Crystal structure of trichloro(*N*-trimethylsilyl)phosphoranimine-trichloroaluminum, $[(CH_3)_3Si(N)PCl_3AlCl_3]$

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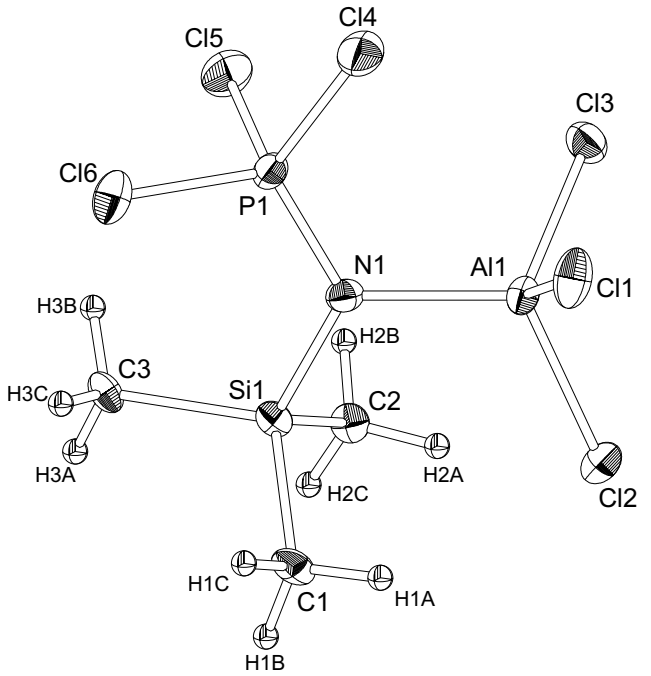

Abstract

$C_3H_9AlCl_6NPSi$, monoclinic, $P12_1/c1$ (No. 14), $a = 15.541(3)$ Å, $b = 12.615(2)$ Å, $c = 16.210(3)$ Å, $\beta = 116.128(2)°$, $V = 2853.3$ Å^3, $Z = 8$, $R_{gt}(F) = 0.077$, $wR_{ref}(F^2) = 0.231$, $T = 100$ K.

Source of material

All manipulations were carried out under inert conditions. To a suspension of 3.1 g (0.023 mol) $AlCl_3$ in 200 ml hexane was added a solution of 10.4 g (0.046 mol) $Me_3SiNPCl_3$ in 200 ml hexane at 195 K. The reaction mixture was allowed to warm up to room temperature, and subsequently refluxed for 1 h. Allowing the as obtained solution to stand at ambient temperature colorless crystals grew overnight.

Discussion

Recently, we reported on single source precursors for the ceramic systems B/P/N/(C) and Al/P/N/(C) [1,2]. The phosphorane iminato complex $[Cl_2AlNPCl_3]_2$ was prepared as a molecular precursor in a two-stage reaction starting from $Me_3SiNPCl_3$ and $AlCl_3$ [2]. During this reaction the title compound $[Me_3SiNPCl_3$-$AlCl_3]$ occurs as an unstable intermediate, which readily decomposes into $[Cl_2AlNPCl_3]_2$. However, under specific reaction conditions it is possible to isolate the donor-acceptor complex $[Me_3SiNPCl_3\ AlCl_3]$ and to get single crystals of it.

The nitrogen atom in $[Me_3SiNPCl_3\ AlCl_3]$ is in an almost trigonal planar coordination, while aluminum, phosphorus, and silicon are nearly tetrahedrally coordinated, respectively. The Al—N distance (194.2(6) pm) is in line with other donor-acceptor complexes between $AlCl_3$ and amines or imines [3,4]. While the P—N distance (160.6(6) pm) is typical for a P—N double bond, all other bond lengths confirm the presence of single bonds (e.g. d(Si—N) = 182.6(6) pm, $\bar{d}$(Si—C) = 187.6(7) pm).

Table 1. Data collection and handling.

Crystal:	colourless, irregular, size 0.25 × 0.30 × 0.35 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	14.23 cm^{-1}
Diffractometer, scan mode:	Bruker AXS SMART 1000, ω
$2\theta_{max}$:	56.66°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	23186, 6573
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5667
$N(param)_{refined}$:	241
Programs:	SHELXTL-NT [5], DIAMOND [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(3A)	4*e*	0.9993	0.7892	0.5872	0.025
H(3B)	4*e*	0.9346	0.8117	0.6395	0.025
H(3C)	4*e*	0.9803	0.9085	0.6084	0.025
H(2A)	4*e*	0.7533	0.7008	0.3802	0.026
H(2B)	4*e*	0.7855	0.6678	0.4850	0.026
H(2C)	4*e*	0.8608	0.6622	0.4424	0.026
H(1A)	4*e*	0.8151	0.9281	0.3385	0.029
H(1B)	4*e*	0.9208	0.8788	0.3841	0.029
H(1C)	4*e*	0.8995	0.9879	0.4221	0.029
H(4A)	4*e*	0.3836	0.8192	0.1879	0.036
H(4B)	4*e*	0.3199	0.8080	0.2427	0.036
H(4C)	4*e*	0.3443	0.9230	0.2169	0.036
H(5A)	4*e*	0.1432	0.9884	0.1217	0.032
H(5B)	4*e*	0.1058	0.8786	0.1435	0.032
H(5C)	4*e*	0.0649	0.9201	0.0398	0.032
H(6A)	4*e*	0.1294	0.6973	–0.0018	0.030
H(6B)	4*e*	0.1898	0.6629	0.1032	0.030
H(6C)	4*e*	0.2415	0.6728	0.0373	0.030

