Formation of aluminacyclobutenes *via* carbon monoxide and isocyanide insertion

Xiaofei Li, Chengbao Ni, Haibing Song and Chunming Cui*

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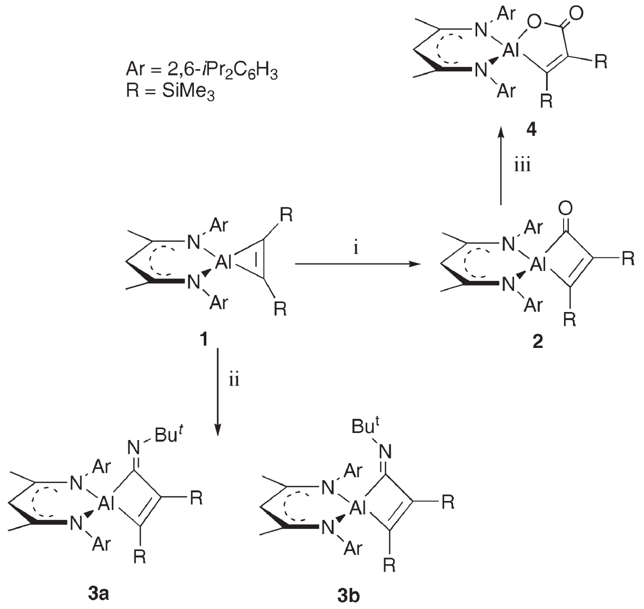
Reaction of LAl[η^2-($CSiMe_3$)$_2$] (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*$Pr_2C_6H_3$) with carbon monoxide and *tert*-butyl isocyanide afforded unique AlC_3 aluminacyclobutenes *via* insertion into one of the aluminium–carbon bonds.

There is increasing interest in strained ring compounds that incorporate heavier main group elements because of their unique structures and high reactivity.[1] In this context, we are interested in the strained aluminium ring systems stabilized by sterically demanding ligands. Recently, several three-membered AlC_2 ring compounds have been reported.[2] It has been demonstrated that the AlC_2 ring compound, LAl[η^2-($CSiMe_3$)$_2$] (**1**, L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*$Pr_2C_6H_3$), can react with a range of small molecules such as carbon dioxide, ketones, nitriles, organic azides, dioxygen and CS_2, leading to either ring expansion or elimination of bis(trimethylacetylene).[2b,3] These studies prompted us to explore the reaction of **1** with carbon monoxide and isocyanides since they are versatile synthons in organic and organometallic synthesis. Although the insertion of CO and isocyanides into transition metal–carbon bonds has been well established,[4] similar studies on the insertion into aluminium–carbon bonds are much less common.[5] To the best of our knowledge, there are only two reports concerning the insertion of CO and an isocyanide into aluminium–carbon bonds, namely the insertion of CO into the aluminium–carbon bond of tri-*tert*-butylaluminium[6] and the double insertion of *tert*-butyl isocyanide into the Al–C bond of Cp'_3Al (Cp′ = C_5Me_4H).[7] The facile insertion of CO and *tert*-butyl isocyanide in these two cases may result from the three-coordinate environment of the aluminium centers. Herein we report on the syntheses and characterization of the AlC_3 aluminacyclobutene rings generated from the insertion reactions of CO and *tert*-butyl isocyanide with **1**.

When a red black solution of **1** was exposed to a purified CO atmosphere (1 atm, moisture and oxygen should be strictly excluded) in *n*-hexane at room temperature, the colour change of the solution to yellow was observed within 2 min. Compound **2** was obtained in high yield after additional stirring for 20 min followed by a standard workup (Scheme 1). The reaction of **1** with *tert*-butyl isocyanide in *n*-hexane proceeds rapidly at −78 °C to give orange crystals of **3** after crystallization from diethyl ether. Compounds **2** and **3** have been characterized by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy and elemental analysis.† The ^1H NMR spectrum of **2** displays four doublets for the CH*Me*$_2$ groups on the Ar rings because of the non-symmetric AlC_3 ring. The ^{13}C NMR spectrum of **2** shows a singlet at δ 234.8 ppm, attributed to the resonance of Al–*C*(O), which is downfield shifted from those of ketones (197–220 ppm)[8] but significantly upfield from that reported for the bridging acyl group of [*t*-$Bu_2AlC(O)Bu$-*t*]$_2$,[6] indicating terminal acyl coordination[9] and the existence of an α,β-unsaturated acyl unit.[2b] The infrared spectrum of **2** exhibits a band at 1677 cm^{-1} as expected for a terminal acyl moiety.[9] Unfortunately we were unable to obtain crystals suitable for single crystal X-ray analysis for further confirmation because of its extremely high sensitivity to the air and moisture although many attempts have been made. Interestingly, reaction of **2** with dioxygen at −78 °C in diethyl ether results in the selective insertion of one oxygen atom into the Al–C(O) bond with the formation of LAl[OC(O)C($SiMe_3$)($CSiMe_3$)] (**4**), the same product as reported for the reaction of **1** with CO_2.[2b] The formation of **4** has been confirmed by its ^1H NMR spectrum and single crystal X-ray analysis.‡ **4** crystallises in a monoclinic space group, different from that reported previously, but the structural parameters are only marginally different from those reported.[3a]



