metal-organic compounds

Trichlorido(1,3-dimethyl-2,3-dihydro-1*H*-imidazol-2-ylidene-κC^2)-aluminium(III)

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The title compound, [Al(C₅H₈N₂)Cl₃], was prepared by a thermolytic decomposition under high-vacuum conditions and presents a formal adduct of an Arduengo carbene, 1,3-dimethyl-1*H*-imidazol-2-ylidene, and aluminium trichloride. The Al atom adopts a pseudo-tetrahedral CCl₃ coordination environment. All N and C atoms, the Al atom, one of the Cl atoms, and all aromatic H atoms of the molecule lie on a mirror plane. As a result of the mirror symmetry of the molecule, the H atoms of all methyl groups are disordered between symmetry-equivalent positions.

Related literature

For related structurally characterized Arduengo carbene Al*X*₃ (*X* = Cl, I) adducts, see: Stasch *et al.* (2004); Ghadwal *et al.* (2009); Bantu *et al.* (2009). For thermolytic interconversion of sterically non-hindered 1,3-dialkyl-1*H*-imidazolium salts with BF₄⁻ and PF₆⁻ anions into Arduengo carbene adducts with BF₃ and PF₅, see: Tian *et al.* (2012). For the crystal structure of the precursor employed in the synthesis of the title compound, see: Tian *et al.* (2013). For a description of the Cambridge Structural Database, see: Allen (2002).

Experimental

Crystal data

[Al(C₅H₈N₂)Cl₃]	*V* = 1008.85 (14) Å³
M_r = 229.46	*Z* = 4
Orthorhombic, *Pnma*	Mo *K*α radiation
a = 8.9075 (7) Å	μ = 0.94 mm⁻¹
b = 7.3903 (6) Å	*T* = 296 K
c = 15.3253 (12) Å	0.40 × 0.38 × 0.20 mm

Data collection

Bruker SMART APEXII diffractometer	5094 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)	1062 independent reflections
	968 reflections with $I > 2\sigma(I)$
T_{min} = 0.706, T_{max} = 0.835	R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033	66 parameters
$wR(F^2)$ = 0.087	H-atom parameters constrained
S = 1.07	$\Delta\rho_{max}$ = 0.40 e Å⁻³
1062 reflections	$\Delta\rho_{min}$ = −0.43 e Å⁻³

Table 1
Selected bond lengths (Å).

Cl1—Al1	2.1193 (12)	Al1—C1	2.006 (3)
Cl2—Al1	2.1290 (7)	Al1—Cl2ⁱ	2.1291 (7)

Symmetry code: (i) $x, -y + \frac{1}{2}, z$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *SHELXTL* and *OLEX2*.

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supporting information

Trichlorido(1,3-dimethyl-2,3-dihydro-1*H*-imidazol-2-ylidene-*κC²*)aluminium(III)

Chong Tian, Xiaofei Gao, Qiao Chen, Wanli Nie and Maxim V. Borzov

S1. Comment

Structurally characterized Al*X*₃ (*X* = Cl, I) adducts with Arduengo carbenes (ACs) are known since 2004 (Stasch *et al.*, 2004) and are still few (Ghadwal *et al.*, 2009; Bantu *et al.*, 2009). Except of the first described representative, *viz.* trichlorido(1,3,4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-ylidene-*κC²*)aluminium (Stasch *et al.*, 2004), they all present complexes with sterically hindered ACs which bear either mesityl or 2,6-diisopropylphenyl substituents at the N-atoms. Of interest, in all four structurally characterized *X*₃Al—AC adducts, the Al atoms are in a tetrahedral coordination environment as shown by an analysis of the structures compiled in the Cambridge Structural Database (Allen, 2002) [CSD; Version 5.34, release May 2013; 4 entries, 4 fragments].

Preparation of all Al complexes mentioned above includes, as a step, generation of a free AC by deprotonation of a corresponding imidazolium salt with a strong base under mild conditions. This seriously limits the method due to the known thermal instability of sterically non-hindered ACs even in solution. Recently, we developed a facile route to BF₃ and PF₅ adducts with sterically non-hindered ACs by a thermolytic decomposition of related imidazolium salts with [BF₄⁻] and/or [PF₅⁻] anions under high-vacuum conditions [573–673 K, 1.3–2.0×10⁻¹ Pa; Tian *et al.* (2012)]. Heating of an equimolar mixture of 1,3-dimethyl-1*H*-imidazolium (hydrogen difluoride), [C₅H₈N₂⁺][HF₂⁻], (II), and AlCl₃ under the same conditions followed by re-crystallization precedures led to formation of the title compound (I), C₅H₈N₂AlCl₃, in a moderate yield (see Experimental for the details; for the crystal structure of (II), see: Tian *et al.*, 2013).

