Crystal structure of *bis*(dimethylamido)-*bis*(ethyl-3-(penta-fluorophenylamido)but-2-enoate)titanium, $C_{28}H_{30}F_{10}N_4O_4Ti$

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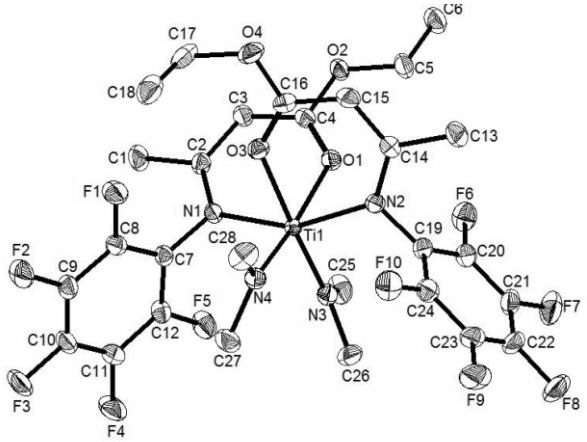
Received May 14, 2012, accepted July 17, 2012, available online July 26, 2012, CCDC no. 1267/3804



Abstract

$C_{28}H_{30}F_{10}N_4O_4Ti$, monoclinic, $P2_1/c$ (no. 14), a = 9.1509(3) Å, b = 12.6138(5) Å, c = 26.7928(9) Å, β = 91.637(2)°, V = 3091.4 Å^3, Z = 4, $R_{gt}(F)$ = 0.0365, $wR_{ref}(F^2)$ = 0.1285, T = 153 K.

Table 1. Data collection and handling.

Crystal:	orange prisms, size 0.08×0.17×0.37 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.78 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	60.22°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	41791, 9051
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6554
$N(param)_{refined}$:	432
Programs:	SHELXS-97 [5]

Source of material

Tetrakis(dimethylamido)titanium was purchased from commercial sources and used as received. 3-pentafluorophenylamino-but-2-enoic acid ethyl ester was synthesized from pentafluoroaniline and ethyl 3-oxobutanoate and prior to use, it was purified by kugelrohr distillation under an atmosphere of argon.

Experimental details

Under an atmosphere of argon, an ice cooled mixture of 3-pentaflurophenylamino-but-2-enoic acid ethyl ester (200 mg, 0.68 mmol) in toluene (10 mL) was slowly added to a cooled solution (273 K) of tetrakis(dimethylamido)titanium (72.4 mg, 0.32 mmol) in *n*-hexane (5 mL) and the resulting mixture was stored at 240 K for 48 h. Afterwards, *n*-hexane (4 mL) was distilled off under vacuum at room temperature and the remaining solution was cooled again to 240 K for 48 h. Finally, a small amount of the solvent (3 mL) was removed under vacuum at room temperature. During that process, orange crystals (184 mg, 0.25 mmol, 79 %) suitable for *X*-ray analysis were formed.

Discussion

Although commercially available tetrakis(dimethylamido)titanium is a well-known catalyst for the hydroamination of alkynes [1] and alkenes [2] it was found that group-4 metal complexes with N,O-chelating amidato ligands show a significantly improved catalytic performance [3]. Inspired by this finding, we planned to use closely related titanium complexes with vinylogous amidato ligands as catalysts for various amination reactions. These complexes are easily accessible via amine elimination from tetrakis(dimethylamido)titanium and beta-enaminones [4]. Herein, we describe a corresponding synthetic procedure that uses 3-pentafluorophenylamino-but-2-enoic acid ethyl ester as the ligand precursor. The resulting titanium complex bears two dimethylamido ligands and two N,O-chelating vinylogous amidato ligands. The crystal structure analysis reveals a monomeric titanium species that is six-coordinate, with a distorted octahedral geometry. Both dimethylamido ligands are located trans to the oxygen atoms of the vinylogous amidato ligands. Studies dealing with the catalytic performance of the title compound for a number of amination reactions are presently underway in our laboratories.

