Organometallics **1995,** *14,* 495−501

Structural Studies on Mesitylaluminum Addition Compounds

Mark S. Lalama, Jeff Kampf, David G. Dick, and John P. Oliver*

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received May 5, 1994[⊗]

Four mesitylaluminum derivatives, $Mes_3Al\cdot(4\text{-picoline})(C_7H_8)_{0.5}$ (**1**), $EtMes_2Al\cdot THF$ (**2**), $Mes_2ClAl\cdot THF$ (**3**), and $[Mes_2Al(\mu\text{-}Cl)]_2$ (**4**) (Mes = 2,4,6-trimethylphenyl), have been prepared and their structures determined by single crystal X-ray diffraction methods. Compound **1** crystallizes in the monoclinic space group $C2/c$ (No. 15): $a = 43.784(15)$ Å, $b = 8.901(1)$ Å, $c = 16.760(2)$ Å, $\beta = 104.02(2)°$, $Z = 8$, $R = 10$, and $R_w = 9.9$. Compound **2** crystallizes in the orthorhombic space group $P2_12_12_1$ (No. 19): $a = 12.057(9)$ Å, $b = 13.490(3)$ Å, $c = 14.037(2)$ Å, $Z = 4$, $R = 5.4$, and $R_w = 3.9$. The halide derivative **3** crystallizes in the primitive monoclinic space group $P2_1/a$ (No. 14): $a = 17.18(1)$ Å, $b = 14.754(2)$ Å, $c = 17.316(2)$ Å, $\beta = 92.74(3)°$, $Z = 8$, $R = 6.5$, and $R_w = 2.4$. The base-free compound **4** exists as a dimer and crystallizes in the space group $P2_1/c$ (No. 14): $a = 12.288(2)$ Å, $b = 15.824(3)$ Å, $c = 9.095(2)$ Å, $\beta = 108.43(2)°$, $Z = 4$, $R = 5.4$, and $R_w = 5.9$. The distortion associated with **1**, **2**, and **3** relative to the parent monomeric molecule, Mes_3Al, is discussed with respect to substitution of the mesityl group for the Cl and Et ligands.

Introduction

Bulky substituents have been widely used in main group chemistry to stabilize highly reactive compounds or species with unique structures.[1−6] The synthesis of such compounds is of current interest due to their novel chemistry and structural features. For example, the halide complexes have been demonstrated to be valuable precursors to divalent Group 3 compounds.[7−10] We have established that Mes_3Al is a three-coordinate, monomeric molecule in which the mesityl group affords a very bulky unit with the ortho methyl groups providing significant steric hindrance/protection of the metal center and preventing formation of the commonly observed carbon-bridged aluminum dimer.[3] The molecule was shown to have an open pocket on either side of the aluminum atom which might accommodate a basic moiety. Seidel established that the THF adduct, $Mes_3Al\cdot THF$,[11] can be formed, and our examination of its structure shows that the THF molecule binds directly to the aluminum.[12] The geometry of the resulting addition compound is distorted from that of other simple adducts. To further explore the effects of the base size and substitution on the geometry around the aluminum atom, we have prepared and structurally characterized $Mes_3Al\cdot(4\text{-picoline})(C_7H_8)_{0.5}$ (**1**), $EtMes_2Al\cdot THF$ (**2**), $Mes_2ClAl\cdot THF$ (**3**), and $[Mes_2Al(\mu\text{-}Cl)]_2$ (**4**). The structural observations resulting from this work are discussed with respect to related Group 13 organometallic complexes containing sterically-demanding ligands.

Experimental Section

(A) General Procedures and Information. The compounds under investigation are both air and water sensitive, so all reactions and manipulations were carried out using standard Schlenk line and glovebox techniques. Argon was purified by passing it through a series of columns containing Deox catalyst (Alfa), sodium hydroxide, and calcium chloride. All solvents used were dried using standard techniques,[13] and all glassware was oven dried. The alkylaluminum halides, $EtAlCl_2$ (1.8 M solution in toluene), $MeAlCl_2$ (1.0 M solution in hexane), 4-picoline, and 2-bromomesitylene were purchased from Aldrich and used as received. Mes_3Al, $Mes_3Al\cdot THF$, and MesMgBr were prepared according to the literature methods.[3,12] Aluminum trichloride was purchased from EM Science and sublimed using a high-vacuum system prior to use. ^1H and ^{13}C NMR spectra were recorded on a General Electric QE 300 NMR or a Varian Gemini-300 spectrometer at ambient temperature. The proton chemical shifts were referenced to C_6D_5H (δ = 7.15 ppm), and the carbon resonances were referenced to C_6D_6 (δ = 128.0 ppm). Elemental analyses on selected compounds were performed by Galbraith Laboratories, Knoxville, TN. Melting points were recorded on a Haake-Buchler apparatus in sealed capillaries and are reported uncorrected. Mass spectrometry data were obtained on a Kratos MS80 RFA mass spectrometer with electron impact ionization at 70 eV, and IR spectra were recorded as Nujol mulls on a Nicolet DX20 FTIR spectrometer.

Synthesis of $Mes_3Al\cdot(4\text{-picoline})(C_7H_8)_{0.5}$ (1). The THF adduct of Mes_3Al (0.500 g, 1.09 mmol) was dissolved in 50 mL of toluene. A 0.11 mL (1.1 mmol) portion of 4-picoline was added at room temperature, and the mixture was stirred overnight. The resulting solution was concentrated, yielding a white product which was recrystallized from hot toluene: mp 169 °C dec; ^1H NMR (C_6D_6, δ, ppm) 1.37 (s, 3H, 4-CH_3-

---

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1994.

(1) Leman, J. T.; Barron, A. R. *Organometallics* **1989,** *8,* 2214.

(2) Petrie, M. A.; Olmstead, M. M.; Hope, H.; Bartlett, R. A.; Power, P. P. *J. Am. Chem. Soc.* **1993,** *115,* 3221.

(3) Jerius, J. T.; Hahn, J. M.; Rahman, A. F. M. M.; Mols, O.; Ilsley, W. H.; Oliver, J. P. *Organometallics* **1986,** *5,* 1812.

(4) Ranaivonjatovo, H.; Escudié, J.; Couret, C.; Declercq, J.-P.; Dubourg, A.; Satgé, J. *Organometallics* **1993,** *12,* 1674.

(5) Beachley, O. T., Jr.; Churchill, M. R.; Pazik, J. C.; Ziller, J. W. *Organometallics* **1986,** *5,* 1814.

(6) Baines, K. M.; Cooke, J. A. *Organometallics* **1992,** *11,* 3487.

(7) Uhl, W. *Z. Naturforsch.* **1988,** *43b,* 1113.

(8) Pluta, C.; Pörschke, K.-R.; Krüger, C.; Hildenbrand, K. *Angew. Chem., Int. Ed. Engl.* **1993,** *32,* 388.

