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The pentacoordinate titanium complex $[TiCl_2(NMe_2)_2(HNMe_2)]$

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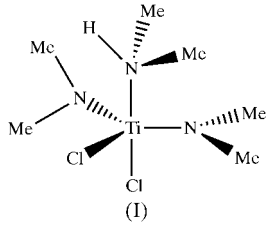
Amido complexes of titanium are useful reagents in a variety of syntheses and as precursors for chemical vapour deposition of TiN. The title compound, dichlorobis(dimethylamido)(dimethylamine)titanium(IV), $[TiCl_2(C_2H_6N)_2(C_2H_7N)]$, crystallizes with one molecule in the asymmetric unit. The neutral complex shows an unusual fivefold coordination of the titanium centre with a distorted trigonal–bipyramidal geometry and the dimethylamine molecule occupying an axial position.

Comment

Crystals of dichlorobis(dimethylamido)(dimethylamine)titanium(IV), (I), were obtained as a side product of the synthesis



(I)

of $Ti(NMe_2)_4$ from $TiCl_4$ and $LiNMe_2$. Sublimation of the residual solid gave crystals of (I) in a low isolated yield.

Experimental

To a solution of dimethylamine (0.50 l, 2.0 *M* in THF, 1.0 mol), cooled to 195 K, was added a solution of *n*-butyllithium (0.63 l, 1.6 *M* in hexane, 1.0 mol). After stirring for 30 min, the solution was warmed to room temperature and stirred for an additional 1 h. After cooling to 195 K, a solution of titanium tetrachloride (0.027 l, 0.25 mol) in hexane (0.10 l) was added slowly to the solution of lithium dimethylamide. The red–brown mixture was warmed to room temperature. Volatiles were removed *in vacuo* and the main product, tetrakis(dimethylamido)titanium(IV) (44 g, 0.20 mol), collected by distillation (343 K at 0.5 Torr; 1 Torr = 133.322 Pa). The solid residue was placed in a large sublimator. Sublimation at room temperature and 0.5 Torr yielded yellow crystals of chlorotris(dimethylamino)-titanium(IV) (1.5 g, 0.01 mol). After yellow crystals no longer formed on the cold finger of the sublimator the apparatus was placed in an oil bath held at 323 K whereupon large orange crystals of dichlorobis-(dimethylamido)(dimethylamine)titanium(IV) (4.6 g, 0.02 mol) formed. Further sublimation at 353 K afforded a crop of red–brown crystals of dichlorobis(dimethylamido)titanium(IV) (3.7 g, 0.02 mol).

Crystal data

$[TiCl_2(C_2H_6N)_2(C_2H_7N)]$	D_x = 1.32 Mg m^{-3}
M_r = 252.04	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 50 reflections
a = 8.3083 (7) Å	θ = 10–12°
b = 11.5075 (9) Å	μ = 1.055 mm^{-1}
c = 13.360 (2) Å	T = 225 (2) K
β = 96.034 (9)°	Irregular block, orange
V = 1270.3 (4) Å^3	0.50 × 0.20 × 0.05 mm
Z = 4	

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.022
$\theta/2\theta$ scans	θ_{max} = 25.97°
Absorption correction: ψ scan (North *et al.*, 1968)	$h = 0 \rightarrow 10$
T_{min} = 0.799, T_{max} = 0.949	$k = 0 \rightarrow 14$
2809 measured reflections	$l = -16 \rightarrow 16$
2486 independent reflections	3 standard reflections
1992 reflections with $I > 3\sigma(I)$	frequency: 50 min
	intensity decay: 0.11%

Refinement

Refinement on F	All H-atom parameters refined
R = 0.030	$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0009F_o^4]$
wR = 0.040	$(\Delta/\sigma)_{max}$ = 0.001
S = 1.294	$\Delta\rho_{max}$ = 0.22 e Å^{-3}
1992 reflections	$\Delta\rho_{min}$ = −0.34 e Å^{-3}
185 parameters	

Table 1
Selected geometric parameters (Å, °).

Ti—Cl1	2.3976 (7)	N1—C2	1.455 (3)
Ti—Cl2	2.3449 (8)	N2—C3	1.456 (3)
Ti—N1	1.855 (2)	N2—C4	1.454 (4)
Ti—N2	1.853 (2)	N3—C5	1.474 (3)
Ti—N3	2.255 (2)	N3—C6	1.476 (3)
N1—C1	1.443 (3)		
Cl1—Ti—Cl2	88.20 (2)	Cl2—Ti—N2	118.38 (7)
Cl1—Ti—N1	93.14 (6)	Cl2—Ti—N3	81.91 (5)
Cl1—Ti—N2	97.90 (7)	N1—Ti—N2	111.22 (9)
Cl1—Ti—N3	169.01 (5)	N1—Ti—N3	89.55 (7)
Cl2—Ti—N1	129.69 (6)	N2—Ti—N3	91.03 (8)

Backgrounds were obtained from analysis of the scan profile (Blessing *et al.*, 1974). All H atoms were refined; N—H = 0.74 (2) Å and C—H = 0.87 (2)–1.08 (3) Å.

Data collection and cell refinement: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977); data reduction: *PROCESS* in *MolEN* (Fair, 1990); program(s) used to solve structure: Patterson and Fourier (*MolEN*); program(s) used to refine structure: *LSFM* in *MolEN*; software used to prepare material for publication: *MolEN*.

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