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Al(1)	4*e*	0.6190(1)	0.9110(2)	0.3813(1)	0.0154(9)	0.017(1)	0.0131(9)	0.0007(7)	0.0039(7)	0.0002(7)
Cl(1)	4*e*	0.5618(1)	1.0677(1)	0.3479(1)	0.0280(9)	0.0183(8)	0.0227(8)	0.0024(7)	–0.0003(7)	0.0023(6)
Cl(2)	4*e*	0.6293(1)	0.8465(2)	0.2642(1)	0.0251(8)	0.038(1)	0.0147(7)	0.0015(7)	0.0076(7)	–0.0006(7)
Cl(3)	4*e*	0.5321(1)	0.8097(1)	0.4192(1)	0.0177(7)	0.0254(8)	0.0247(8)	–0.0025(6)	0.0097(6)	0.0023(7)
P(1)	4*e*	0.7494(1)	0.9415(1)	0.5855(1)	0.0170(8)	0.0219(9)	0.0126(7)	0.0025(7)	0.0055(6)	0.0001(6)
Cl(4)	4*e*	0.6370(1)	1.0213(2)	0.5784(1)	0.0265(9)	0.045(1)	0.0235(9)	0.0117(8)	0.0111(7)	–0.0058(8)
Cl(5)	4*e*	0.7591(2)	0.8170(2)	0.6643(1)	0.035(1)	0.035(1)	0.0237(9)	–0.0001(8)	0.0136(8)	0.0082(7)
Cl(6)	4*e*	0.8597(1)	1.0317(2)	0.6615(1)	0.0282(9)	0.0299(9)	0.0200(8)	–0.0038(7)	0.0038(7)	–0.0063(7)
Si(1)	4*e*	0.8433(1)	0.8432(2)	0.4793(1)	0.0140(8)	0.0154(8)	0.0187(9)	0.0008(6)	0.0079(7)	0.0008(7)
C(3)	4*e*	0.9523(4)	0.8375(5)	0.5920(5)	0.011(3)	0.016(3)	0.023(3)	0.004(2)	0.006(3)	0.002(2)
C(2)	4*e*	0.8062(5)	0.7014(5)	0.4422(5)	0.019(3)	0.014(3)	0.019(3)	–0.001(2)	0.008(3)	0.000(2)
C(1)	4*e*	0.8732(5)	0.9184(6)	0.3961(5)	0.017(3)	0.019(3)	0.025(3)	0.001(3)	0.012(3)	0.011(3)
N(1)	4*e*	0.7435(4)	0.9111(4)	0.4874(4)	0.018(3)	0.017(3)	0.015(3)	0.002(2)	0.009(2)	0.001(2)
Al(2)	4*e*	0.1336(1)	0.9072(2)	–0.1312(1)	0.0144(9)	0.0170(9)	0.0125(9)	–0.0007(7)	0.0041(7)	0.0003(7)
Cl(7)	4*e*	0.0082(1)	0.8338(2)	–0.1349(1)	0.0165(7)	0.0299(9)	0.0217(8)	–0.0045(6)	0.0054(6)	0.0023(7)
Cl(8)	4*e*	0.0990(1)	1.0660(1)	–0.1806(1)	0.0239(8)	0.0185(8)	0.0217(8)	0.0021(6)	0.0054(7)	0.0032(6)
Cl(9)	4*e*	0.1852(1)	0.8125(2)	–0.2093(1)	0.0287(9)	0.0302(9)	0.0203(8)	0.0018(7)	0.0117(7)	–0.0077(7)
P(2)	4*e*	0.3413(1)	0.9413(1)	0.0074(1)	0.0141(8)	0.0191(8)	0.0150(8)	–0.0017(6)	0.0061(6)	0.0000(6)
Cl(10)	4*e*	0.4128(1)	1.0373(1)	0.1120(1)	0.0193(8)	0.0215(8)	0.0235(8)	–0.0051(6)	0.0051(6)	–0.0050(6)
Cl(11)	4*e*	0.4270(1)	0.8173(2)	0.0291(1)	0.0201(8)	0.0256(9)	0.0315(9)	0.0033(7)	0.0116(7)	–0.0044(7)
Cl(12)	4*e*	0.3445(1)	1.0158(2)	–0.0986(1)	0.0224(8)	0.042(1)	0.0223(8)	–0.0082(8)	0.0103(7)	0.0083(7)
Si(2)	4*e*	0.2193(1)	0.8447(2)	0.0854(1)	0.0166(8)	0.0162(9)	0.0137(8)	–0.0012(7)	0.0067(7)	–0.0002(6)
C(4)	4*e*	0.3299(5)	0.8493(6)	0.1964(5)	0.028(4)	0.027(4)	0.014(3)	–0.005(3)	0.005(3)	0.000(3)
C(5)	4*e*	0.1218(5)	0.9164(6)	0.0993(5)	0.025(3)	0.023(3)	0.022(3)	0.002(3)	0.015(3)	–0.001(3)
C(6)	4*e*	0.1917(5)	0.7025(5)	0.0521(5)	0.024(3)	0.017(3)	0.020(3)	0.000(3)	0.010(3)	0.003(3)
N(2)	4*e*	0.2366(4)	0.9107(4)	–0.0075(4)	0.017(3)	0.015(3)	0.017(3)	–0.001(2)	0.010(2)	0.002(2)

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