(9) Uhl, W.; Vester, A.; Kaim, W.; Poppe, J. *J. Organomet. Chem.* **1993,** *454,* 9.

(10) Wehmschulte, R. J.; Ruhlandt-Senge, K.; Olmstead, M. M.; Hope, H.; Sturgeon, B. E.; Power, P. P. *Inorg. Chem.* **1993,** *32,* 2983.

(11) Seidel, W. *Z. Anorg. Allg. Chem.* **1985,** *524,* 101.

(12) De Mel, V. S. J.; Oliver, J. P. *Organometallics* **1989,** *8,* 827.

(13) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*; John Wiley & Sons: New York, 1986.

0276-7333/95/2314-0495$09.00/0

pyridine), 2.10 (s, 1.5H, PhCH_3), 2.26 (s, 9H, *p*-Me of Mes), 2.44 (s, 18H, *o*-Me of Mes), 5.96 (d, 2H, J_{H-H} = 5 Hz, *m*-H of 4-picoline), 6.89 (s, 6H, *m*-H of Mes), 6.99–7.13 (m, 2.5H, toluene), 8.41 (d, 2H, J_{H-H} = 5 Hz, *o*-H of 4-picoline); $^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm) 21.26 (*p*-Me of Mes), 25.94 (*o*-Me of Mes), 21.36 (Me-pyridine), 20.55 (Ph*Me*), 125.06, 125.64, 128.32, 128.50, 129.27, 136.29, 146.18, 149.41, 150.24 (aryl).

Synthesis of $EtMes_2Al·THF$ (2). A solution of $EtAlCl_2$ in toluene (1.8 M, 58.2 mL, 103 mmol) was added dropwise to 2 equiv of the mesityl Grignard reagent at 0 °C. The reaction mixture was refluxed for 2 h and stirred overnight. The solvent was removed under vacuum and the crude product extracted twice with hot toluene (~300 mL). The volume of the toluene extract was reduced by 50%, resulting in the precipitation of a crude product identified primarily as magnesium salts. The supernatant was decanted and the toluene removed under vacuum, yielding a white solid which was washed with pentane. The solid was recrystallized from benzene at approximately 5 °C, collected, and identified as $EtMes_2Al·THF$: yield, 75%; mp 166–169 °C; ^1H NMR (C_6D_6, δ, ppm) 0.50 (q, 2H, $-CH_2CH_3$), 1.07 (m, 4H, 3,4-H of THF), 1.21 (t, 3H, $-CH_2CH_3$), 2.25 (s, 6H, *p*-Me), 2.43 (s, 12H, *o*-Me), 3.57 (m, 4H, 2,5-H of THF), 6.85 (s, 4H, *m*-H); ^{13}C NMR (C_6D_6, δ, ppm) 7.02 ($-CH_2CH_3$), 10.65 ($-CH_2CH_3$), 21.28 (*p*-Me), 24.84 (THF), 25.50 (*o*-Me), 71.40 (THF), 127.69 (*m*-Ar), 136.22 (*p*-Ar), 145.39 (*o*-Ar), 147.06 (*ipso*-C). Anal. Calcd (found) for $C_{24}H_{35}AlO$: C, 78.65 (76.42); H, 9.63 (9.28).

Synthesis of $Mes_2ClAl·THF$ (3). A solution of $AlCl_3$ in THF was prepared by placing THF (~150 mL) in a flask which was then cooled to −78 °C. The $AlCl_3$ (13.30 g, 100 mmol) was added slowly with stirring. The solution was brought to room temperature and added dropwise to 2 equiv of the mesityl Grignard solution at 0 °C. After addition of the aluminum halide, the mixture was allowed to warm to room temperature and then was refluxed for 2 h and allowed to stir overnight. The solvent was removed under reduced pressure, and the remaining solid was extracted with warm toluene (~60 °C, ~800 mL). Concentration of this solution followed by addition of pentane yielded a white solid which was recrystallized from toluene at −20 °C and identified as $Mes_2ClAl·THF$: yield, 70%; mp 155–159 °C; ^1H NMR (C_6D_6, δ, ppm) 1.01 (m, 4H, 3,4-H of THF), 2.22 (s, 6H, *p*-Me), 2.56 (s, 12H, *o*-Me), 3.67 (m, 4H, 2, 5-H of THF), 6.85 (s, 4H, *m*-H); ^{13}C NMR (C_6D_6, δ, ppm) 20.90 (*p*-Me), 24.41 (THF), 25.37 (*o*-Me), 72.39 (THF), 127.88 (*m*-Ar), 137.18 (*p*-Ar), 142.90 (*ipso*-C), 145.41 (*o*-Ar). Anal. Calcd (found) for $C_{22}H_{30}AlClO$: C, 70.86 (69.75), H, 8.11 (8.11).

Preparation of $[Mes_2Al(\mu\text{-}Cl)]_2$ (4). Trimesitylaluminum (0.500 g, 1.30 mmol) was added to 0.5 equiv of $AlCl_3$ in benzene. The mixture was stirred overnight, during which time the trihalide disappeared. The solvent was removed under reduced pressure, and the residue was recrystallized from hexane at −20 °C: yield, 0.670 g, 57%; mp 160–161 °C; ^1H NMR (C_6D_6, δ, ppm) 2.10 (s, 6H, *p*-Me of Mes), 2.44 (s, 12H, *o*-Me of Mes), 6.67 (s, 4H, aryl of Mes); $^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm) 21.19 (*p*-Me of Mes), 25.15 (*o*-Me of Mes), 127.38, 128.32, 139.30, 145.34 (aryl); IR (Nujol, ν, cm^{-1}) 1603 (s), 1057 (m), 1027 (m), 951 (w), 845 (s), 614 (s), 541 (m); MS (EI, *m*/*e*, relative intensity) 549 (M^+ − Cl − Me − H, 0.1), 446 (M^+ − Mes − Cl, 0.5), 300 (Mes_2AlCl, 14.5), 285 (Mes_2AlCl − Me, 3.4), 265 (Mes_2Al, 36.7), 181 (MesAlCl, 6.8).

Synthesis of $Mes_2MeAl·THF$ (5). A 1.0 M hexane solution of $MeAlCl_2$ (51.5 mL, 52 mmol) was added dropwise to 2 equiv of MesMgBr in THF at 0 °C. The reaction mixture was refluxed for 2 h and stirred overnight. The product was isolated using the procedure described for **3**: yield, 75%; mp 136–140 °C; ^1H NMR (C_6D_6, δ, ppm) −0.06 (s, 3H, $AlCH_3$), 0.96 (m, 4H, THF), 2.27 (s, 6H, *p*-Me), 2.48 (s, 12H, *o*-Me), 3.50 (br, 4H, THF), 6.89 (s, 4H, *m*-H); ^{13}C NMR (C_6D_6, δ, ppm) −4.46 ($AlCH_3$), 21.26 (*p*-Me), 24.75 (THF), 25.61 (*o*-Me), 71.52 (THF), 127.79 (*m*-Ar), 136.35 (*p*-Ar), 145.46 (*o*-Ar), 147.37 (*ipso*-C).