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	0.6197	0.9231	0.1328	0.046
H(1B)	4*e*	0.5300	0.9918	0.1717	0.046
H(1C)	4*e*	0.4703	0.9796	0.1153	0.046
H(3)	4*e*	0.4028	0.9059	0.2260	0.029
H(5A)	4*e*	0.2848	0.6083	0.2928	0.032
H(5B)	4*e*	0.1357	0.6755	0.2947	0.032
H(6A)	4*e*	0.3728	0.6920	0.3657	0.045
H(6B)	4*e*	0.2180	0.6391	0.3766	0.045
H(6C)	4*e*	0.2290	0.7640	0.3670	0.045
H(13A)	4*e*	–0.1290	0.4277	0.1977	0.044
H(13B)	4*e*	–0.1647	0.5167	0.2382	0.044
H(13C)	4*e*	–0.0188	0.4474	0.2442	0.044
H(15)	4*e*	–0.1320	0.6818	0.2138	0.030
H(17A)	4*e*	0.0923	0.9263	0.1386	0.041
H(17B)	4*e*	–0.0466	0.9963	0.1527	0.041
H(18A)	4*e*	–0.0361	0.8595	0.0685	0.058
H(18B)	4*e*	–0.0318	0.9863	0.0661	0.058
H(18C)	4*e*	–0.1770	0.9269	0.0829	0.058
H(25A)	4*e*	0.5521	0.4811	0.1927	0.051
H(25B)	4*e*	0.5551	0.6067	0.1844	0.051
H(25C)	4*e*	0.6477	0.5306	0.1494	0.051
H(26A)	4*e*	0.5313	0.4334	0.0843	0.050
H(26B)	4*e*	0.3570	0.4224	0.0824	0.050
H(26C)	4*e*	0.4508	0.3706	0.1275	0.050

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Table 2. continued.

Atom	Site	x	y	z	U_{iso}
H(27A)	4*e*	0.2772	0.5185	0.0049	0.050
H(27B)	4*e*	0.4136	0.5739	0.0332	0.050
H(27C)	4*e*	0.3083	0.6421	–0.0032	0.050

Table 2. continued.

Atom	Site	x	y	z	U_{iso}
H(28A)	4*e*	0.0684	0.6960	0.0252	0.051
H(28B)	4*e*	0.0041	0.6334	0.0716	0.051
H(28C)	4*e*	0.0404	0.5710	0.0215	0.051

