6.63, N 16.10; found: C 58.56, H 6.55, N 16.07.

$Al[9\text{-fluorenolato}][C_4H_3N(CH_2NMe_2)\text{-}2][9\text{-}(2\text{-dimethylaminomethylene-}2H\text{-pyrrol-5-yl})\text{-}9H\text{-fluoren-9-oato}]$ (3): A solution of 9-fluorenone (1.972 g, 10.9 mmol) in diethyl ether (20 mL) was added dropwise to a Schlenk flask containing **1** (1.50 g, 5.47 mmol) in diethyl ether (20 mL) precooled to 0 °C. The reaction mixture was stirred at room temperature for 5 h and then the resulting pale pink suspension was filtered to yield a crude solid. The solid was dried under vacuum and recrystallized from a diethyl ether/methylene chloride solution to yield **3** (2.75 g) as dark red crystals in 80 % yield. ^1H NMR ($CDCl_3$): $\delta = 2.28$ (s, 3 H; NMe_2), 2.50 (s, 3 H; NMe_2), 3.14 (s, 3 H; NMe_2), 3.19 (s, 3 H; NMe_2), 3.30 (d, ^2J(H,H) = 12.6 Hz, 1 H; CH_aH$_b$N), 4.13 (d, ^2J(H,H) = 12.6 Hz, 1 H; CH$_a$$H_b$N), 5.27 (s; C$H_2Cl_2$), 5.79 (m, 1 H; 2H-pyrrole ring CH), 5.82 (s, 1 H; CHO), 6.08 (m, 1 H; pyrrole CH), 6.22 (m, 1 H; pyrrole CH), 6.53 (m, 1 H; pyrrole CH), 7.01 (d, 1 H; 2H-pyrrole ring CH), 7.04–7.39 (m, 10 H; phenyl CH), 7.50 (d, 1 H; phenyl CH), 7.65 (m, 3 H; phenyl CH), 7.71 (d, 1 H; phenyl CH), 7.89 (d, 1 H; phenyl CH), 8.19 ppm (s, 1 H; =CHNMe$_2$); ^{13}C NMR ($CDCl_3$): $\delta = 40.93$ (q, J(C,H) = 139 Hz; NMe_2), 46.66 (q, J(C,H) = 139 Hz; NMe_2), 46.95 (q, J(C,H) = 139 Hz; NMe_2), 47.58 (q, J(C,H) = 139 Hz; NMe_2), 53.41 (t, J(C,H) = 177 Hz; CH$_2$Cl$_2$), 58.83 (t, J(C,H) = 138 Hz; CH$_2$NMe$_2$), 76.41 (d, J(C,H) = 133 Hz; CHO), 82.96 (s; OC), 103.33 (d, J(C,H) = 165 Hz; pyrrole CH), 108.48 (d, J(C,H) = 164 Hz; pyrrole CH), 114.16 (d, J(C,H) = 172 Hz; 2H-pyrrole ring CH), 119.34 (d, J(C,H) = 157 Hz; phenyl CH), 119.57 (d, J(C,H) = 157 Hz; phenyl CH), 119.61 (d, J(C,H) = 157 Hz; phenyl CH), 119.72 (d, J(C,H) = 157 Hz; phenyl CH), 123.93 (d, J(C,H) = 157 Hz; phenyl CH), 124.09 (d, J(C,H) = 189 Hz; 2H-pyrrole CH), 124.28 (d, J(C,H) = 178 Hz; pyrrole CH), 125.23 (d, J(C,H) = 157 Hz; phenyl CH), 125.86 (d, J(C,H) = 157 Hz; phenyl CH), 126.39 (d, J(C,H) = 157 Hz; phenyl CH), 126.58 (d, J(C,H) = 157 Hz; phenyl CH), 126.94 (d, J(C,H) = 157 Hz; phenyl CH), 127.29 (d, J(C,H) = 157 Hz; phenyl CH), 127.33 (d, J(C,H) = 157 Hz; phenyl CH), 127.66 (d, J(C,H) = 157 Hz; phenyl CH), 127.86 (d, J(C,H) = 157 Hz; phenyl CH), 127.96 (d, J(C,H) = 157 Hz; phenyl CH), 128.26 (d, J(C,H) = 157 Hz; phenyl CH), 136.17 (s; pyrrole C_{ipso}), 138.94 (s; phenyl C_{ipso}), 139.17 (s; phenyl C_{ipso}), 139.41 (s; phenyl C_{ipso}), 140.32 (s; phenyl C_{ipso}), 150.80 (s; phenyl C_{ipso}), 150.89 (s; phenyl C_{ipso}), 151.29 (d, J(C,H) = 169 Hz; =CHNMe$_2$), 151.50 (s; phenyl C_{ipso}), 152.05 (s; phenyl C_{ipso}), 168.51 ppm (s; 2H-pyrrole C_{ipso}); elemental analysis calcd for $C_{40}H_{37}N_4O_2Al{\cdot}0.2\,CH_2Cl_2$: C 74.31, H 5.80, N 8.62; found: C 74.43, H 5.78, N 8.02.