(B) X-ray Data Collection and Structure Refinement. Crystals of suitable quality were prepared using the procedures described above. Crystals of **1**–**4** were sealed in thin-walled glass capillaries under an argon atmosphere. Diffraction data for **1** and **4** were collected on a Nicolet $P2_1$ diffractometer using Mo Kα radiation. Data for **2** were collected on a Nicolet P3/V diffractometer using Cu radiation while data for **3** were obtained from a Nicolet R3 diffractometer using Mo Kα radiation. The initial orientation matrices were obtained from machine-centered reflections selected from rotation photographs. These data were used to determine the crystal systems. Rotation photographs around each axis were consistent with monoclinic (**1**, **3**, **4**) and orthorhombic (**2**) crystal systems. Ultimately, 25 high-angle reflections were used to determine the final cell constants and orientation matrices. Systematic absences indicated that **1** could belong to the space group *C*2/*c* or *Cc*. Wilson statistics suggested a centrosymmetric structure, and therefore the space group *C*2/*c* was chosen. The assignment of this space group was confirmed by successful refinement of the structure. The space groups $P2_12_12_1$, $P2_1/a$ and $P2_1/c$ were unambiguously determined from systematic absences for **2**, **3**, and **4**, respectively. No absorption corrections were applied to the data since in all cases the absorption coefficients are small (1–8 cm^{-1}). Three standard reflections were collected every 97 reflections, revealing that **1**, **2**, **3**, and **4** decayed 1, 3, 7, and 6%, respectively. Selected X-ray data and structural parameters are listed in Table 1.

For **2** and **3**, the data reduction was carried out using SHELXTL programs,[14] and the data refinement was performed with SHELX-76.[15] Structures **1** and **4** were refined using SHELXTL PC.[16] Scattering factors[17] for neutral non-hydrogen atoms were used and the data were corrected for Lorentz and polarization effects. Direct methods were used to determine the heavy atom positions for all four compounds. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. Full-matrix, least-squares refinement of positional and thermal parameters for non-hydrogen atoms was carried out by minimizing the function $\sum(w|F_o| - |F_c|)^2$. The methyl groups were treated as rigid rotors, with a C−H bond distance of 0.96 Å and H−C−H angles of 109.4°. Their isotropic thermal parameters were fixed either at 1.2 times the isotropic thermal parameter of the contiguous carbon atom (**2** and **3**) or at 0.08 Å^2 (**1** and **4**). All hydrogen atom positional parameters were allowed to ride with their parent carbon atoms during subsequent refinement.

In the final cycles of refinement in **1**, the Al and N atoms were refined anisotropically. All other atoms were refined isotropically because of the limited size of the data set. In **2**, **3**, and **4**, all non-hydrogen atoms were refined anisotropically. The asymmetric unit of **1** contains one independent molecule and one-half of a molecule of toluene in the asymmetric unit, the atoms of which occupy general positions. The toluene molecule was disordered and was located near the center of inversion. Its position was located from a difference Fourier map. It occupied two positions with interchange of the toluene methyl group. It was refined as a rigid group, with d_{ring} = 1.395 ± 0.05 Å and d_{methyl} = 0.96 Å, with a 50% occupancy factor for the two orientations of the toluene. One and two independent molecules occur in the asymmetric units of **2** and **3**, respectively, and one-half of the dimer in the asymmetric unit of **4**. All observed reflections were used for the refinement of **1**, but three, six, and two reflections were excluded during the refinement of **2**, **3**, and **4**, respectively. The residual

---

[14] Sheldrick, G. M. *SHELXTL*; University of Göttingen: Göttingen, Federal Republic of Germany, 1978.

[15] Sheldrick, G. M. *SHELX-76*; University Chemical Laboratory: Cambridge, England, 1976.

[16] *SHELXTL PC*; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1990.

[17] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV (present distributor, D. Reidel: Dordrecht).

Table 1. Selected Experimental Parameters for the X-ray Diffraction Study of $Mes_3Al{\cdot}(4\text{-picoline})(C_7H_8)_{0.5}$ (1), $EtMes_2Al{\cdot}THF$ (2), $Mes_2ClAl{\cdot}THF$ (3), and $[Mes_2Al(\mu\text{-}Cl)]_2$ (4)

	1	2	3	4
formula	$C_{36.5}H_{40}NAl$	$C_{24}H_{35}OAl$	$C_{22}H_{30}OClAl$	$C_{18}H_{22}AlCl$
mol wt	519.71	366.52	372.91	300.81
space group	$C2/c$ (No. 15)	$P2_12_12_1$ (No. 19)	$P2_1/a$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	43.784(15)	12.057(9)	17.18(1)	12.288(2)
b (Å)	8.901(1)	13.490(3)	14.754(2)	15.824(3)
c (Å)	16.760(2)	14.027(2)	17.316(2)	9.095(2)
β (deg)	104.02(2)	90.00	92.74(3)	108.43(2)
V (Å^3)	6337(2)	2281(2)	4384(3)	1678.2(5)
Z	8	4	8	4
D_{calc} (g/cm^3)	1.089	1.067	1.130	1.191
radiation (Å)	Mo Kα	Cu Kα	Mo Kα	Mo Kα
2θ range (deg)	4.5−45.0	0−110	5−50	5−50
F(000) (electrons)	2232	800	1600	640
no. of data collected	4310	3297	7935	3201
no. of unique reflns	4172	2882	7074	2945
no. of obsd reflns	1875 ($F_o \geq 4\sigma F_o$)	2465 ($F_o \geq 4\sigma F_o$)	3396 ($F_o \geq 3\sigma F_o$)	1450 ($F_o \geq 4\sigma F_o$)
μ (cm^{-1})	0.88	8.04	2.18	2.69
refined variables	326	236	452	175
R^a	0.10	0.0542 (0.0561)^c	0.065	0.054
$R_w{}^b$	0.099	0.0391 (0.0405)^c	0.024	0.059
max shift/esd	0.000	0.003	0.002	0.000

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [c] Bracketed values are for the opposite enantiomer.

