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計畫主持人：黃瑞賢

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報告

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**Insertion Reactions of Carbon Dioxide into Aluminum Hydride Bond of
Aluminum Complexes Containing Substituted Ketiminate Ligands**

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Abstract

Reaction of ketiminate ligand **1** with an excess of LiAlH_4 generates an aluminum hydride complex **2**, which was ready react with carbon dioxide at room temperature in dichloromethane to yield a novel aluminum formate complex **3**.

Keywords

Ketiminate, aluminum hydride, carbon dioxide, formate

中文摘要

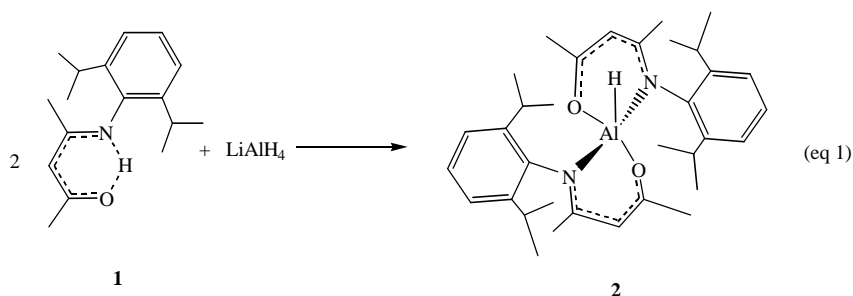
酮胺配位基 **1** 與過量之 LiAlH_4 反應產生一鋁氫化合物 **2**。化合物 **2** 再室溫下於 CH_2Cl_2 中與二氧化碳反應得到一不常見甲醯基錯化合物 **3**。

關鍵字

酮胺，鋁氫化合物，二氧化碳，甲醯基

The emission of carbon dioxide is considering as the largest source for the global warming. Hence, the re-using carbon dioxide as a C1 source is a current research area which is not only in reducing the dependant of fossil fuel consuming but also in reducing the global greenhouse effect.¹ Various methods have been developed for the CO₂ activation and the using transition metal complexes as catalysts are in common.² One way to convert CO₂ into functionalized organic molecules is by inserting the CO₂ into transition metal hydride bond. Reactions between CO₂ and transition metal hydride bonds have been reported in many metals, which mainly are focus on late transition metals.³ The reaction of CO₂ with lithium aluminum hydride to form a reduced formic acid was known,⁴ however, the insertion of CO₂ into aluminum hydride bond and structure characterized has not been seen. In this report, we present the synthesis and characterization of aluminum hydride complexes containing substituted ketimine ligands and their reactions with carbon dioxide.

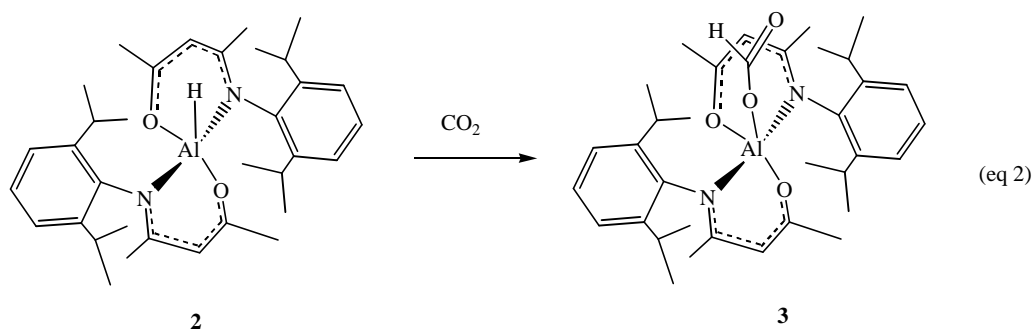
Compound **1** can be easily synthesized in high yield via imine condensation by reacting 1:1 ratio of 2,4-pentandione and 2,6-diisopropylaniline in methanol.⁵



