

solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP/PC* (Siemens, 1990). Software used to prepare material for publication: *SHELXL93*.

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Chloro(dibenzylamine-*N*)dimethylaluminium(III)

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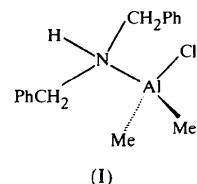
(Received 4 August 1997; accepted 13 November 1997)

Abstract

The addition of dibenzylamine to Me_2AlCl gives the title alane adduct, $[\text{Me}_2\text{ClAl}(\text{NHBz}_2)]$ or $[\text{AlCl}(\text{CH}_3)_2(\text{C}_{14}\text{H}_{15}\text{N})]$. The coordination geometry about the Al atom is distorted tetrahedral in both the crystalline phase and in solution.

Comment

We recently reported (Armstrong *et al.*, 1996) that the reaction of the simple alane amine adduct $[\text{Me}_3\text{Al}(\text{NHBz}_2)]$, (II), with the lithium amide LiNBz_2 affords the novel heterobimetallic adduct $[\text{Me}_3\text{Al}(\text{Bz}_2\text{NLi})(\text{NHBz}_2)]$, which still retains coordinated amine. In a follow-up study (Armstrong *et al.*, 1998), we showed that the presence of this amine could be used to advantage to promote a subsequent intramolecular methane elimination/amine insertion process that generates the lithium alkylaluminium secondary amide $[\text{Me}_2\text{Al}(\text{Bz}_2\text{N}_2\text{Li})(\text{thf})]$ (thf is tetrahydrofuran). As a prerequisite to investigating variations of this reaction sequence, we have been synthesizing and characterizing dibenzylamine adducts of a number of different alanes. In the course of this work, we have crystallized the chloro derivative of (II), $[\text{Me}_2\text{ClAl}(\text{NHBz}_2)]$, (I), whose structure is reported here.



The crystal structure consists of discrete molecular units, with no intermolecular contacts of significantly less than the sum of van der Waals radii. The coordination geometry about the Al atom is distorted tetrahedral, the largest deviation from ideal geometry being the wide $\text{C}1\text{—Al}1\text{—C}2$ angle of $122.8(1)^\circ$ (Table 1). A similar steric widening of the Me—Al—Me angle is found in the two other known structures containing the Me_2ClAlN moiety (Atwood & Jegier, 1996; Sun *et al.*, 1995). That the tetrahedral arrangement persists in pyridine solution is confirmed by ^{27}Al NMR spectroscopy [see *Experimental* and Akitt (1989)]. Comparing the Al—N distance in (I) [$2.020(2)$ Å] with those in these two complexes shows that of (I) to be a longer bond than that of the primary amine analogue $[\text{Me}_2\text{ClAl}(\text{NH}_2\text{Bu})]$, [$1.993(4)$ Å] and that a better match is found with that in $[\text{Me}_2\text{ClAl}(5,6\text{-benzoquinoline})]$ [$2.016(3)$ Å].

The greater electronegativity of the Cl ligand and the subsequent lower electron density on the metal centre results in the Al—N bond length of (I) being slightly shorter than that of $2.058(2)$ Å in the closely related complex (II). The molecular conformation of (I) is broadly similar to that of (II). Examination of the torsion angles shows that the Me_2ClAl fragment is *anti* with respect to the phenyl ring of one benzyl group [$\text{Al}1\text{—N}1\text{—C}10\text{—C}11 = 179.4(2)^\circ$] and that the orientation about the Al—N bond is such that the other benzyl group lies *anti* to the Cl atom [$\text{Cl}1\text{—Al}1\text{—N}1\text{—C}3 = 171.6(1)^\circ$].

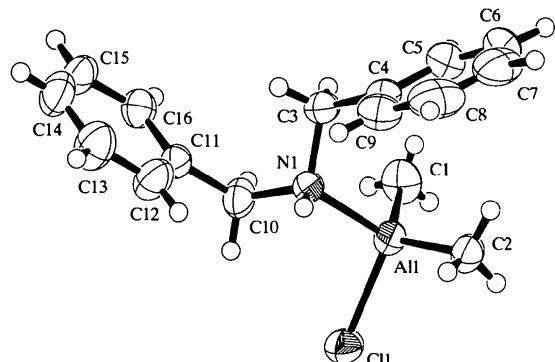


Fig. 1. ORTEPII (Johnson, 1976) view of (I). Non-H atoms are shown as 50% ellipsoids and H atoms as small spheres of arbitrary size.