Table 2. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\times 10^3$) for the Non-Hydrogen Atoms of $Mes_3Al{\cdot}(4\text{-picoline})$ (1)

Atom	x	y	z	$U_{eq}{}^a$
Al(1)	3841(1)	1731(4)	7931(2)	38(1)
N(1)	3675(2)	0(9)	7143(4)	37(4)
C(1)	4021(2)	3360(11)	7356(5)	34(3)
C(2)	4223(2)	4360(12)	7865(6)	38(3)
C(3)	4421(3)	5372(12)	7588(6)	47(3)
C(4)	4424(3)	5378(12)	6750(6)	45(3)
C(5)	4222(3)	4473(12)	6230(6)	44(3)
C(6)	4022(2)	3494(12)	6502(6)	39(3)
C(7)	4240(3)	4460(14)	8788(6)	57(3)
C(8)	4651(3)	6425(14)	6458(7)	70(4)
C(9)	3801(3)	2593(13)	5847(7)	58(3)
C(11)	3422(2)	2090(12)	8221(6)	38(3)
C(12)	3254(2)	3447(13)	8104(6)	44(3)
C(13)	2945(3)	3586(14)	8208(7)	63(4)
C(14)	2803(3)	2370(14)	8478(7)	61(4)
C(15)	2963(3)	1022(14)	8611(7)	62(4)
C(16)	3266(3)	867(12)	8486(6)	45(3)
C(17)	3385(3)	4862(13)	7799(7)	67(4)
C(18)	2469(3)	2504(18)	8590(9)	111(6)
C(19)	3406(3)	−693(12)	8667(7)	58(4)
C(21)	4196(2)	736(11)	8720(6)	37(3)
C(22)	4452(2)	45(12)	8470(6)	37(3)
C(23)	4664(3)	−880(13)	8956(6)	49(3)
C(24)	4651(2)	−1247(12)	9754(7)	47(3)
C(25)	4433(3)	−488(12)	10060(6)	45(3)
C(26)	4211(2)	445(12)	9572(6)	37(3)
C(27)	4505(3)	424(13)	7605(6)	54(3)
C(28)	4881(3)	−2348(13)	10278(7)	67(4)
C(29)	3990(2)	1285(12)	9993(6)	51(3)
C(31)	3817(2)	−1336(13)	7181(6)	40(3)
C(32)	3698(2)	−2513(12)	6654(6)	39(3)
C(33)	3423(3)	−2318(12)	6079(6)	42(3)
C(34)	3266(2)	−972(12)	6043(6)	43(3)
C(35)	3398(3)	130(12)	6593(6)	43(3)
C(36)	3293(3)	−3555(14)	5484(8)	79(4)
C(40) (Tol)	2482(3)	2585(24)	4405(5)	50
C(41) (Tol)	2747(3)	2892(25)	5031(7)	50
C(42) (Tol)	2729(3)	2811(25)	5853(6)	50
C(43) (Tol)	2457(4)	2245(27)	6039(6)	50
C(44) (Tol)	2210(3)	1712(23)	5414(8)	50
C(45) (Tol)	2228(4)	1826(25)	4590(7)	50
C(46) (Tol)	2483(4)	2864(26)	3497(6)	50

[a] $U_{eq} = {}^1/_3\Sigma_i\Sigma_j U_{ij}\, a_i{}^*a_j{}^*\bar{a}_i\bar{a}_j$.

electron densities of **1**−**4** are of no chemical significance. Positional and thermal parameters of the non-hydrogen atoms are presented in Tables 2−5. Selected bond distances and angles are given in Table 6. Complete listings of crystal and X-ray data collection parameters, bond distances and angles, hydrogen atom parameters, and anisotropic thermal parameters are deposited as supplementary material.

Results and Discussion

The monomeric aluminum compounds $EtMes_2Al{\cdot}THF$ (**2**), $Mes_2ClAl{\cdot}THF$ (**3**), and $Mes_2MeAl{\cdot}THF$ (**5**) were prepared by reaction of the Grignard reagent, MesMgBr, in THF with $EtAlCl_2$, $AlCl_3$, and $MeAlCl_2$, respectively. The chloro-bridged dimer $[Mes_2Al(\mu\text{-}Cl)]_2$ (**4**) was obtained through the exchange reaction of Mes_3Al and $AlCl_3$ in benzene. The halide adduct **3** was prepared previously from $MgMes_2$ and $AlCl_3$.[11] The picoline derivative $Mes_3Al{\cdot}(4\text{-picoline})(C_7H_8)_{0.5}$ (**1**) was obtained by the displacement of the THF in $Mes_3Al{\cdot}THF$ by addition of 4-picoline. These five products are obtained in good yields and in pure form as colorless crystalline materials by recrystallization from hydrocarbon solvents. The adducts are readily characterized by their ^1H and ^{13}C NMR spectra. Integration of the ^1H NMR spectra reveal that 1:1 adducts are formed with THF and 4-picoline. The proton and carbon chemical shifts of the mesityl, ethyl, and methyl ligands occur in the expected regions. Coordination of THF is indicated by the large upfield shift of the 3,4-protons from 1.73 ppm in free THF to 0.96−1.07 ppm for **2**, **3**, and **5**. This observation has been noted for several aluminum compounds containing halide, silyl, and organic ligands.[18] Large upfield shifts are also noted for the proton resonances of **1**. The methyl group and ortho protons of 4-picoline move upfield by approximately 1.0 ppm to 1.37 and 5.96 ppm, respectively.

All of these compounds are sensitive to moisture and oxygen. They possess greater kinetic stability than the base-free compounds, and the mixed ligand derivatives **2**, **3**, and **5** can be isolated in reasonably pure form, showing their stability toward redistribution of the organic groups. The compounds have slight solubility

---

(18) Sierra, M. L.; de Mel, V. S. J.; Oliver, J. P. *Organometallics* **1989**, *8*, 2312.

Table 3. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $EtMes_2Al·THF$ (2)

Atom	x	y	z	U_{eq}[a]
Al1	0.5047(1)	0.36047(9)	0.11641(9)	0.0635(5)
C1	0.5094(5)	0.5036(3)	0.0784(3)	0.064(2)
C2	0.4154(4)	0.5385(4)	0.0281(3)	0.070(2)
C3	0.4090(5)	0.6346(4)	−0.0068(4)	0.084(2)
C4	0.4923(6)	0.7006(4)	0.0047(4)	0.085(2)
C5	0.5850(5)	0.6719(4)	0.0541(3)	0.081(2)
C6	0.5941(4)	0.5743(4)	0.0919(3)	0.071(2)
C7	0.3180(4)	0.4703(4)	0.0091(4)	0.109(3)
C8	0.4862(5)	0.8064(3)	−0.0348(3)	0.121(3)
C9	0.7006(4)	0.5473(4)	0.1449(4)	0.101(3)
C10	0.5183(4)	0.2646(3)	0.0064(3)	0.062(2)
C11	0.4819(5)	0.1654(4)	0.0145(4)	0.081(2)
C12	0.4923(5)	0.0971(4)	−0.0589(4)	0.096(3)
C13	0.5382(5)	0.1217(5)	−0.1426(4)	0.099(3)
C14	0.5772(5)	0.2165(4)	−0.1554(4)	0.089(2)
C15	0.5659(4)	0.2867(4)	−0.0803(4)	0.072(2)
C16	0.4298(5)	0.1313(4)	0.1089(4)	0.138(3)
C17	0.5484(6)	0.0462(4)	−0.2234(4)	0.171(4)
C18	0.6133(4)	0.3885(4)	−0.0987(3)	0.102(3)
C19	0.3900(4)	0.3413(4)	0.2163(3)	0.083(2)
C20	0.3683(5)	0.4251(5)	0.2768(4)	0.140(4)
O1	0.6369(3)	0.3202(3)	0.1842(2)	0.075(1)
C21	0.7317(4)	0.2670(4)	0.1442(4)	0.097(3)
C22	0.7881(5)	0.2192(5)	0.2265(5)	0.130(3)
C23	0.7561(6)	0.2772(7)	0.3080(4)	0.192(5)
C24	0.6478(5)	0.3203(5)	0.2881(4)	0.121(3)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}\, a_i^* a_j^* \bar{a}_i \bar{a}_j$.