Scheme 1 *Reagents and conditions*: i. CO, *n*-hexane, r.t.; ii. CNBu^t, *n*-hexane, −78 °C; iii. O_2, diethyl ether, −78 °C.

The NMR spectrum of **3** indicates the formation of two isomers because of the two possible orientations of the *tert*-butyl group (Scheme 1). The two isomers are stable, and cannot be interconverted in hot toluene. It should be noted that the ratio (*ca.* 2 : 1 estimated from the ^1H NMR spectrum) of the two

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State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. China. E-mail: cmcui@nankai.edu.cn; Fax: +86-22-23503461; Tel: +86-22-23503461

isomers is independent on the reaction temperatures (−78 °C to room temperature). Attempts to separate **3a** and **3b** by repeated crystallisation failed because of their very similar physical properties (solubility and appearance). However, the ^{1}H NMR spectrum of the mixture could be partially distinguished despite the overlaps of the resonances of the aromatic protons and C*H*Me$_2$ groups of the two molecules. The proton NMR spectrum of the major isomer shows three singlets at δ 0.48, 0.55 and 0.80 ppm with the same integration, attributed to the resonances of the two SiMe$_3$ groups and the *t*-butyl group while the spectrum of the minor one shows resonances at δ −0.14, 0.52 and 1.42 ppm. The down and upfield shifts of one of the SiMe$_3$ groups and the *t*-butyl group in the ^{1}H NMR spectrum of the major isomer may result from intramolecular H···H interactions among the two groups. The chemical shifts for the other protons and the resonances found in the ^{13}C NMR spectrum of the two isomers are quite close to each other. Based on these observations, we, tentatively, assign **3a** as the major isomer because of the existence of steric repulsion between the *t*-butyl and its neighboring SiMe$_3$ group. The iminoacyl resonances in the ^{13}C NMR spectrum of **3** appear at δ 197.5 and 194.6 ppm, which are in the reported range for those found in terminal iminoacyl complexes.[9] The molecular structure of one isomer has been characterized by single crystal X-ray analysis, which disclosed that the molecular array corresponds to **3b**.‡

The structure of **3b** is shown in Fig. 1. The most striking feature of **3b** is the almost planar AlC$_3$ ring (mean deviation from the plane: 0.0236 Å), which is arranged nearly perpendicular to the N1–Al1–N2 plane (the angle between the C30–Al1–C32 and N1–Al1–N2 planes: 91.6°). The aluminium atom adopts a distorted tetrahedral geometry because of the geometric constraints of the two fused rings around the aluminium atom. The iminoacyl group is coordinated to the aluminium atom in an η^1 fashion and the Al1–C30 bond length (1.9842(19) Å) is in line with a Al–C (sp^2 hybrid) single bond.[2b] The N3–C30 bond length (1.285(2) Å) is in the range for iminoacyl groups. The C30–C31 bond length (1.519(2) Å) is consistent with a C–C single bond, and the C31–C32 bond length (1.374(3) Å) indicates double bonding. The *trans* α,β-unsaturated iminoacyl moiety N3–C30–C31–C32 is not planar (torsion angle: 10.8°) probably due to the sterically demanding ligands on the AlC$_3$ four-membered ring.

