Synthesis and Reactivity of Bis-Pentamethylcyclopentadienyl Diiododialane $(Cp^*AlI)_2$: An Aluminum(II) Precursor to $(Cp^*Al)_4$†

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SUPPORTING INFORMATION

Experimental

General Considerations. All reactions were performed using standard Schlenk-line techniques or in an MBraun dry box (<1 ppm O_2/H_2O) unless noted otherwise. All glassware were dried at 150°C for at least 12 hours, or flame dried under a vacuum prior to use. Pentane, hexane, diethyl ether, and toluene were purified by passage through a column of activated alumina and degassed with argon prior to use.[1] Deuterated benzene was vacuum transferred from sodium/benzophenone. NMR spectra were recorded at ambient temperature on Bruker AVB-400 or DRX-500 spectrometers. ^{1}H and $^{13}C\{^{1}H\}$ chemical shifts are given relative to residual solvent peaks and coupling constants (*J*) are given in Hz. ^{27}Al NMR chemical shifts are referenced to an external standard of 1M $Al(NO_3)_3$ in H_2O/D_2O (δ 0). Infra-red samples were prepared as Nujol mulls and taken between KBr disks. Melting points were determined using sealed capillaries prepared under nitrogen and are uncorrected. Cp^*SiMe_3,[2] $Cp^*AlI_2{\bullet}Et_2O$,[3] and $Ar''N_3$ ($Ar'' = C_6H_3$-2,6-Mes_2, Mes = C_6H_2-2,4,6-$(CH_3)_3$)[4] were prepared by the literature procedures. GaI_3 was prepared from its elements and recrystallized from hot toluene. Unless otherwise noted, all other reagents were acquired from commercial sources and used as received. Elemental Analyses were determined at the Microanalytical Laboratory of the College of Chemistry, University of California, Berkeley. X-ray structural determinations were performed at CHEXRAY, University of California, Berkeley.

Crystallographic Analysis. Single crystals of **1** and **2** were coated in Paratone-N oil, mounted on a Kaptan loop, transferred to a Siemens SMART diffractometer or a Bruker APEX CCD area detector,[5] centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that has been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrices and cell constants were determined by collection of 60 30 second frames, followed by spot integration and least-squares refinement. An arbitrary hemisphere of data was collected and the raw data were integrated using SAINT.[6] Cell dimensions reported were calculated from all reflections with $I > 10\sigma$. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Data were analyzed for agreement and possible absorption using XPREP.[7] An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS.[8] The structures were solved using SHELXS[9] and refined on all data by full-matrix least squares with SHELXL-97.[10] Thermal parameters for all non-hydrogen atoms were refined anisotropically. ORTEP diagrams were created using the ORTEP-3 software package.[11] A summary of the X-ray diffraction data is presented in Table 1.

Single-crystal diffraction data for **3** were collected using synchrotron radiation at the Advanced Light Source at Lawrence Berkeley National Laboratory. A crystal was coated in Paratone-N oil and mounted on a Kaptan loop, transferred to a Bruker D8 controller, and cooled in a dinitrogen stream. Data were collected using a Bruker Platinum 200 with an APEX2 v1.0-27 detector. Initial lattice parameters were obtained from a least-squares analysis of more than 30 centered reflections; these parameters were later refined against all data. A full hemisphere of data was collected. Data were integrated using Bruker SAINT[6] and corrected for Lorentz and polarization effects using SADABS.[8] Space group assignments were made on the basis of systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined against all data using the SHELXTL 5.0 software package. Thermal parameters for all non-hydrogen atoms were refined anisotropically. A summary of the X-ray diffraction data is presented in Table 1.