Experimental

All manipulations were carried out under a dry oxygen-free argon atmosphere using standard Schlenk techniques. Me₂AlCl (10 mmol, 1 M solution in hexane) and additional hexane (5 ml) were chilled in an ice bath and then dibenzylamine (10 mmol) was added dropwise, producing a white precipitate. The solvents were removed and the white solid was recrystallized from a toluene–hexane–tetrahydrofuran mixture (1:3:1) giving X-ray quality crystals on standing overnight at room temperature. Yield 2.38 g (82%). M.p. 412–414 K. NMR (d^5 -pyridine). ¹H (400 MHz): –0.19 [s, (CH₃)₂Al], 2.40 (s, NH), 3.86 (s, PhCH₂), 7.29 (t, *p*-phenyl), 7.39 (t, *m*-phenyl), 7.49 (d, *o*-phenyl). ¹³C (100 MHz): 6.7 [br, (CH₃)₂Al], 54.0 (PhCH₂), 127.7–130.0 (phenyl ring), 142.2 [*ipso*-C(Ph)]. ²⁷Al (104 MHz): 155.3, $w_{1/2}$ = 2620 Hz.

Crystal data

[AlCl(CH₃)₂(C₁₄H₁₅N)]

M_r = 289.78

Triclinic

$P\bar{1}$

a = 9.720 (2) Å

b = 9.735 (2) Å

c = 10.111 (2) Å

α = 93.12 (2)°

β = 112.80 (2)°

γ = 108.05 (2)°

V = 821.8 (3) Å³

Z = 2

D_x = 1.171 Mg m^{–3}

D_m not measured

Data collection

Rigaku AFC-7S diffractometer

$\omega/2\theta$ scans

Absorption correction: none

4008 measured reflections

3787 independent reflections

2514 reflections with

$I > 1.5\sigma(I)$

Mo $K\alpha$ radiation

λ = 0.71069 Å

Cell parameters from 24 reflections

θ = 18.5–21.3°

μ = 0.273 mm^{–1}

T = 295 K

Block

0.50 × 0.40 × 0.40 mm

Colourless

Refinement

Refinement on F

R = 0.036

wR = 0.043

S = 1.614

2514 reflections

257 parameters

All H atoms refined

w = $1/\sigma^2(F)$

$(\Delta/\sigma)_{\text{max}} = 0.002$

$\Delta\rho_{\text{max}} = 0.23 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.22 \text{ e } \text{\AA}^{-3}$

Extinction correction:

Zachariasen (1968) type

2, Gaussian isotropic

Extinction coefficient:

$6.5(6) \times 10^{-6}$

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (Å, °)

C11—Al1	2.2027 (8)	N1—C3	1.502 (3)
Al1—N1	2.020 (2)	N1—C10	1.505 (3)
Al1—C1	1.979 (3)	C3—C4	1.502 (3)
Al1—C2	1.946 (2)		
C11—Al1—N1	101.84 (5)	Al1—N1—C3	113.0 (1)
C11—Al1—C1	110.0 (1)	Al1—N1—C10	112.1 (1)
C11—Al1—C2	107.00 (8)	C3—N1—C10	110.7 (2)
N1—Al1—C1	103.9 (1)	N1—C3—C4	112.9 (2)
N1—Al1—C2	109.43 (9)	N1—C10—C11	114.8 (2)
C1—Al1—C2	122.8 (1)		
C11—Al1—N1—C3	–171.6 (1)	Al1—N1—C10—C11	–179.4 (2)
C11—Al1—N1—C10	–45.7 (2)	C3—N1—C10—C11	–52.2 (3)
Al1—N1—C3—C4	–63.1 (2)	C4—C3—N1—C10	170.2 (2)

The title crystal was mounted in a Lindemann capillary under an argon atmosphere. The structure was solved by direct methods and Fourier techniques, with all atoms located from a series of difference syntheses. Non-H atoms were treated anisotropically and H atoms isotropically. Final refinement to convergence was by full-matrix least squares. Refinement on F with all positive intensities or on F^2 with all intensities gave no significant change in parameters and only marginal changes in s.u.'s compared with those reported here. All calculations were performed on a Silicon Graphics Indy R4600.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1985). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *SIR* (Burla *et al.*, 1989). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1362). Services for accessing these data are described at the back of the journal.

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Tetraethylammonium (2,2-Dicyano-1,1-ethylenedithiolato-S,S')bis(triphenylphosphino-P)copper(I), $(\text{Et}_4\text{N})[\text{Cu}(\text{PPh}_3)_2\{\text{S}_2\text{C}_2(\text{CN})_2\}]$

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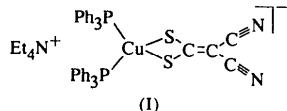
(Received 28 August 1996; accepted 4 July 1997)

Abstract

The crystal structure of the copper(I) compound $(\text{C}_8\text{H}_{20}\text{N})[\text{Cu}(\text{C}_4\text{N}_2\text{S}_2)(\text{C}_{18}\text{H}_{15}\text{P})_2]$ consists of discrete $[\text{Et}_4\text{N}]^+$ cations and $[\text{Cu}(\text{PPh}_3)_2\{\text{S}_2\text{C}_2(\text{CN})_2\}]^-$ anions. The Cu atom in the anion is tetrahedrally coordinated by two phosphine ligands and two S atoms from the 2,2-dicyano-1,1-ethylenedithiolate ligand. The average Cu—P and Cu—S distances are 2.278 (5) and 2.423 (5) Å, respectively.