Compound (I) presents a formal adduct of an Arduengo carbene, 1,3-dimethyl-1*H*-imidazol-2-ylidene, and aluminium trichloride. The Al-atom adopts a pseudo-tetrahedral coordination environment, defined by the three Cl atoms and the carbene C atom (Table 1). All N- and C-atoms, the Al-atom, one of the Cl-atoms, and all aromatic H-atoms of the molecule lie on a mirror plane at (*x*, 1/4, *z*). The H-atoms of methyl groups are disordered between symmetry equivalent positions (Fig. 1).

S2. Experimental

Acetonitrile and toluene solvents were kept over and distilled from CaH₂ and/or Na/K alloy under Ar atmosphere, respectively. AlCl₃ was sublimed in high vacuum prior to use. ¹H NMR spectra were recorded on a Varian 400 INOVA instrument in CD₃CN at 400 MHz and 298 K, with the signal of the residual solvent protons [δ(H) = 1.94 p.p.m.] used as an internal reference.

The imidazolium salt (II) was prepared by a reaction of AgF (1.27 g, 10.0 mmol) and 1,3-dimethyl-1*H*-imidazolium iodide (2.24 g, 10.0 mmol) in distilled water (25 ml). The precipitate of AgI was filtered off, the filtrate was concentrated till dryness, and dried on the high-vacuum line (1.3–2.0×10⁻¹ Pa) at 323 K. Recrystallization from an ethanol/acetone mixture (1: 1) followed by double recrystallization from dry acetonitrile gave 0.93 g (6.8 mmol, 68%) of (II) as colorless crystals. ¹H NMR δ p.p.m.: 3.85 (s, 6H, CH₃), 7.44 (s, 2H, CH=CH), 9.45 (s, 1H, NCHN).

Compound (I): Crystalline (II) (0.93 g, 6.8 mmol) and $AlCl_3$ (0.91 g, 6.8 mmol) were placed into a small apparatus for distillation of high-melting compounds, the system was connected to the high-vacuum line ($1.3–2.0 \times 10^{-1}$ Pa) through a liq. N_2 cooled trap, evacuated, and heated. At approximately 423 K, the signs of melting were observed and then a strongly exothermic reaction accompanied by a gas evolution started. The temperature of the reaction mixture was then increased up to 573 K and the crude product was collected in the receiver as a reddish oil (reaction vessel temperature 573–673 K). The crude compound of (I) (1.03 g, 4.5 mmol, 66%) was allowed to crystallize in a refrigerator (270 K, 7 days). ^{1}H NMR δ p.p.m.: 3.98 (s, 6H, CH_3), 7.24 (s, 2H, CH=CH). Single crystal of (I) suitable for the X-ray diffraction analysis were grown by recrystallization of crude (I) from dry toluene, mounted in a Lindemann glass capillary (Ø 0.5 mm, glove box, N_2 atmosphere) and sealed off.