$(Cp^*AlI)_2$ (1): A solution of $Cp^*AlI_2{\bullet}Et_2O$ (4.6 g, 9.9 mmol) in toluene (35 mL) was added to Na/K alloy prepared by mixing Na° (88 mg, 3.8 mmol) and K° (0.27 g, 7.1 mmol) in toluene (10 mL) and stirred for 48 h at room temperature. Following filtration, the yellow solution was concentrated to 10 mL *in vacuo*. Storage at -10 °C for several days followed by filtration afforded yellow blocks of pure **1** (2.0 g, 36%). ^1H NMR (500 MHz, C_6D_6): δ 1.80 (s, 15H, $C_5(CH_3)_5$). ^{13}C NMR (125 MHz, C_6D_6): δ 116.98, 11.69. ^{27}Al NMR (130 MHz, C_6D_6): δ -41.75. IR (cm^{-1}): 1029 (m), 796 (m), 668 (w), 616 (w), 588 (w), 528 (s). Anal. Calcd for $C_{20}H_{30}Al_2I_2$: C, 41.54; H, 5.23. Found: C, 41.33; H, 5.04. M.p. = 159–162 °C.

$[Cp^*AlMe(\mu\text{-}I)]_2$ (2): MeLi (1.1 mL, 1.6 M in diethyl ether, 1.8 mmol) was added to a dry schlenk flask, evaporated, suspended in toluene (10 mL), and cooled to -78 °C. A solution of **1** (0.50 g, 0.87

mmol) was prepared in toluene (10 mL) and added to the MeLi/toluene suspension. The mixture was allowed to warm with the cold bath to room-temperature while stirring over 16 h. The volatile components were removed *in vacuo*, and the solids were extracted with pentane (20 mL). Following filtration, the pentane extract was concentrated *in vacuo* until crystallization was incipient. Storage at -10 °C for 7 days afforded the product as X-ray quality colorless needles (85 mg, 32%). ^{1}H NMR (500 MHz, C_6D_6): δ 1.64 (s, 30 H, $C_5(CH_3)_5$), -0.48 (s, 6 H, CH_3). ^{13}C NMR (125 MHz, C_6D_6): δ 10.19, 115.74. ^{27}Al NMR (130 MHz, C_6D_6): δ -7.22. IR (cm^{-1}): 1182 (m), 1066 (w), 1024 (m), 950 (w), 888 (w), 799 (w), 700 (s), 660 (s), 587 (m), 443 (s). Anal. Calcd for $C_{22}H_{36}Al_2I_2$: C, 43.44; H, 5.97. Found: C, 42.27; H, 5.82. M.p. = 94–97 °C.

Alternative synthesis of (Cp*Al)$_4$: A solution of **1** (0.50 g, 0.87 mmol) in toluene (5 mL) was added to Na/K alloy prepared from Na° (14 mg, 0.63 mmol) and K° (44 mg, 1.1 mmol) in toluene (1 mL) and stirred for 16 h at room temperature. The solution was filtered and concentrated to 3 mL *in vacuo*. Storage at -35°C for several days followed by filtration afforded the product [Cp*Al]$_4$ as yellow cubes (95 mg, 33%). Analytical data for [Cp*Al]$_4$ were consistent with those reported in the literature.[12, 13]