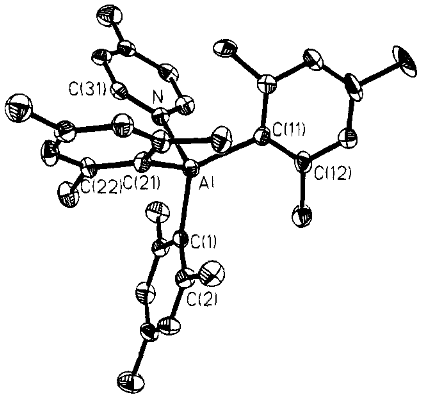

Figure 1. ORTEP diagram of $Mes_3Al·(4\text{-picoline})(C_7H_8)_{0.5}$ (**1**) with 30% thermal ellipsoids. The hydrogen atoms have been omitted for clarity. The lattice solvent molecule is not shown.

Table 4. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $Mes_2ClAl·THF$ (3)

Atom	x	y	z	U_{eq}[a]
Al1	0.8566(1)	0.0287(1)	0.5943(1)	0.0632(9)
Cl1	0.9733(1)	0.0696(1)	0.64062(9)	0.0639(7)
C1	0.8673(4)	−0.1020(4)	0.5678(4)	0.055(3)
C2	0.8588(4)	−0.1418(5)	0.4932(4)	0.056(3)
C3	0.8841(4)	−0.2298(5)	0.4803(4)	0.064(3)
C4	0.9157(4)	−0.2836(5)	0.5385(5)	0.066(3)
C5	0.9196(4)	−0.2491(5)	0.6129(4)	0.069(3)
C6	0.8970(4)	−0.1607(5)	0.6273(4)	0.066(3)
C7	0.8206(4)	−0.0918(4)	0.4257(3)	0.089(4)
C8	0.9461(4)	−0.3781(4)	0.5212(4)	0.105(4)
C9	0.9010(4)	−0.1295(4)	0.7109(4)	0.104(4)
C10	0.7689(4)	0.0814(5)	0.6506(4)	0.064(3)
C11	0.7702(5)	0.1700(5)	0.6821(4)	0.068(4)
C12	0.7064(6)	0.2050(5)	0.7179(4)	0.075(4)
C13	0.6385(6)	0.1587(6)	0.7243(5)	0.086(4)
C14	0.6341(5)	0.0725(6)	0.6939(5)	0.090(4)
C15	0.6977(5)	0.0351(5)	0.6585(4)	0.075(4)
C16	0.8404(4)	0.2305(5)	0.6751(4)	0.104(4)
C17	0.5694(5)	0.2027(5)	0.7600(4)	0.129(5)
C18	0.6855(4)	−0.0612(5)	0.6276(4)	0.113(4)
O1	0.8520(3)	0.1007(3)	0.5039(3)	0.065(2)
C19	0.9183(4)	0.1216(5)	0.4552(4)	0.084(4)
C20	0.8814(6)	0.1692(7)	0.3866(5)	0.157(6)
C21	0.8030(6)	0.1891(7)	0.3999(6)	0.143(6)
C22	0.7805(4)	0.1464(5)	0.4708(5)	0.103(4)
Al2	0.8834(1)	0.1869(1)	0.0690(1)	0.0593(9)
Cl2	1.0076(1)	0.1516(1)	0.0863(1)	0.0724(8)
C23	0.8827(4)	0.3193(4)	0.0502(4)	0.055(3)
C24	0.8604(4)	0.3653(5)	−0.0185(4)	0.066(3)
C25	0.8718(4)	0.4587(5)	−0.0257(4)	0.072(4)
C26	0.9027(4)	0.5107(5)	0.0329(5)	0.072(4)
C27	0.9219(4)	0.4674(6)	0.1011(4)	0.078(4)
C28	0.9120(4)	0.3743(5)	0.1111(4)	0.063(3)
C29	0.8222(4)	0.3154(4)	−0.0877(4)	0.121(4)
C30	0.9163(4)	0.6115(4)	0.0232(4)	0.105(4)
C31	0.9331(4)	0.3327(4)	0.1899(4)	0.099(4)
C32	0.8091(4)	0.1303(5)	0.1389(4)	0.054(3)
C33	0.8193(4)	0.0443(5)	0.1729(4)	0.062(3)
C34	0.7644(5)	0.0061(5)	0.2195(4)	0.070(4)
C35	0.6961(5)	0.0498(6)	0.2338(4)	0.070(4)
C36	0.6840(5)	0.1333(5)	0.2000(4)	0.080(4)
C37	0.7390(5)	0.1738(5)	0.1544(4)	0.065(3)
C38	0.8912(4)	−0.0134(4)	0.1599(4)	0.102(4)
C39	0.6352(4)	0.0060(5)	0.2823(4)	0.115(4)
C40	0.7166(4)	0.2659(4)	0.1202(4)	0.098(4)
O2	0.8646(3)	0.1191(3)	−0.0232(3)	0.063(2)
C41	0.9205(4)	0.1023(5)	−0.0822(4)	0.094(4)
C42	0.8749(6)	0.0625(8)	−0.1474(5)	0.136(6)
C43	0.8055(7)	0.0243(7)	−0.1177(6)	0.161(7)
C44	0.7927(4)	0.0677(5)	−0.0441(5)	0.106(4)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}\, a_i^* a_j^* \bar{a}_i \bar{a}_j$.

in hexane, moderate solubilty in aromatic solvents, and high solubility in polar solvents.