$Al[1,1\text{-diphenylmethoxyl}][C_4H_3N(CH_2NMe_2)\text{-}2][1\text{-}(2\text{-dimethylaminomethylene-}2H\text{-pyrrol-5-yl})\text{-}1,1\text{-diphenylmethoxyl}]$ (4): A solution of benzophenone (0.80 g, 4.39 mmol) in methylene chloride (20 mL) was added dropwise to a Schlenk flask containing **1** (0.60 g, 2.18 mmol) in methylene chloride (20 mL) precooled to 0 °C. The reaction was stirred at room temperature for 5 h and then the solution was dried under vacuum. The resulting solid was recrystallized from a toluene solution to generate **4** (0.96 g) as orange crystals in 69 % yield. ^1H NMR ($CDCl_3$): $\delta = 2.33$ (s, 3 H; NMe_2), 2.48 (s, 3 H; NMe_2), 2.54 (s, 3 H; NMe_2), 2.98 (s, 3 H; NMe_2), 3.43 (d, ^2J(H,H) = 12.6 Hz, 1 H; CH_aH$_b$N), 4.31 (d, ^2J(H,H) = 12.6 Hz, 1 H; CH$_a$$H_b$N), 5.26 (s, 1 H; Ph$_2CH$O), 6.03 (m, 1 H; pyrrole CH), 6.06 (m, 1 H; pyrrole CH), 6.27 (m, 1 H; pyrrole CH), 6.63 (d, 1 H; 2H-pyrrole ring CH), 6.86–6.89 (m, 2 H; 2H-pyrrole ring CH + phenyl CH), 7.01–7.35 (m, 17 H; phenyl CH); 7.43 (s, 1 H; =CHNMe$_2$), 7.64 (m, 1 H; phenyl CH), 7.67 ppm (m, 1 H; phenyl CH); ^{13}C NMR ($CDCl_3$): $\delta = 40.4$ (q, J(C,H) = 140 Hz; NMe_2), 46.5 (q, J(C,H) = 138 Hz; NMe_2), 46.6 (q, J(C,H) = 138 Hz; NMe_2), 47.2 (q, J(C,H) = 140 Hz; NMe_2), 58.8 (t, J(C,H) = 138 Hz; CH$_2$NMe$_2$), 76.0 (d, J(C,H) = 139 Hz; Ph$_2$$C$HO), 79.6 (s; O$CPh_2$), 102.8 (d, J(C,H) = 165 Hz; pyrrole CH), 107.7 (d, J(C,H) = 164 Hz; pyrrole CH), 116.2 (d, J_{CH} = 171 Hz; 2H-pyrrole ring CH), 124.2 (d, J(C,H) = 178 Hz; pyrrole CH), 125.1 (s; 2H-pyrrole ring C_{ipso}), 125.4 (d, J(C,H) = 158 Hz; phenyl CH), 125.6 (d, J(C,H) = 158 Hz; phenyl CH), 125.9 (d, J(C,H) = 158 Hz; phenyl CH), 126.0 (d, J(C,H) = 158 Hz; phenyl CH), 126.1 (d, J(C,H) = 158 Hz; phenyl CH), 126.2 (d, J(C,H) = 158 Hz; phenyl CH), 126.9 (d, J(C,H) = 158 Hz; phenyl CH), 127.2 (d, J(C,H) = 158 Hz; phenyl CH), 127.3 (d, J(C,H) = 177 Hz; 2H-pyrrole ring CH), 127.4 (d, J(C,H) = 158 Hz; phenyl CH), 127.5 (d, J(C,H) = 158 Hz; phenyl CH), 127.6 (d, J(C,H) = 158 Hz; phenyl CH), 135.8 (s; pyrrole C_{ipso}), 148.6 (s; phenyl C_{ipso}), 149.3 (s; phenyl C_{ipso}), 149.5 (s; phenyl C_{ipso}), 150.0 (s; phenyl C_{ipso}), 152.5 (d, J(C,H) = 171 Hz; =CHNMe$_2$), 168.1 ppm (s; 2H-pyrrole C_{ipso}); elemental analysis calcd for $C_{40}H_{41}N_4O_2Al$: C 75.45, H 6.49, N 8.80; found: C 74.98, H 6.19, N 8.25.