S3. Refinement

The H atoms were treated as riding atoms with distances C—H = 0.96 (CH_3), 0.93 Å ($C_{Ar}H$) and $U_{iso}(H) = 1.5 \, U_{eq}(C)$, 1.2 $U_{eq}(C)$, respectively. The H-atoms of the methyl groups are disordered due to the mirror symmetry of the aromatic ring; hance they were refined with half-occupancy.
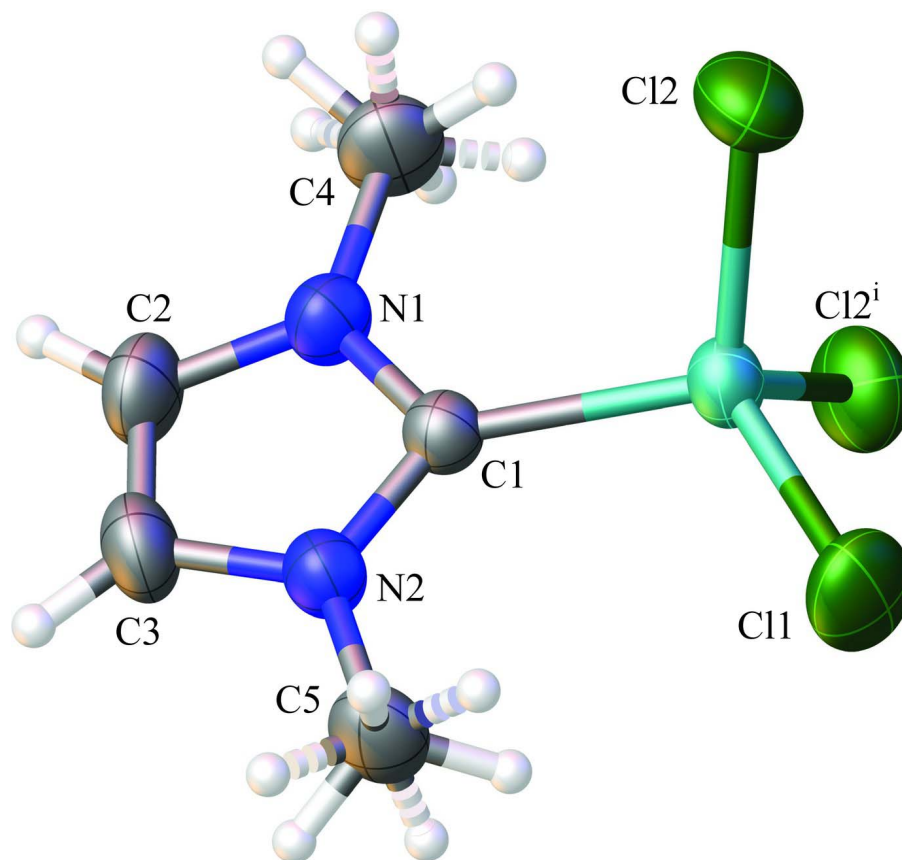

Figure 1

The molecular structure of compound (I). Thermal displacement ellipsoids are shown at the 50% probability level. Bonds to symmetry-equivalent disordered H-atoms are dashed. [Symmetry code: (i) x, $-y + 1/2$, z.]

Trichlorido(1,3-dimethyl-2,3-dihydro-1*H*-imidazol-2-ylidene-*κC*²)aluminium(III)

Crystal data

[Al(C₅H₈N₂)Cl₃]	$F(000) = 464$
$M_r = 229.46$	$D_x = 1.511$ Mg m⁻³
Orthorhombic, *Pnma*	Mo *Kα* radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ac 2n	Cell parameters from 4672 reflections
$a = 8.9075$ (7) Å	$\theta = 2.7–28.3°$
$b = 7.3903$ (6) Å	$\mu = 0.94$ mm⁻¹
$c = 15.3253$ (12) Å	$T = 296$ K
$V = 1008.85$ (14) Å³	Block, colourless
$Z = 4$	0.40 × 0.38 × 0.20 mm

Data collection

Bruker SMART APEXII diffractometer	5094 measured reflections
Radiation source: fine-focus sealed tube	1062 independent reflections
Graphite monochromator	968 reflections with $I > 2\sigma(I)$
Detector resolution: 8.333 pixels mm⁻¹	$R_{int} = 0.022$
phi and *ω* scans	$\theta_{max} = 26.0°$, $\theta_{min} = 2.6°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)	$h = -7 \rightarrow 10$
	$k = -9 \rightarrow 9$
$T_{min} = 0.706$, $T_{max} = 0.835$	$l = -18 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.033$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.087$	
$S = 1.07$	H-atom parameters constrained
1062 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2 + 0.7006P]$ where $P = (F_o^2 + 2F_c^2)/3$
66 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.40$ e Å⁻³
	$\Delta\rho_{min} = -0.43$ e Å⁻³

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	$U_{iso}*/U_{eq}$	Occ. (<1)
Cl1	−0.07057 (9)	0.2500	0.44325 (6)	0.0726 (3)	
Cl2	0.18333 (7)	0.01243 (9)	0.31551 (4)	0.0633 (2)	
Al1	0.15020 (9)	0.2500	0.39170 (5)	0.0399 (2)	
N1	0.4590 (3)	0.2500	0.46678 (15)	0.0428 (5)	

N2	0.3009 (3)	0.2500	0.57221 (14)	0.0405 (5)	
C1	0.3100 (3)	0.2500	0.48390 (17)	0.0362 (6)	
C2	0.5401 (3)	0.2500	0.5426 (2)	0.0546 (8)	
H2	0.6441	0.2500	0.5474	0.066*	
C3	0.4420 (4)	0.2500	0.6082 (2)	0.0537 (8)	
H3	0.4649	0.2500	0.6675	0.064*	
C4	0.5262 (4)	0.2500	0.3794 (2)	0.0589 (8)	
H4A	0.4611	0.1877	0.3395	0.088*	0.50
H4B	0.6217	0.1899	0.3813	0.088*	0.50
H4C	0.5399	0.3725	0.3600	0.088*	0.50
C5	0.1634 (4)	0.2500	0.6240 (2)	0.0569 (8)	
H5A	0.0870	0.3169	0.5938	0.085*	0.50
H5B	0.1825	0.3054	0.6796	0.085*	0.50
H5C	0.1303	0.1277	0.6327	0.085*	0.50