The results of the crystallographic study show that the three addition compounds $Mes_3Al·(4\text{-picoline})(C_7H_8)_{0.5}$ (**1**), $EtMes_2Al·THF$ (**2**), and $Mes_2ClAl·THF$ (**3**) have structures comparable to those of other amine and ether trialkyl- and triarylaluminum adducts.[19] A more detailed analysis of each of these structures follows. In **1**, a single molecular unit of $Mes_3Al·(4\text{-picoline})$ along with one-half of a molecule of toluene constitutes the asymmetric unit. The presence of the toluene has been confirmed by ^1H and ^{13}C NMR spectroscopy, but the coordinates for this molecule did not refine well. An ORTEP drawing of **1** is shown in Figure 1. The ORTEP diagrams for **2** and **3** are shown in Figures 2 and 3, respectively. The geometry around the Al atom in each of these can be described as a distorted tetrahedron. The six angles at the Al atom fall in the range of 94.2(4)–121.4(3)° for **1** and are similar to those observed in $Mes_3Al·THF$,[12] which fall between 91.4 and 120.3°. In **2** and **3**, where one of the Mes moieties has been replaced by an ethyl group or chlorine atom, the angles fall in the range of 97.4(2)–120.8(2)° for **2** and 98.6(2)–124.8(3)° for **3**. This wide distribution of angles can be attributed to steric interactions between the mesityl groups or the other substituents bound to the aluminum. The C–Al–N, C–Al–O, and Cl–Al–O angles for **1**, **2**, and **3** are listed in Table 6. The average C–Al–N angle is 102°. In **2** the average of the C–Al–O angles is 103.5°, and in **3** the average value of the C–Al–O angles is 106.4°, but if the Cl–Al–O angles are included, the average ligand to oxygen angle becomes 103.4°. The corresponding C–Al–C and C–Al–O angles in $Mes_3Al·THF$ average 116.2 and 101.5°,[12] and those in $(Me_3Al)_2·C_4H_8O_2$,

---

[19] Oliver, J. P. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; John Wiley: New York, 1985; Vol. 2, pp 789–826.

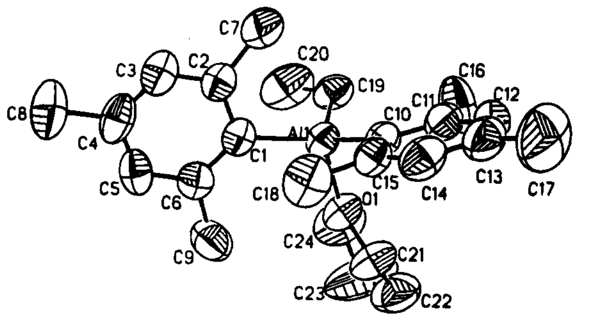

Figure 2. ORTEP diagram of EtMes$_2$Al·THF (**2**) with 50% thermal ellipsoids. The hydrogen atoms have been omitted for clarity.

Table 5. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (×10^3) for the Non-Hydrogen Atoms of [Mes$_2$Al(μ-Cl)]$_2$ (4)

Atom	x	y	z	U_{eq}[a]
Al(1)	−1197(1)	119(1)	567(2)	36(1)
Cl(1)	539(1)	830(1)	898(1)	43(1)
C(1)	−2354(3)	921(3)	−672(5)	35(2)
C(2)	−2369(4)	1720(3)	12(5)	40(2)
C(3)	−3158(4)	2330(3)	−735(6)	46(2)
C(4)	−3952(4)	2184(3)	−2166(6)	49(2)
C(5)	−3960(3)	1401(3)	−2832(5)	45(2)
C(6)	−3195(3)	774(3)	−2126(5)	39(2)
C(7)	−1566(4)	1920(3)	1607(5)	55(2)
C(8)	−4796(4)	2878(4)	−2946(7)	76(3)
C(9)	−3311(4)	−77(3)	−2928(6)	62(2)
C(11)	−1389(3)	−525(3)	2317(5)	37(2)
C(12)	−480(3)	−932(3)	3456(5)	38(2)
C(13)	−697(4)	−1481(3)	4527(5)	44(2)
C(14)	−1795(4)	−1635(3)	4571(5)	43(2)
C(15)	−2682(4)	−1223(3)	3498(5)	45(2)
C(16)	−2511(3)	−680(3)	2386(5)	43(2)
C(17)	756(3)	−773(3)	3577(5)	54(2)
C(18)	−2017(5)	−2247(3)	5712(6)	63(2)
C(19)	−3574(4)	−298(4)	1253(7)	78(3)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}\, a_i^* a_j^* \bar{a}_i \bar{a}_j$.

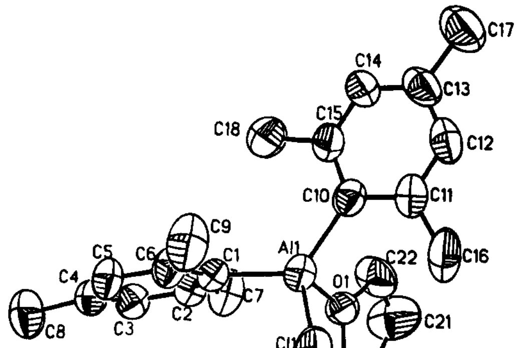

Figure 3. ORTEP diagram of Mes$_2$ClAl·THF (**3**) with 50% thermal ellipsoids. The hydrogen atoms have been omitted for clarity.

116.8 and 100.4°.[20] The deviations between the smallest L−Al−L (94°) and the largest (125°) angles in **1**, **2**, and **3** are nearly the same (Table 6) and are similar to that in Mes$_3$Al·THF.[12] Further, there is no pattern discernible in the distribution. These findings lead to the conclusion that the structures of addition compounds with two or three mesityl groups bound to the aluminum are determined by the steric requirements of the mesityl group. The sum of the L−Al−L angles (L = C, Cl) provides a measure of the planarity of the L$_3$Al unit. In **1**, **2**, and **3**, the sum is 347.8, 344.6, and 343.7° (av). These values are typical for aluminum addition compounds, with the small decrease indicating a small decrease in the steric interaction with substitution of Et or Cl for a Mes group.

The Al−C distances of **1**−**4** (Table 6) are in the range of 2.004−2.033 Å for the organic derivatives and 1.966 to 1.993 Å for those containing a chlorine atom and are typical of Al-C single bond lengths for a variety of organoaluminum compounds as noted earlier.[3,21] The average Al−Cl bond length in **3**, 2.206 Å, is longer by ~0.05 Å than that of MesAlCl$_2$·THF[21] and ~0.05 Å longer than the bond in AlCl$_3$·2THF[22] but is within the range expected for single Al−Cl bonds. The Al−N distance in **1** (2.045(8) Å) is similar to the Al−N distance in Me$_3$Al·quinuclidine (2.06(1) Å),[23] but longer than the distances found in Me$_2$IAl·NMe$_3$ (2.02 Å),[24] Cs$^+$[Me$_3$Al·N$_3$]$^-$ (1.97(1) Å)[25] and Me$_3$Al·NCCH$_3$ (2.02(1) Å).[26]