$C_{68}H_{80}N_4Al_2I_2$ (3): A solution of Ar''N$_3$ (0.18 g, 0.52 mmol) in toluene (2 mL) was added to a flask containing a solution of (Cp*AlI)$_2$ (0.15 g, 0.26 mmol) in toluene (10 mL), which had been cooled to -78 °C. The solution was allowed to warm to room temperature with stirring over 16 h. Volatiles were removed *in vacuo*, pentane was added (20 mL) and the solution was filtered. Following evaporation of the solvent, the product was isolated as an orange powder (0.19 g, 58%). Crystals suitable for X-ray structural analysis were obtained after storing a concentrated solution of **3** in pentane at -10 °C for 7 days. ^{1}H NMR (400 MHz, C_6D_6): δ 7.06 (d, *J* = 7.2 Hz, 1 H, Ar*H*), 6.94 (m, 2 H, Ar*H*), 6.85 (s, 2 H, Ar*H*), 6.78 (s, 3 H, Ar*H*), 6.77 (s, 1 H, Ar*H*), 6.73 (s, 2 H, Ar*H*), 6.09 (m, 1 H, vinyl *H*), 5.36 (br s, 1 H, vinyl *H*), 3.01 (t, *J* = 4.2 Hz, 1 H, sp^3 ring *H*), 2.58 (s, 3 H, CH_3), 2.37 (s, 6 H, CH_3), 2.35 (s, 3 H, CH_3), 2.28 (s, 6 H, CH_3), 2.18 (s, 6 H, CH_3), 2.13 (s, 6 H, CH_3), 2.11 (s, 3 H, CH_3), 2.04 (s, 6 H, CH_3), 1.60 (s, 15 H, $C_5(CH_3)_5$), 1.48 (s, 3 H, CH_3), 1.42 (s, 3 H, CH_3), 1.33 (s, 3 H, CH_3), 1.10 (s, 3 H, CH_3). ^{13}C NMR (125 MHz, C_6D_6): δ 10.50, 11.03, 11.41, 12.72, 20.94, 21.13, 21.35, 21.52, 21.58, 21.85, 21.95, 76.09, 115.25, 117.40, 126.03, 126.17, 126.48, 129.67, 129.84, 130.00, 130.63, 131.00, 131.42, 132.14, 133.84, 135.31, 135.72, 136.11, 136.35, 136.73, 136.81, 137.04, 137.30, 137.58, 137.90, 138.28, 139.81, 142.30. IR (cm^{-1}): 2670 (w), 2135 (w), 2089 (w), 1655 (m), 1612 (m), 1579 (w), 1340 (m), 1299 (m), 1262 (s), 1213 (m), 1087 (m), 1066 (m), 1029 (m), 923 (w), 866 (m), 849 (s), 801 (s), 740 (w), 629 (w), 615 (w), 590 (w), 553 (w), 528 (w), 509 (w), 449 (w). Anal. Calcd for $C_{68}H_{80}N_4Al_2I_2$: C, 64.76; H, 6.39; N, 4.44. Found: C, 64.71; H, 6.68; N, 3.90. M.p. = 171–175 °C.

Cp*GaI$_2$•Et$_2$O (4). The literature procedure for synthesizing Cp*GaI$_2$ was modified.[14] A suspension of GaI$_3$ (5.0 g, 11 mmol) in *n*-hexane (30 mL) was brought to reflux under an inert atmosphere provided by an argon-filled balloon. On a schlenk-line, a solution of Cp*SiMe$_3$ (2.3 g, 11 mmol) in *n*-hexane (15 mL) was prepared, and added dropwise to the solution of GaI$_3$ by cannula. After 0.5 hrs the red solution was decanted via cannula, while at reflux, without transferring the black decomposition products. Following evaporation of the volatile components Et$_2$O was added (10 mL), resulting in a yellow solution. Filtration and storage at -35 °C resulted in yellow crystals of pure **5**, which were isolated by filtration and used immediately (4.4 g, 82%). ^{1}H NMR (500 MHz, C_6D_6): δ 0.76 (t, *J* = 7 Hz, 6 H, $(CH_2C\mathit{H}_3)_2O$), 1.80 (s, 15 H, $C_5(C\mathit{H}_3)_5$), 3.48 (q, *J* = 7 Hz, 4 H, $(C\mathit{H}_2CH_3)_2O$). ^{13}C NMR (125 MHz, C_6D_6): δ 12.12, 13.86, 68.24, 121.16. Samples of **5** were extremely unstable and found to decompose in the solid state in under 5 minutes. An infra-red spectrum, melting point, and elemental analysis could not be determined.