Comment

In an attempt to prepare a new series of transition metal compounds with phosphine ligands, we isolated a mononuclear copper(I) compound, $(\text{Et}_4\text{N})[\text{Cu}(\text{PPh}_3)_2\{\text{S}_2\text{C}_2(\text{CN})_2\}]$, (I).



The crystal structure of (I) consists of discrete $[\text{Et}_4\text{N}]^+$ cations and $[\text{Cu}(\text{PPh}_3)_2\{\text{S}_2\text{C}_2(\text{CN})_2\}]^-$ anions. The univalent Cu atom of the anion is tetrahedrally coordinated

by two phosphine ligands and two S atoms from the 2,2-dicyano-1,1-ethylenedithiolate ligand. 2,2-Dicyano-1,1-ethylenedithiolate acts as a chelating ligand; the S—Cu—S angle is 74.5 (5)°. The P—Cu—P angle of 123.74 (6)° is much bigger than the S—Cu—P angles, which range from 107.65 (6) to 118.32 (6)°. The average Cu—P and Cu—S distances are 2.278 (5) and 2.423 (5) Å, respectively; the Cu—S bond lengths are comparable with those found in $\text{Cu}\{\text{S}_2\text{C}_2(\text{CN})_2\}$ compounds (McCandlish *et al.*, 1968; Zhang & Yu, 1987). Fig. 1 depicts the anion structure.

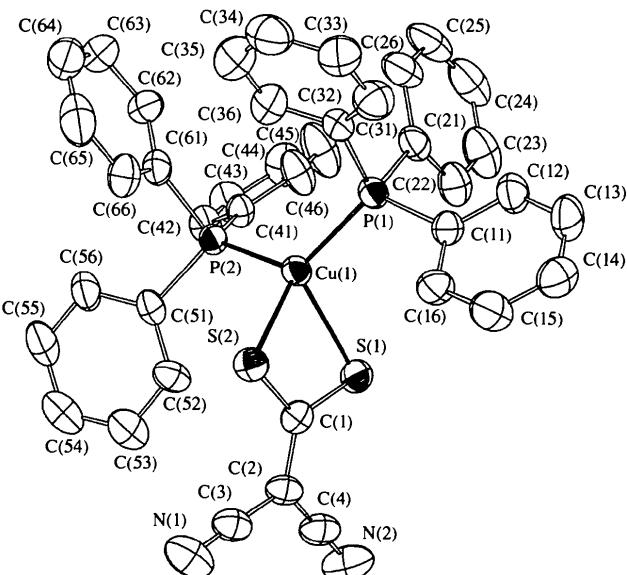


Fig. 1. The structure of $[\text{Cu}(\text{PPh}_3)_2\{\text{S}_2\text{C}_2(\text{CN})_2\}]^-$ with displacement ellipsoids plotted at the 50% probability level.

Experimental

The title compound was obtained from the reaction of PPh_3 , $\text{K}_2\text{S}_2\text{C}_2(\text{CN})_2$, CuCl and Et_4NCl in CH_3OH , and recrystallized from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$.

Crystal data

$(\text{C}_8\text{H}_{20}\text{N})[\text{Cu}(\text{C}_4\text{N}_2\text{S}_2)(\text{C}_{18}\text{H}_{15}\text{P})_2]$	Mo $K\alpha$ radiation
$M_r = 858.6$	$\lambda = 0.71073 \text{ \AA}$
Triclinic	Cell parameters from 25 reflections
$P\bar{1}$	$\theta = 9.0\text{--}12.5^\circ$
$a = 10.532 (2) \text{ \AA}$	$\mu = 0.667 \text{ mm}^{-1}$
$b = 12.384 (2) \text{ \AA}$	$T = 296 \text{ K}$
$c = 18.095 (5) \text{ \AA}$	Prism
$\alpha = 88.71 (2)^\circ$	$0.35 \times 0.20 \times 0.20 \text{ mm}$
$\beta = 99.55 (2)^\circ$	Colourless
$\gamma = 99.99 (2)^\circ$	
$V = 2293.4 (13) \text{ \AA}^3$	
$Z = 2$	
$D_x = 1.244 \text{ Mg m}^{-3}$	
D_m not measured	