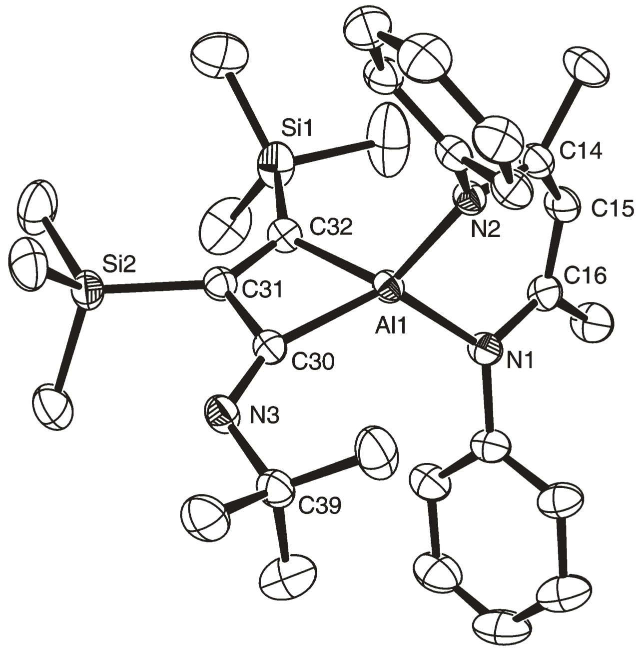

Fig. 1 Thermal ellipsoid drawing of **3b** (30% probability). Hydrogen atoms and *i*Pr groups on the Ar rings have been omitted. Selected bond distances (Å) and angles (°): Al1–C30 1.9842(19), Al1–C32 1.989(2), Al1–N1 1.9020(16), Al1–N2 1.9141(15), C30–C31 1.519(2), C31–C32 1.374(3), N3–C30 1.285(2), N3–C39 1.480(2); N1–Al1–N2 95.88(7), C30–Al1–C32 72.94(8), N1–Al1–C30 125.36(7), N2–Al1–C32 117.81(7), C30–C31–C32 109.31(16), C30–N3–C39 119.71(16).

In summary, the facile insertion of CO and isocyanide into an Al–C bond of the four coordinate aluminium AlC$_2$ ring is remarkable, demonstrating that ring strain could induce new reactivity for higher coordinate aluminium species. The formed AlC$_3$ aluminacyclobutenes are unique and new additions to strained aluminium ring systems. Compounds **2** and **3** may undergo interesting insertion reactions with a number of unsaturated small molecules to generate novel aluminium ring systems because of the two distinct Al–C bonds and the ring strain. Investigation of new reactions of **2** and **3** is currently being undertaken.