Alternative synthesis of Cp*GaGa(I)$_2$Cp*. A solution of **5** (1.0 g, 2.0 mmol) in toluene (10 mL) was added to Na/K alloy prepared from Na° (18 mg, 0.78 mmol) and K° (57 mg, 1.5 mmol) in toluene (5 mL). The solution was stirred at room-temperature for 12 h, filtered, and stored at -10 °C for seven days. The product was isolated as pale yellow crystals following filtraton (0.18 g, 27%). Analytical data for (Cp*GaGa(I)$_2$Cp*) were consistent with those reported in the literature.[15]

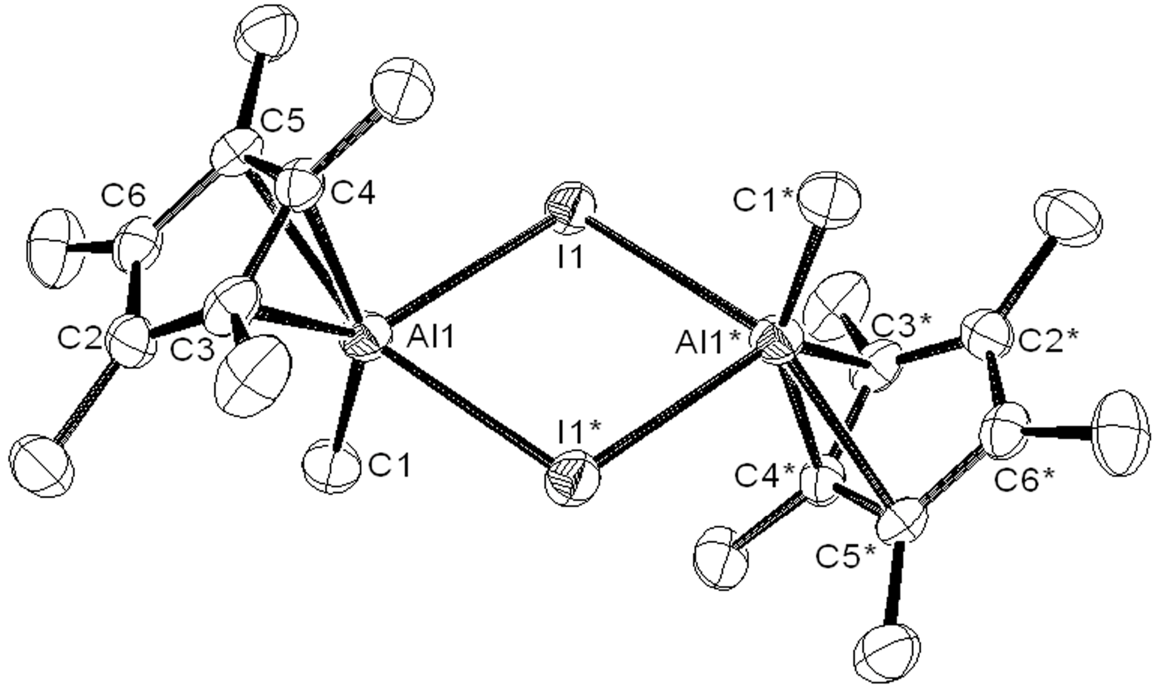

Figure S1. Molecular structure of [Cp*AlMe(μ-I)]$_2$, **2**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogens have been removed for clarity.

Table S1. Summary of crystallographic data collection and refinement for **1**, **2**, and **3**.

