

SUPPORTING INFORMATION

Remarkable Room-Temperature Insertion of Carbon Monoxide into an Aluminum-Carbon Bond of Tri-*tert*-butylaluminum

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Experimental Section

General Procedures. All reactions were performed under an atmosphere of purified nitrogen using standard inert atmosphere techniques. Hexane and tetrahydrofuran were distilled from calcium hydride and sodium benzophenone ketyl, respectively, prior to use. Toluene was distilled from sodium. CDCl_3 was dried by storage over activated molecular sieves. Carbon monoxide enriched in ^{13}C (99 atom %) was purchased from Isotec and used as received. Tri-*tert*-butylaluminum was prepared as previously described.^{1,2} Solution NMR spectra were recorded on a Varian Unity 400 spectrometer using CDCl_3 as the internal lock. Chemical shifts are reported relative to tetramethylsilane. Melting points were obtained using a Thomas Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Preparation of $[\text{}^t\text{Bu}_2\text{AlC(O)}^t\text{Bu}]_2$ (1**).** Carbon monoxide was bubbled through a solution of tri-*tert*-butylaluminum (0.337 g, 1.70 mmol) in hexanes (15 mL) for 5 minutes. The initially clear, colorless solution changed to yellow almost immediately. The solution was stirred at room temperature for 12 h and filtered to isolate the first crop of product. The filtrate was stored at $-20\text{ }^\circ\text{C}$ overnight. Isolation of the second crop of product by filtration and recrystallization of the combined product from THF afforded yellow crystals of **1**. Yield: 0.231 g, 60.1%. ^1H NMR (C_6D_6 , 400 MHz): δ 1.12 (s, 18H, ^tBu), 0.97 (s, 9H, ^tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100.6 MHz): δ 327.1 (s, CO), 51.64 (s, $\text{C}(\text{CH}_3)_3$), 31.04 (s, $\text{AlC}(\text{CH}_3)_3$), 24.96 (s, $\text{C}(\text{CH}_3)_3$), 15.44 (bs, $\text{AlC}(\text{CH}_3)_3$). IR (KBr, ν_{CO}): 1527 cm^{-1} . Anal. calcd for $\text{C}_{13}\text{H}_{27}\text{AlO}$: C, 68.98; H, 12.03; Al, 11.92. Found: C, 68.96; H, 12.87; Al, 13.17.

Preparation of $[\text{}^t\text{Bu}_2\text{Al}^{13}\text{C(O)}^t\text{Bu}]_2$ (1- ^{13}C**).** Compound **1- ^{13}C** was prepared using the same procedure described for compound **1**, but using ^{13}C -enriched carbon monoxide. Yield:

62%. ^1H NMR (C_6D_6 , 400 MHz): δ 1.12 (s, 18H, ^tBu), 0.97 (d, $^3J_{\text{C-H}} = 4.4$ Hz, 9H, ^tBu).

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100.6 MHz): δ 327.06 (s, CO), 51.63 (d, $^1J_{\text{C-C}} = 19.9$ Hz, $\text{C}(\text{CH}_3)_3$), 31.04 (s, $\text{AlC}(\text{CH}_3)_3$), 24.95 (d, $^3J_{\text{C-C}} = 2.5$ Hz, $\text{C}(\text{CH}_3)_3$), 15.46 (bs, $\text{AlC}(\text{CH}_3)_3$). IR (KBr, $\nu(^{13}\text{CO})$): 1493 cm^{-1} .

Reaction of $^t\text{Bu}_3\text{Al}\cdot\text{THF}$ with CO. To a solution of approximately 0.20 g $^t\text{Bu}_3\text{Al}$ in toluene (15 mL) was added two drops of THF. Carbon monoxide was bubbled through the solution for 5 minutes and the solution was stirred overnight under CO atmosphere. Removal of volatiles from the colorless solution yielded a residue identified as $^t\text{Bu}_3\text{Al}\cdot\text{THF}$ by NMR spectroscopy.

Reaction of $^t\text{Bu}_3\text{Al}\cdot\text{OEt}_2$ with CO. The reaction was conducted as described above using diethyl ether in place of THF. No reaction was observed between CO and $^t\text{Bu}_3\text{Al}\cdot\text{OEt}_2$.

X-ray Crystallography. Crystals of **1** were grown from a THF solution at room temperature. The X-ray diffraction data were collected on a Siemens three-circle platform diffractometer equipped with a 1K CCD detector. The frame data were acquired with the SMART³ software using Mo $K\alpha$ radiation ($\lambda = 0.710\ 73\ \text{\AA}$). Cell constants were determined with SAINT PLUS 6.45⁴ from the complete dataset. A complete hemisphere was scanned on ω (0.3°) with run times of 60 s/frame. A total of 1267 frames were collected for each dataset. An additional 50 frames, identical to the first 50 frames, were collected to determine crystal decay. The frames were integrated using the SAINT PLUS 6.45⁴ software and the data were corrected for absorption and decay using the SADABS program.⁵ The structure was solved by direct methods and refined by least-squares methods on F^2 using SHELXL-97.⁶ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located and refined with isotropic displacement parameters. Details of data collection and refinement are

provided in Table 1. Further details, including atomic coordinates, distances, and angles, are found in the CIF file.

References

- (1) Uhl, W. Z. *Anorg. Allg. Chem.* **1989**, 570, 37.
- (2) (a) Lehmkuhl, H.; Olbrysch, O.; Nehl, H. *Liebigs Ann. Chem.* **1973**, 708. (b) Lehmkuhl, H.; Olbrysch, O. *Liebigs Ann. Chem.* **1973**, 715.
- (3) *SMART, Software for the CCD Detector System*; Siemens Analytical Instruments Division: Madison, WI, 1995.
- (4) *SAINT PLUS 6.45, Software for the CCD Detector System*; Bruker Analytical Instruments Division: Madison, WI, 2003.
- (5) Sheldrick, G. M. *SADABS: Absorption Correction Program*; University of Göttingen: Göttingen, Germany, 1996.
- (6) Sheldrick, G. M. *SHELXL-97: Program for Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

Table 1. Summary of X-ray Crystallographic Data

1	
formula	C ₂₆ H ₅₄ Al ₂ O ₂
fw	452.65
crystal system	monoclinic
space group	P2(1)/n
<i>a</i> , Å	8.5511(9)
<i>b</i> , Å	11.6180(13)
<i>c</i> , Å	14.657(2)
α , deg	90
β , deg	90.712(6)
γ , deg	90
<i>V</i> , Å ³	1456.0(3)
<i>Z</i>	2
<i>D</i> _{calcd} , g cm ^{−3}	1.032
<i>T</i> , °C	−153
μ (Mo K α), cm ^{−1}	1.18
λ , Å	0.710 73
transm coeff	1.000–0.823
2 θ limits, deg	4.5–52
total no. of data	8377
no. of unique data	2858
no. of obsd data ^a	2593
no. of params	244
<i>R</i> 1 ^{a,b}	0.0612
w <i>R</i> 2 ^{a,c}	0.1156
max, min peaks, e/Å ³	0.375, −0.286

^a $I > 2\sigma(I)$. ^b $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^c $wR2 = [\sum [w (F_o^2 - F_c^2)^2] / \sum [w (F_o^2)^2]]^{1/2}$.