$Al[C_4H_3N(CH_2NMe_2)\text{-}2]\ [C_4H_3N(CH_2NHMe_2)\text{-}2]\ [1,2\text{-diphenylethene-}1,2\text{-diolate}]$ (5): A solution of benzil (0.92 g, 4.37 mmol) in diethyl ether (20 mL) was added dropwise to a Schlenk flask containing **1** (1.20 g, 4.37 mmol) in diethyl ether (20 mL) precooled to 0 °C. The reaction mixture was stirred at room temperature for 0.5 h and then the solvents were removed under reduced pressure. The resulting solid was recrystallized from a diethyl ether/methylene chloride solution to generate **5** (1.48 g) as brown crystals in 71 % yield. A very small amount of diethyl ether was observed in the NMR spectra. ^1H NMR ($CDCl_3$, 240 K): $\delta = 1.26$ (t; Et_2O), 1.36 (s, 3 H; NMe_2), 2.59 (s, 3 H; NMe_2), 2.66 (s, 3 H; NMe_2), 2.95 (s, 3 H; NMe_2), 3.12–3.19 (m, 1 H; CH_2N) 3.39 (d, ^2J(H,H) = 13.2 Hz, 1 H; CH_aH$_b$N), 3.50–3.59 (m; CH_2N and Et_2O overlap), 3.74 (d, ^2J(H,H) = 13.2 Hz, 1 H; CH$_a$$H_b$N), 6.07–6.12 (m, 3 H; pyrrole CH), 6.32 (m, 1 H; pyrrole CH), 7.03–7.26 (m, 7 H; pyrrole ring CH + phenyl CH), 7.35–7.39 (m, 3 H; phenyl CH), 7.58–7.60 (m, 2 H; phenyl CH), 12.74 ppm (s, 1 H; OHN); ^{13}C NMR ($CDCl_3$, 240 K): $\delta = 15.26$ (q, J(C,H) = 126 Hz; Et_2O), 38.43 (q, J(C,H) = 141 Hz; NMe_2), 42.12 (q, J(C,H) = 141 Hz; NMe_2), 46.10 (q, J(C,H) = 139 Hz; NMe_2), 47.49 (q, J(C,H) = 134 Hz; NMe_2), 56.26 (t, J(C,H) = 139 Hz; CH$_2$NMe$_2$), 58.09 (t, J(C,H) = 139 Hz; CH$_2$NMe$_2$), 65.94 (t, J(C,H) = 138 Hz; Et_2O), 103.63 (d, J(C,H) = 167 Hz; pyrrole CH), 106.45 (d, J(C,H) = 167 Hz; pyrrole CH), 109.42 (d, J(C,H) = 167 Hz; pyrrole CH), 112.83 (d, J(C,H) = 167 Hz; pyrrole CH), 124.19 (d, J(C,H) = 178 Hz; pyrrole CH), 125.17 (d, J(C,H) = 160 Hz; pyrrole CH), 125.23 (d, J(C,H) = 159 Hz; phenyl CH), 125.81 (s, pyrrole C_{ipso}), 126.58 (d, J(C,H) = 159 Hz; phenyl CH), 126.83 (d, J(C,H) = 159 Hz; phenyl CH), 127.26 (d, J(C,H) = 159 Hz; phenyl CH), 127.69 (d, J(C,H) = 160 Hz; phenyl CH), 130.62 (d, J(C,H) = 179 Hz; pyrrole CH), 133.61 (s; pyrrole C_{ipso}), 135.14 (s; CO), 137.78 (s; phenyl C_{ipso}), 138.37 (s; CO), 139.26 ppm (s; phenyl C_{ipso}); elemental analysis calcd for $C_{28}H_{33}N_4O_2Al$: C 69.40, H 6.86, N 11.56; found: C 68.69, H 6.80, N 10.73.

Crystallographic structural determination of 1, 3, 4, and 5: Crystal data collection, refinement parameter, and bond lengths and angles are listed in Table 1. The crystals were mounted in capillaries, transferred to a goniostat, and were collected at 150 K. Data were collected on a Bruker SMART CCD diffractometer with graphite-monochromated $\mathrm{Mo}_{K\alpha}$ radiation. Structure determinations were performed by using the SHELXTL package of programs. All refinements were carried out by full-matrix least-squares by using anisotropic displacement parameters for all nonhydrogen atoms. All the hydrogen atoms are included as calculated positions into the refinements.

CCDC-181787 (**1**), CCDC-279564 (**3**), CCDC-279565 (**4**), and CCDC-279566 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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