The reaction of compound **1** with excess of LiAlH₄ in diethyl ether at $-78\text{ }^{\circ}\text{C}$ and stirred at $-10\text{ }^{\circ}\text{C}$ for 2 h generates **2** in 76 % yield after a re-crystallization of the reaction solution in diethyl ether at $-20\text{ }^{\circ}\text{C}$ (eq 1).⁶ The ¹H NMR spectrum of complex **2** in C₆D₆ exhibits a C₂ symmetry with the two methyl resonances of the ligand backbone appeared at δ 1.50 and 1.32, respectively. The N–Ar rotation of complex **2** in solution at ambient temperature is slow due to highly steric hindrance of the isopropyl and the methyl group of the backbone of the ligands. The ¹H and ¹³C NMR spectra of complex **2** clearly present the results as shown by two sets of isopropyl resonances. However, the hydride resonance was not observed, presumably due to the interaction of hydrogen with Al ($I = 5/2$).⁷ Solid state IR spectrum indicates that the $\nu_{\text{Al-H}}$ stretching frequency appeared at 1788 cm^{-1} . Moreover, a deuterated complex **2**, **2-D**, synthesized by reacting LiAlD₄ and ketimine **1**, exhibits exactly the same ¹H NMR spectroscopic data with complex **2** and the stretching frequency of $\nu_{\text{Al-D}}$ shifted to 1297 cm^{-1} , which was estimated at 1287 cm^{-1} by calculation. Complex **2** can be recrystallized from diethyl ether solution at $-20\text{ }^{\circ}\text{C}$, which crystal structure was determined.⁸ The ORTEP plot and selected bond

lengths and angles of complex **2** were depicted in Figure 1. The structure of complex **2** exhibits a five-coordinated trigonal bipyramidal structure, with the two nitrogen atoms of ketimate backbone occupying the axial positions while the two oxygen atoms and hydride taking the trigonal planar. Complex **2** is not thermal stable, which decomposed at 80 °C in C₆D₆ forming an un-identified compounds.

The aluminum hydride complex **2** is reactive toward polar functional groups such as carbon dioxide. In a reaction of complex **2** or **2D** with CO₂ in diethyl ether solution, the reaction was completed within minutes after the CO₂ gas was bubbled into the solution (eq 2). Exothermic reaction was observed while the reaction proceeded and the reaction was complete after the solution temperature back to room temperature. An aluminum formate complex **3** or **3D** can be isolated in 93 % yield from the diethyl ether solution at -20 °C.⁹ Complex **3** is very thermal stable which remained unchanged under vacuum at 100 C for h.



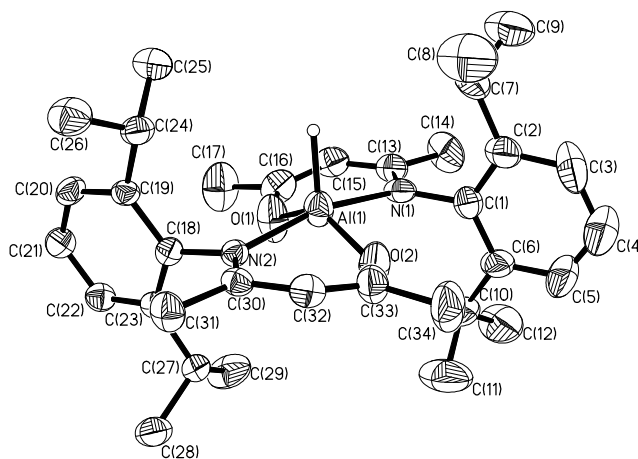
The ketimate backbone of **3** exhibits the same pattern of ¹H and ¹³C NMR resonances with that of **2**. However, ¹H NMR spectrum of **3** exhibits a single at δ 8.0 indicative of a formate proton, which was not observed for complex **3D**. Again the ¹³C{¹H} NMR spectrum shows a singlet at δ 163.8 for the carbonyl carbon of formate complex **3**. A single crystal of **3** suitable for structure determination by X-ray crystallography was obtained from a diethyl ether/dichloromethane mix solution at -20 °C.¹⁰ An ORTEP drawing of **3** and selected bond distances and angles are shown in Figure 2. The structure of complex **3** also exhibits as a five-coordinated trigonal bipyramidal structure. However, the most distinct structural difference of **3** from **2** is the two oxygen atoms of the two ketimate backbones are taking the axial position with an angle of 171.20(8)°, while which the two nitrogen atoms of the two ketimate backbones of **2** occupied the axial positions. Moreover, a series of ketimate aluminum halide and alkyl compounds¹¹ are all shown a O—O trans geometry, similar to that of compound **3**.