The Al−O distances in **2** and **3** are 1.934(4) and 1.894(5) Å (av) and are listed, along with Al−O distances for other adducts, in Table 7. The Al−O bond distances listed fall into three groups: those associated with trialkyl addition compounds with Al−O bond distances greater than 2.0 Å, those with aryl groups bound to aluminum which fall in the broad range of 1.9−1.97 Å and those with a halogen atom bound to aluminum with Al−O distances less than 1.9 Å. The Lewis acidity of the compounds follows this same pattern, with increasing acidity corresponding to decreasing Al−O bond length. On this basis, the increased Lewis acidity of **3** accounts for the shorter Al−O distance observed in this compound. The Al-O distance in MesAlCl$_2$·THF, at 1.852(1) Å, is the shortest in the mesityl derivatives while (Trip)AlBr$_2$·OEt$_2$ shows an Al−O distance of 1.865(11) Å.[21] The C−Al−O angle also appears to be correlated with the Lewis acidity of the aluminum derivative. As the acidity of the metal increases, the Al−O length decreases, and a corresponding increase in the C−Al−O angle is observed. Steric repulsion between the base and the mesityl groups does not affect the Al−O distance of ether adducts. In the adducts Me$_3$Al·OMe$_2$[27] and (Me$_3$Al)$_2$·*p*-dioxane,[20] the Al−O bond distances are 2.014(14) and 2.02(2) Å, respectively, while shorter distances are found for Bz$_3$Al·OEt$_2$[28] (1.901(4) Å) and (*o*-Tol)$_3$Al·OEt$_2$[29] (1.928(3) Å). In the mesityl derivatives Mes$_3$Al·THF,[12] **2**, and **3**, the Al−O bond distances are 1.969(5), 1.934(4), and 1.898(5) Å, respectively.

The structural determination of **4** completes the series Mes$_2$MCl (M = Al, Ga, In). An ORTEP diagram is

---

[20] Atwood, J. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1967**, *89*, 5362.

[21] Petrie, M. A.; Power, P. P.; Dias, H. V. R.; Ruhlandt-Senge, K.; Waggoner, K. M.; Wehmschulte, R. J. *Organometallics* **1993**, *12*, 1086.

[22] Cowley, A. H.; Cushner, M. C.; Davis, R. E.; Riley, P. E. *Inorg. Chem.* **1981**, *20*, 1179.

[23] Whitt, C. D.; Parker, L. M.; Atwood, J. L. *J. Organomet. Chem.* **1971**, *32*, 291.

[24] Atwood, J. L.; Milton, P. A. *J. Organomet. Chem.* **1973**, *52*, 275.

[25] Atwood, J. L.; Newberry, W. R. J., III. *J. Organomet. Chem.* **1975**, *87*, 1.

[26] Atwood, J. L.; Seale, S. K.; Roberts, D. H. *J. Organomet. Chem.* **1973**, *51*, 105.

[27] Haaland, A.; Samdal, S.; Stokkeland, O.; Weidlein, J. *J. Organomet. Chem.* **1977**, *134*, 165.

[28] Rahman, A. F. M. M.; Siddiqui, K. F.; Oliver, J. P. *J. Organomet. Chem.* **1987**, *319*, 161.

[29] Barber, M.; Liptak, D.; Oliver, J. P. *Organometallics* **1982**, *1*, 1307.

Table 6. Selected Bond Distances (Å) and Angles (deg) for $Mes_3Al{\cdot}(4\text{-picoline})(C_7H_8)_{0.5}$ (1), $EtMes_2Al{\cdot}THF$ (2), MesClAl·THF (3), and $[Mes_2Al(\mu\text{-}Cl)]_2$ (4)

				$Mes_2ClAl{\cdot}THF$ (**3**)					
$Mes_3Al{\cdot}(4\text{-picoline})(C_7H_8)_{0.5}$ (**1**)		$EtMes_2Al{\cdot}THF$ (**2**)		molecule 1		molecule 2		$[Mes_2Al(\mu\text{-}Cl)]_2$ (**4**)	
Al−C1	2.005(11)	Al−C1	2.004(4)	Al1−C1	1.993(7)	Al2−C23	1.980(7)	Al1−C1	1.972(4)
Al−C11	2.033(12)	Al−C10	2.020(5)	Al1−C10	1.992(8)	Al2−C32	1.985(7)	Al1−C11	1.966(5)
Al−C19	1.990(10)	Al−C19	1.986(5)	Al1−Cl1	2.207(3)	Al2−Cl2	2.204(3)	Al1−Cl1	2.346(2)
Al−N	2.045(8)	Al−O	1.934(4)	Al1−O1	1.890(5)	Al2−O2	1.898(5)	Al1−Cl1A	2.315(2)
Cl−Al−C11	118.9(4)	C1−Al−C10	114.3(2)	C1−Al1−C10	124.8(3)	C23−Al2−C32	121.1(3)	C1−Al1−C11	123.1(2)
C1−Al−C21	107.8(4)	C1−Al−C19	109.5(2)	C10−Al1−Cl1	114.3(2)	C32−Al2−Cl2	117.7(2)	Cl1−Al1−Cl1A	85.2(1)
C11−Al−C21	121.1(4)	C10−Al−C19	120.8(2)	C1−Al1−Cl1	104.8(2)	C23−Al2−Cl2	104.7(2)	Al1−Cl1−Al1A	94.8(1)
C1−Al−N	110.7(4)	C1−Al−O	112.2(2)	C1−Al1−O1	110.7(3)	C23−Al2−O2	112.5(3)		
C11−Al−N	94.2(4)	C10−Al−O	97.4(2)	C10−Al1−O1	100.5(3)	C32−Al2−O2	101.7(2)		
C21−Al−N	101.1(4)	C19−Al−O	101.0(2)	Cl1−Al1−O1	98.6(2)	Cl2−Al2−O2	96.6(2)		

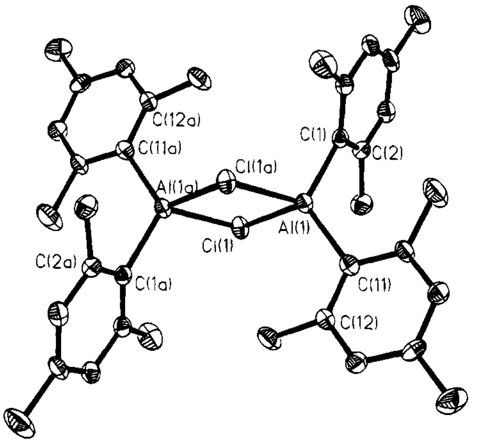

Figure 4. ORTEP diagram of $[Mes_2Al(\mu\text{-}Cl)]_2$ (**4**) with 30% thermal ellipsoids. The hydrogen atoms have been omitted for clarity.