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0355 (4)	0.1078 (8)	0.0747 (6)	0.000	0.0014 (4)	0.000
Cl2	0.0725 (4)	0.0603 (4)	0.0570 (4)	0.0022 (3)	−0.0091 (3)	−0.0172 (3)
Al1	0.0347 (4)	0.0493 (5)	0.0356 (4)	0.000	−0.0053 (3)	0.000
N1	0.0334 (12)	0.0518 (14)	0.0430 (12)	0.000	0.0001 (10)	0.000
N2	0.0395 (12)	0.0463 (13)	0.0357 (11)	0.000	−0.0021 (9)	0.000
C1	0.0334 (13)	0.0405 (14)	0.0348 (12)	0.000	−0.0006 (10)	0.000
C2	0.0343 (15)	0.071 (2)	0.0590 (18)	0.000	−0.0129 (14)	0.000
C3	0.0503 (17)	0.068 (2)	0.0431 (15)	0.000	−0.0162 (14)	0.000
C4	0.0402 (16)	0.084 (2)	0.0524 (17)	0.000	0.0116 (14)	0.000
C5	0.0509 (18)	0.081 (2)	0.0387 (15)	0.000	0.0058 (13)	0.000

Geometric parameters (Å, º)

Cl1—Al1	2.1193 (12)	C2—C3	1.332 (5)
Cl2—Al1	2.1290 (7)	C2—H2	0.9300
Al1—C1	2.006 (3)	C3—H3	0.9300
Al1—Cl2[i]	2.1291 (7)	C4—H4A	0.9600
N1—C1	1.352 (3)	C4—H4B	0.9600
N1—C2	1.368 (4)	C4—H4C	0.9600
N1—C4	1.468 (4)	C5—H5A	0.9600
N2—C1	1.356 (3)	C5—H5B	0.9600
N2—C3	1.373 (4)	C5—H5C	0.9600
N2—C5	1.460 (4)		
C1—Al1—Cl1	113.32 (9)	N2—C1—Al1	131.37 (19)
C1—Al1—Cl2	106.74 (5)	C3—C2—N1	107.2 (3)
Cl1—Al1—Cl2	109.45 (3)	C3—C2—H2	126.4
C1—Al1—Cl2[i]	106.74 (5)	N1—C2—H2	126.4
Cl1—Al1—Cl2[i]	109.45 (3)	C2—C3—N2	107.3 (3)
Cl2—Al1—Cl2[i]	111.11 (5)	C2—C3—H3	126.4

C1—N1—C2	110.7 (2)	N2—C3—H3	126.4
C1—N1—C4	125.3 (2)	N1—C4—H4A	109.5
C2—N1—C4	124.0 (2)	N1—C4—H4B	109.5
C1—N2—C3	110.3 (2)	N1—C4—H4C	109.5
C1—N2—C5	126.4 (2)	N2—C5—H5A	109.5
C3—N2—C5	123.3 (2)	N2—C5—H5B	109.5
N1—C1—N2	104.6 (2)	N2—C5—H5C	109.5
N1—C1—Al1	124.02 (19)		
C2—N1—C1—N2	0.0	Cl2^i—Al1—C1—N1	−59.45 (4)
C4—N1—C1—N2	180.0	Cl1—Al1—C1—N2	0.0
C2—N1—C1—Al1	180.0	Cl2—Al1—C1—N2	−120.55 (4)
C4—N1—C1—Al1	0.0	Cl2^i—Al1—C1—N2	120.55 (4)
C3—N2—C1—N1	0.0	C1—N1—C2—C3	0.0
C5—N2—C1—N1	180.0	C4—N1—C2—C3	180.0
C3—N2—C1—Al1	180.0	N1—C2—C3—N2	0.0
C5—N2—C1—Al1	0.0	C1—N2—C3—C2	0.0
Cl1—Al1—C1—N1	180.0	C5—N2—C3—C2	180.0
Cl2—Al1—C1—N1	59.45 (4)		

Symmetry code: (i) x, $-y+1/2$, z.