The intriguing reactivity of compound **2** toward CO₂ has been carefully calculated. Four structures are considered and calculated for their energies, which are the N—N trans and O—O trans form of complex **2**, and N—N trans and O—O trans form of complex **3** as shown in Scheme 1.

- Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (c) Yin, X.; Moss, J. R. *Coord. Chem. Rev.* **1999**, *181*, 747. (d) Tsai, J. –C.; Nicholas, K. M. *J. Am. Chem. Soc.* **1992**, *114*, 5117. (d) McLoughlin, M. A.; Keder, N. L.; Harrison, W. T. A.; Flesher, R. J.; Mayer, H. A.; Kaska, W. C. *Inorg. Chem.* **1999**, *38*, 3223. (e) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1985**, *24*, 924. (f) Bradley, M. G.; Robert, D. A.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 379. (g) Whittlesey, M. K.; Perutz, R. W.; Moore, M. H. *Organometallics* **1996**, *15*, 5166.
4. Parks, J. E.; Holm, R. H. *Inorg. Chem.* **1968**, *7*, 1408.
 5. ^1H NMR (C_6D_6) for **2**: δ 1.04-1.38 (m, 24H, CHMe_2), 1.32 (s, 6H, CMe), 1.50 (s, 6H, CMe), 3.13 (m, 2H, CHMe_2), 3.40 (m, 2H, CHMe_2), 5.06 (s, 2H, CMeCHCMe), 7.15 (m, 6H, Ph). ^{13}C NMR (C_6D_6) for **2**: δ 23.4, 24.0, 24.3, 24.5, 24.6, 25.9, 28.2, 28.5, 100.1, 123.5, 123.9, 125.6, 129.4, 142.0, 142.2, 145.2, 173.0, 177.2. Anal. Calcd. for $\text{C}_{34}\text{H}_{49}\text{N}_2\text{O}_2\text{Al}$: C, 74.96; H, 9.07; N, 5.14. Found: C, 74.14; H, 8.92; N, 6.20.
 6. Similar phenomena have been seen, for example: Coles, M. P.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 5183.
 7. Crystal data for **2**: $\text{C}_{34}\text{H}_{49}\text{AlN}_2\text{O}_2$, $mw = 544.73$, $T = 150(1)$ K, Rhombohedral, space group $R\bar{3}m$, $a = 36.358(3)$ Å, $b = 36.358(3)$ Å, $c = 13.0454(14)$ Å, $V = 14935(2)$ Å³, $z = 18$.
 8. ^1H NMR (CDCl_3) for **3**: δ 1.03-1.14 (m, 24H, CHMe_2), 1.18 (s, 6H, CMe), 1.65 (s, 6H, CMe), 2.82 (m, 2H, CHMe_2), 3.05 (m, 2H, CHMe_2), 5.21 (s, 2H, CMeCHCMe), 7.03-7.23 (m, 6H, Ph), 8.23 (s, COH). ^{13}C NMR (CDCl_3) for **3**: δ 23.7, 23.9, 24.3, 24.8 Br, two peaks overlapping), 25.3, 27.3, 28.2, 100.1, 123.1, 123.9, 125.6, 140.6, 143.0, 145.1, 163.8, 177.8, 180.6. Anal. Calcd. for $\text{C}_{35}\text{H}_{49}\text{N}_2\text{O}_4\text{Al}$: C, 71.4; H, 8.39; N, 4.76. Found: C, 71.83; H, 8.90; N, 5.05. The ^1H and ^{13}C NMR spectra of **3D** is similar to that of **3** excepting that the formate proton of **3** at δ 8.01 was not seen in that of **3D** and the carbonyl carbon of **3** at δ 163.8 was not observed in that of **3D** presumably due to the nuclear quadrupole interaction of deuterium ($I = 1$).
 9. Crystal data for **3**: $\text{C}_{35}\text{H}_{49}\text{AlN}_2\text{O}_4$, $mw = 588.74$, $T = 150(2)$ K, Triclinic, space group $R\bar{1}$, $a = 10.4508(13)$ Å, $b = 12.1431(14)$ Å, $c = 14.4459(17)$ Å, $\alpha = 69.713(2)^\circ$, $\beta = 84.803(2)^\circ$, $\gamma = 71.539(2)^\circ$, $V = 1630.7(3)$ Å³, $z = 2$.
 10. Yu, R. –C.; Chang, J. –C.; Hung, C. –H.; Hunag, J. –H.; Lee, H. –I; Chen, J. –T. *Inorg. Chem.* **2002**, In press.
 11. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
 12. The comparison of bond distances and angles of calculated structures and single