Table 7. Structural Parameters of Aluminum Adducts as a Function of Lewis Acidity

Compound	C−Al−O (deg)	Al−O (Å)	Al−C (Å)
$Me_3Al{\cdot}OMe_2$[a]	98.7	2.014	1.973
$(Me_3Al)_2{\cdot}p\text{-dioxane}$[b]	100.4	2.02	1.97
$Mes_3Al{\cdot}THF$[c]	101.3	1.969	2.017
$Ph_2AlSi(SiMe_3)_3{\cdot}THF$[d]	103.2	1.927	1.985
$EtMes_2Al{\cdot}THF$[e]	103.5	1.934	2.012, 1.986 (Et)
$(o\text{-}Tol)_3Al{\cdot}OEt_2$[f]	103.8	1.928	1.990
$Bz_3Al{\cdot}OEt_2$[g]	105.6	1.901	1.986
$Mes_2ClAl{\cdot}THF$[e]	106.4	1.894	1.988
$TripAlBr_2{\cdot}OEt_2$[h]	107.6	1.865	1.976
$MesAlCl_2{\cdot}THF$[h]	115.2	1.852	1.969

[a] Reference 27. [b] Reference 20. [c] Reference 12. [d] Reference 18. [e] This work. [f] Reference 29. [g] Reference 28. [h] Reference 21.

shown in Figure 4. Like the Ga and In analogues, **4** exists in the solid state as a dimer containing a planar Al_2Cl_2 core. It is isomorphous with the gallium analogue.[21] The Al−Cl distances are 2.346(2) and 2.315(2) Å, and, like the Ga compound, the core is asymmetric. This feature has also been noted for $[Trip_2Al(\mu\text{-}Br)]_2$.[21] $[Mes_2In(\mu\text{-}Cl)]_2$ displays equivalent In−Cl bonds.[1] The average Al−Cl distance of **4** (2.329) is longer than the single Al−Cl bond in compounds such as **3** (2.206(4) Å), $EtCl_2Al{\cdot}P(SiMe_3)_3$ (2.114(4) and 2.156(4) Å), and $i\text{-}Bu_2ClAl{\cdot}P(SiMe_3)_3$ (2.179(4) Å)[30] but comparable to the distances observed for the bridging halides such as those in $[Me_2Al(\mu\text{-}Cl)]_2$ (2.303 Å).[31] The endocyclic Al−Cl−Al and Cl−Al−Cl angles are 90.6 and 89.4° and the exocyclic C−Al−C angle is 126.9°. The comparable endocyclic angles in the three compounds, $[Mes_2M(\mu\text{-}Cl)]_2$ (M = Al, Ga, and In), are 94.8, 95.9, and 96.5° (M−Cl−M) and 85.2, 84.1, and 83.5° (Cl−M−Cl), and the C−M−C angles are 122.7(2), 126.6(2), and 131.0°, respectively. In $[Trip_2Al(\mu\text{-}Br)]_2$, the exocyclic angle is 130.0(4)°.[21] These observations indicate that the intramolecular interactions between the Ar groups in $[Ar_2M(\mu\text{-}X)]_2$ have very little effect on either the endo- or the exocyclic angles in these compounds.

There are four major factors which determine the stability of Group 13 addition compounds: the Lewis acidity of the metal, which follows the order Al > Ga > In; the modification of the Lewis acidity by the substituents bound to the metal, which decreases from X > Ar > R (X = halogen; Ar = aryl, R = alkyl); the basicity of the ligand; and the steric interactions, which include those on the metal and that between the incoming base and the substituents bound to the metal. In the present system, the adducts $Mes_3Al{\cdot}OEt_2$, $Mes_3Al{\cdot}THF$, and $Mes_3Al{\cdot}4$-picoline increase in stability as a function of the basicity of the ligand. Diethyl ether and THF can be removed readily, while 4-picoline cannot be removed without additional decomposition of the compound. This order follows that expected for the bases. The heavier homologues Mes_3Ga[5] and Mes_3In[1] do not form stable adducts with Et_2O or THF. Similarly, in the neopentyl series, Np_3Al binds Et_2O,[32] Np_3Ga does not form a stable adduct with Et_2O but does with THF,[33] and Np_3In forms addition compounds only with very strong bases such as NMe_3.[34] The latter sequence follows the order of acidity expected for the metals.

Study of the organoaluminum derivatives in the absence of a coordinating ligand provides additional insight into the steric interactions. The ability of these compounds to form dimeric or trimeric aggregates is well established. The stability of the dimer in the series $[Ph_2Al(\mu\text{-}Ph)]_2 \geq [(2\text{-}MeC_6H_4)_2Al(\mu\text{-}2MeC_6H_4)]_2 > Mes_3Al$ decreases in the order shown, with Mes_3Al observed only as a monomer. The observation that $[Mes_2Al(\mu\text{-}Cl)]_2$ and $[Mes_2Ga(\mu\text{-}Cl)]_2$ are dimeric with chlorine bridges supports the earlier suggestion that the steric interference that prevents dimerization occurs at the bridging site. With more sterically demanding ligands,

---

(30) Wells, R. L.; McPhail, A. T.; Self, M. F.; Laske, J. A. *Organometallics* **1993**, *12*, 3333.

(31) Brendhaugen, K.; Haaland, A.; Novak, D. P. *Acta Chem. Scand.* **1974**, *A28*, 45.

(32) Beachley, O. T., Jr.; Victoriano, L. *Organometallics* **1988**, *7*, 63.

(33) Beachley, O. T., Jr.; Pazik, J. C. *Organometallics* **1988**, *7*, 1516.

(34) Beachley, O. T., Jr.; Spiegel, E. F.; Kopasz, J. P.; Rogers, R. D. *Organometallics* **1989**, *8*, 1915.

such as those found in $Trip_2GaCl$[21] and $Mes^*{}_2InBr$,[35] the halide derivatives are monomeric, indicating that the bulky substituents interact, preventing bridge formation.

Study of the $Ar_nR_{3-n}Al$ systems such as Mes_2MeAl and Mes_2EtAl is complicated by the exchange of groups and the possible formation of dimeric species with alkyl and/or aryl bridges. It is clear from the formation of the mixed species **2** and **5** stabilized by THF that mixed derivatives can be prepared.

In other compounds with bulky substituents, such as Np_3Al and $(Me_3SiCH_2)_3Al$, which are isostructural, the neopentyl derivative is monomeric,[32] while the (trimethylsilyl)methyl derivative is involved in a monomer−dimer equilibrium in solution.[36] Substitution of a hydride for one of the bulky substituents permits the formation of an equilibrium between dimers and trimers for $[Np_2Al(\mu\text{-}H)]_n$[32] and the formation of trimers for $(Me_3SiCH_2)_2AlH$.[37]

The mixed mesityl−alkyl derivatives remain to be studied, but with the reduced steric requirements of the methyl group, one may find associated species in solution.

Supplementary Material Available: Complete listings of crystal and X-ray data collection parameters, bond distances and angles, anisotropic thermal parameters for the non-hydrogen atoms, and atomic coordinates and isotropic thermal parameters for the hydrogen atoms (22 pages). Ordering information is given on any current masthead page.

OM940350S

---

(35) Rahbarnoohi, H.; Heeg, M. J.; Oliver, J. P. *Organometallics* **1994**, *13*, 2123.

(36) Nyathi, J. Z.; Ressner, J. M.; Smith, J. D. *J. Organomet. Chem.* **1974**, *70*, 35.

(37) Beachley, O. T., Jr.; Tessier-Youngs, C. *Organometallics* **1983**, *2*, 796.