Crystal Data	1	2	3•(*n*-pentane)$_{0.5}$
empirical formula	$C_{20}H_{30}Al_2I_2$	$C_{22}H_{36}Al_2I_2$	$C_{70.5}H_{86}Al_2I_2N_4$
formula weight (g/mol)	578.2	608.27	1297.19
T (°K)	113(2)	157(2)	150(2)
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1$/n	$P2_1$/n	$P\bar{1}$
a (Å)	8.7521(12)	8.516(3)	10.6194(10)
b (Å)	14.660(2)	9.716(4)	15.9477(15)
c (Å)	18.022(2)	15.352(6)	21.317(2)
α (°)	90	90	105.315(2)
b (°)	93.253(2)	92.465(5)	94.491(2)
g (°)	90	90	102.408(1)
volume (Å^3)	2308.7(5)	1269.1(9)	3365.5(5)
Z	4	2	2
density (calcd) (M g/m^3)	1.664	1.592	1.280
crystal habit, color	plate, yellow	plate, colorless	rod, yellow
absorption coefficient (cm^{-1})	2.801	2.552	1.246
crystal size (mm)	0.51 x 0.47 x 0.06	0.70 x 0.15 x 0.15	0.15 x 0.10 x 0.06
radiation	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å	synchrotron, 0.77490 Å
θ range for data collection (°)	3.45 to 24.72	3.38 to 24.70	2.50 to 30.21
no. reflns collected	10124	5355	41370
no. of data/restrnts/params	3886/0/227	2127/0/124	15352/9/752
goodness-of-fit on F^2	1.047	1.049	1.033
R_{int}	0.0202	0.0324	0.0727
R_1, wR_2 ($I > 2\sigma(I)$)	0.0202, 0.0528	0.0187, 0.0500	0.0563, 0.1330
R_1, wR_2 (all data)	0.0231, 0.0537	0.0205, 0.0509	0.0868, 0.1503
largest diff. peak and hole (e Å-3)	0.746, -0.944	0.368, -0.353	1.000, -1.206

Table S2. Selected Bond Distances (Å) and Angles (deg) for **1**, **2**, and **3**.

1		**2**		**3**			
Al(1)-Al(2)	2.5321(10)	Al(1)–C(1)	1.942(2)	Al(1)–I(1)	2.5637(13)	I(1)–Al(1)–N(1)	102.90(12)
Al(1)–Cp$_{cent1}$	1.8924(7)	Al(1)–C(2)	2.479(2)	Al(1)–N(1)	1.734(3)	Al(1)–N(1)–C(1)	172.6(3)
Al(2)–Cp$_{cent2}$	1.8914(7)	Al(1)–C(3)	2.263(2)	N(1)–C(1)	1.271(5)	C(6)–C(1)–C(2)	115.3(3)
Al(1)–I(1)	2.6400(8)	Al(1)–C(4)	2.103(2)	C(1)–C(2)	1.491(6)	C(1)–C(2)–C(3)	120.6(4)
Al(2)–I(2)	2.6384(8)	Al(1)–C(5)	2.258(2)	C(2)–C(3)	1.354(5)	C(2)–C(3)–C(4)	123.8(4)
Cp$_{cent1}$–Al(1)-I(1)	128.74(3)	Al(1)–C(6)	2.464(2)	C(3)–C(4)	1.473(5)	C(3)–C(4)–C(5)	113.2(3)
Cp$_{cent1}$–Al(1)–Al(2)	132.19(4)	Al(1)–I(1)	2.8231(13)	Al(2)–C(4)	2.004(4)	C(4)–Al(2)–I(2)	117.20(12)
I(1)–Al(1)–Al(2)	98.70(3)	Al(1)–I(1)–Al(1*)	93.99(2)	Al(2)–I(2)	2.4867(12)	I(2)–Al(2)–N(3)	122.98(8)
Cp$_{cent2}$–Al(2)-I(2)	129.28(3)	I(1)–Al(1)–I(1*)	86.01(2)	Al(2)–N(2)	1.928(3)	N(2)–Al(2)–N(4)	66.16(13)
Cp$_{cent2}$–Al(2)–Al(1)	130.54(4)	C(1)–Al(1)–I(1)	99.86(9)	Al(2)–N(3)	2.400(3)	N(2)–N(3)–N(4)	107.2(3)
I(2)–Al(2)–Al(1)	99.77(3)	C(1)–Al(1)–C(4)	152.01(10)	Al(2)–N(4)	1.942(3)		
				N(2)–N(3)	1.327(4)		
				N(3)–N(4)	1.297(4)		
				N(2)–C(45)	1.419(4)		
				N(4)–C(35)	1.486(5)		

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