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Notes and references

† **2**: A solution of **1** (0.25 g, 0.4 mmol) in *n*-hexane at room temperature was exposed to dry carbon monoxide under normal pressure. A colour change to yellow was observed within 2 min. It was stirred at room temperature for an additional 20 min under a CO atmosphere. All volatiles were removed to give a pale yellow solid, which was washed with *n*-hexane to afford **2**: yield 72%; mp 126 °C (dec.); anal. found for $C_{38}H_{59}AlN_2OSi_2$: C 70.63, H, 9.53. Calc. C 70.98, H, 9.41; ^{1}H NMR (C_6D_6, 400 MHz): δ −0.07 (s, 9H, SiMe$_3$), 0.43 (s, 9H, Si*Me*$_3$), 1.03 (d, 6H, *J* = 6.80 Hz, CH*Me*$_2$), 1.08 (d, 6H, *J* = 6.80 Hz, CH*Me*$_2$), 1.19 (d, 6H, *J* = 6.80 Hz, CH*Me*$_2$), 1.36 (d, 6H, *J* = 6.80 Hz, CH*Me*$_2$), 1.43 (s, 6H, β-C*Me*), 3.13 (sept, 2H, C*H*Me$_2$), 3.26 (sept, 2H, C*H*Me$_2$), 4.74 (s, 1H, γ-C*H*), 6.97 (m, 2H, Ar–*H*), 7.04 (m, 4H, Ar–*H*); ^{13}C NMR (C_6D_6): δ 1.23 (Si*Me*$_3$), 2.66 (Si*Me*$_3$), 22.13 (CH*Me*$_2$), 23.02 (CH*Me*$_2$), 25.86 (CH*Me*$_2$), 26.80 (CH*Me*$_2$), 30.21 (C*Me*), 31.07 (*C*HMe$_2$), 123.4, 126.8, 128.6, 129.6, 142.3, 145.5, 146.8, 148.9, 150.4 (Al*CC*, Ar–*C*), 234.8 (*C*O); IR ν/cm^{-1}: 1677 (s, AlCO). **3**: To a solution of **1** (0.20 g, 0.32 mmol) in *n*-hexane (15 mL) was added neat *tert*-butyl isocyanide (0.027 g, 0.32 mmol) at −78 °C. The colour of the solution turned into orange immediately. The resulting mixture was allowed to warm up to room temperature and was stirred for 30 min. All volatiles were removed and the remaining solid was crystallised from diethyl ether at −25 °C to give orange crystals of **3**: yield 57%; mp 145 °C (dec.); anal. found for $C_{42}H_{68}AlN_3Si_2$: C 72.26, H 9.96. Calc. C 72.25, H 9.82; ^{1}H NMR (C_6D_6): δ −0.14, 0.48 (s, 1 : 2, 9H, Si*Me*$_3$), 0.52, 0.55 (s, 1 : 2, 9H, Si*Me*$_3$), 0.80 (s 6H, C*Me*$_3$), 1.01 (d, 2H, *J* = 6.40 Hz, CH*Me*$_2$), 1.04 (d, 2H, *J* = 6.80 Hz, CH*Me*$_2$), 1.13 (d, 6H, *J* = 6.80 Hz, CH*Me*$_2$), 1.17 (d, 4H, *J* = 6.80 Hz, CH*Me*$_2$), 1.20 (d, 2H, *J* = 6.80 Hz, CH*Me*$_2$), 1.26 (d, 4H, *J* = 6.80 Hz, CH*Me*$_2$), 1.39 (d, 2H, *J* = 6.80 Hz, CH*Me*$_2$), 1.42 (s, 3H, C*Me*$_3$), 1.47 (d, 6H, C*Me*), 2.29 (m, 4H, C*H*Me$_2$), 4.96, 5.09 (s, 1H, 1 : 2, γ-CH), 7.04–7.09 (m, 6H, Ar–H); ^{13}C NMR (C_6D_6): δ 2.04, 2.73, 3.28 (Si*Me*$_3$), 23.90, 24.33, 24.54, 24.72, 24.85, 25.07, 25.15, 25.85, 26.64 (*Me*, CH*Me*$_2$), 27.81, 29.03, 29.11, 29.24, 30.30 (*C*HMe$_2$ and C*Me*$_3$), 55.75, 55.48 (*C*Me$_3$), 100.48, 101.42 (γ-C), 124.23, 124.29, 125.12, 125.29, 127.41, 127.47, 139.00, 140.57, 140.82, 142.94, 144.91, 145.40 (Ar–*C*), 170.75, 171.27, 172.54 (N*C*Me and *C*SiMe$_3$), 194.62, 197.47 (Al*C*(N)). IR ν/cm^{-1}: 1587 (s, AlCN)

‡ Crystal data for **3b**·Et$_2$O: $C_{46}H_{78}AlN_3OSi_2$, *M* = 772.27, triclinic, space group $P\bar{1}$, $a = 10.672(3)$, $b = 13.588(4)$, $c = 18.468(6)$ Å, $\alpha = 72.022(4)$, $\beta = 87.112(4)$, $\gamma = 80.639(4)^\circ$, $V = 2513.3(14)$ Å^3, $Z = 2$, $D_c = 1.020$ g cm^{-3}, $F(000) = 848$, 13739 reflections measured (8763 unique). $R1$ [$I > 2\sigma(I)$] = 0.0442, w$R2$ (all data) = 0.1361, GOF = 1.019 for 497 parameters and 0 restraints. CCDC 296206. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b601056c **4**: $C_{38}H_{59}AlN_2O_2Si_2$,

M = 659.03, monoclinic, space group $P2_1/n$, a = 16.1975(18), b = 11.3234(12), c = 22.709(2) Å, β = 104.540(2)°, V = 4031.7(8) Å^3, Z = 4, D_c = 1.086 g cm^{-3}, F(000) = 1432, 22056 reflections measured (8091 unique). $R1$ [$I > 2\sigma(I)$] = 0.0537, w$R2$ (all data) = 0.1552, GOF = 0.995 for 422 parameters and 0 restraints The X-ray data were collected on a Bruker Smart-Apex II diffractometer using graphite monochromated Mo-Kα (λ = 0.71073 Å) at 294(2) K. The structure was solved by direct methods (SHELXS-97)[10] and refined by full matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97).[11]

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