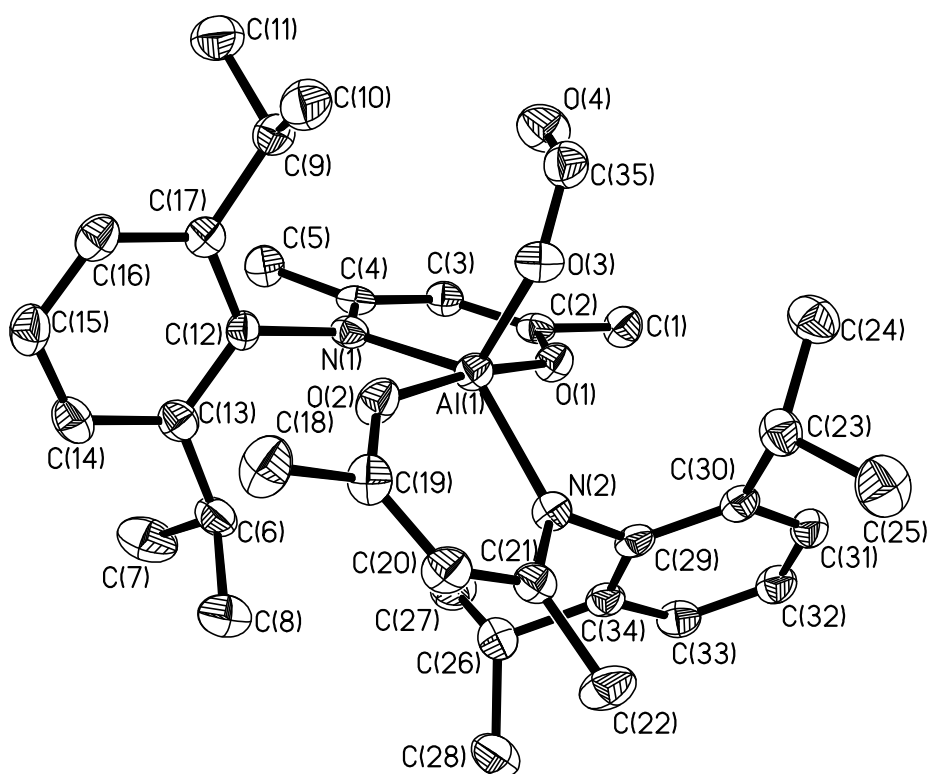
crystal structures were listed in the supporting information.

Figure 1. The ORTEP drawing of complex **2** and selected bond distances and angles. Al(1)–H(1) 1.61(3); Al(1)–O(2) 1.757(3); Al(1)–O(1) 1.763(3); Al(1)–N(2) 2.064(3); Al(1)–N(1) 2.079(3); H(1)–Al(1)–O(2) 114.5(11); H(1)–Al(1)–O(1) 111.8(11); O(2)–Al(1)–O(1) 133.6(2); H(1)–Al(1)–N(2) 99.0(1); O(2)–Al(1)–N(2) 88.21(13); O(1)–Al(1)–N(2) 86.96(13); H(1)–Al(1)–N(1) 95.3(11); O(2)–Al(1)–N(1) 85.31(14); O(1)–Al(1)–N(1) 88.3(1); N(2)–Al(1)–N(1) 165.69(13)



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Figure 2. The ORTEP drawing of complex 3 and selected bond distances and angles. Al(1)–O(3) 1.798(2); Al(1)–O(1) 1.807(2); Al(1)–O(2) 1.813(2); Al(1)–N(1) 1.956(2); Al(1)–N(2) 1.997(2); O(4)–C(35) 1.213(3); O(3)–C(35) 1.296(3); O(3)–Al(1)–O(1) 96.95(8); O(3)–Al(1)–O(2) 91.77(8); O(1)–Al(1)–O(2) 171.20(8); O(3)–Al(1)–N(1) 116.10(8); O(1)–Al(1)–N(1) 90.45(7); O(2)–Al(1)–N(1) 86.73(7); O(3)–Al(1)–N(2) 108.30(8); O(1)–Al(1)–N(2) 87.00(7); O(3)–C(35)–O(4) 127.6(3)



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