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}
Ti(1)	4*e*	0.27543(3)	0.63030(2)	0.13203(1)	0.0163(1)	0.0149(1)	0.0153(1)	–0.00052(9)	0.00155(9)	–0.0008(1)
O(1)	4*e*	0.3065(1)	0.66635(9)	0.20765(4)	0.0245(5)	0.0188(6)	0.0168(5)	–0.0030(4)	0.0012(4)	–0.0015(4)
O(2)	4*e*	0.3113(1)	0.7637(1)	0.27788(4)	0.0368(6)	0.0207(6)	0.0150(5)	–0.0045(5)	0.0048(5)	–0.0004(5)
O(3)	4*e*	0.1124(1)	0.74406(9)	0.13727(4)	0.0195(5)	0.0192(6)	0.0258(6)	0.0006(4)	0.0020(4)	–0.0004(5)
O(4)	4*e*	–0.0722(1)	0.8407(1)	0.16626(5)	0.0283(6)	0.0221(7)	0.0429(8)	0.0074(5)	0.0074(5)	–0.0025(6)
N(1)	4*e*	0.4134(1)	0.7682(1)	0.12428(5)	0.0196(5)	0.0186(7)	0.0155(6)	–0.0017(5)	0.0014(5)	0.0009(5)
N(2)	4*e*	0.1094(1)	0.5310(1)	0.16326(5)	0.0201(5)	0.0165(7)	0.0197(7)	–0.0025(5)	0.0025(5)	–0.0014(5)
N(3)	4*e*	0.4318(1)	0.5290(1)	0.13284(5)	0.0217(6)	0.0217(7)	0.0238(7)	0.0022(5)	0.0035(5)	0.0033(6)
N(4)	4*e*	0.2201(2)	0.6092(1)	0.06312(5)	0.0290(6)	0.0204(7)	0.0178(7)	–0.0024(5)	–0.0002(5)	–0.0022(5)
C(1)	4*e*	0.5217(2)	0.9437(2)	0.14307(7)	0.0434(9)	0.0232(9)	0.0263(9)	–0.0128(7)	0.0075(7)	–0.0001(7)
C(2)	4*e*	0.4374(2)	0.8462(1)	0.15749(6)	0.0221(6)	0.0179(8)	0.0203(8)	–0.0028(5)	0.0004(6)	0.0009(6)
C(3)	4*e*	0.3929(2)	0.8433(1)	0.20648(6)	0.0335(8)	0.0193(8)	0.0188(8)	–0.0057(6)	0.0043(6)	–0.0026(6)
C(4)	4*e*	0.3341(2)	0.7529(1)	0.22864(6)	0.0200(6)	0.0217(8)	0.0159(7)	0.0007(5)	0.0007(5)	–0.0004(6)
C(5)	4*e*	0.2418(2)	0.6767(2)	0.30301(6)	0.0335(8)	0.0259(9)	0.0202(8)	–0.0062(7)	0.0044(7)	0.0042(7)
C(6)	4*e*	0.2677(2)	0.6945(2)	0.35782(7)	0.0387(9)	0.033(1)	0.0187(8)	–0.0031(7)	0.0019(7)	0.0034(7)
C(7)	4*e*	0.4649(2)	0.7869(1)	0.07569(6)	0.0212(6)	0.0176(8)	0.0173(7)	–0.0038(5)	0.0008(5)	0.0005(6)
C(8)	4*e*	0.3861(2)	0.8483(1)	0.04160(6)	0.0221(6)	0.0229(9)	0.0205(8)	0.0023(6)	0.0022(6)	0.0007(6)
C(9)	4*e*	0.4325(2)	0.8663(1)	–0.00648(6)	0.0303(7)	0.0248(9)	0.0186(8)	–0.0006(6)	–0.0013(6)	0.0042(7)
C(10)	4*e*	0.5611(2)	0.8212(2)	–0.02176(6)	0.0311(8)	0.030(1)	0.0155(7)	–0.0023(7)	0.0046(6)	0.0022(7)
C(11)	4*e*	0.6416(2)	0.7592(1)	0.01095(6)	0.0222(7)	0.0280(9)	0.0239(8)	0.0011(6)	0.0061(6)	–0.0008(7)
C(12)	4*e*	0.5947(2)	0.7431(1)	0.05908(6)	0.0211(6)	0.0244(9)	0.0211(8)	–0.0002(6)	0.0003(6)	0.0040(7)
C(13)	4*e*	–0.0865(2)	0.4814(2)	0.22021(7)	0.0254(7)	0.031(1)	0.032(1)	–0.0029(7)	0.0090(7)	0.0053(8)
C(14)	4*e*	–0.0047(2)	0.5625(1)	0.19013(6)	0.0185(6)	0.0241(9)	0.0184(7)	–0.0024(6)	0.0002(5)	–0.0002(6)
C(15)	4*e*	–0.0547(2)	0.6661(2)	0.19206(7)	0.0212(6)	0.0279(9)	0.0266(9)	0.0021(6)	0.0069(6)	–0.0018(7)
C(16)	4*e*	0.0023(2)	0.7487(1)	0.16384(7)	0.0195(6)	0.0217(9)	0.0258(8)	0.0028(6)	–0.0007(6)	–0.0053(7)
C(17)	4*e*	–0.0159(2)	0.9287(2)	0.13749(9)	0.0314(8)	0.0164(9)	0.054(1)	0.0032(7)	0.0032(8)	–0.0030(8)
C(18)	4*e*	–0.0699(2)	0.9250(2)	0.08411(9)	0.0328(9)	0.029(1)	0.054(1)	0.0056(7)	0.0031(9)	0.007(1)
C(19)	4*e*	0.1376(2)	0.4208(1)	0.16239(6)	0.0218(6)	0.0188(8)	0.0251(8)	–0.0023(6)	0.0054(6)	0.0009(7)
C(20)	4*e*	0.2266(2)	0.3708(1)	0.19849(7)	0.0256(7)	0.0226(9)	0.0272(9)	–0.0032(6)	0.0050(6)	0.0016(7)
C(21)	4*e*	0.2589(2)	0.2645(2)	0.19608(8)	0.0293(8)	0.0228(9)	0.040(1)	0.0014(6)	0.0109(7)	0.0106(8)
C(22)	4*e*	0.2017(2)	0.2038(2)	0.15769(8)	0.0362(9)	0.0149(8)	0.053(1)	–0.0018(7)	0.0221(9)	0.0005(8)
C(23)	4*e*	0.1126(2)	0.2496(2)	0.12160(8)	0.0353(8)	0.0220(9)	0.037(1)	–0.0099(7)	0.0140(8)	–0.0095(8)
C(24)	4*e*	0.0816(2)	0.3567(1)	0.12429(7)	0.0288(7)	0.0237(9)	0.0260(9)	–0.0067(6)	0.0039(7)	–0.0021(7)
C(25)	4*e*	0.5570(2)	0.5376(2)	0.16772(8)	0.0249(7)	0.043(1)	0.034(1)	0.0062(7)	–0.0005(7)	0.0127(9)
C(26)	4*e*	0.4437(2)	0.4308(2)	0.10442(8)	0.0354(9)	0.0215(9)	0.045(1)	0.0049(7)	0.0161(8)	–0.0010(8)
C(27)	4*e*	0.3124(2)	0.5838(2)	0.02104(7)	0.047(1)	0.032(1)	0.0210(9)	–0.0080(8)	0.0084(7)	–0.0066(8)
C(28)	4*e*	0.0708(2)	0.6290(2)	0.04372(8)	0.0366(9)	0.032(1)	0.032(1)	–0.0001(8)	–0.0147(8)	–0.0076(8)
F(1)	4*e*	0.2620(1)	0.89484(9)	0.05514(4)	0.0291(5)	0.0384(7)	0.0287(6)	0.0135(4)	0.0059(4)	0.0060(5)
F(2)	4*e*	0.3549(1)	0.9290(1)	–0.03760(4)	0.0421(6)	0.0443(7)	0.0222(5)	0.0116(5)	–0.0012(4)	0.0117(5)
F(3)	4*e*	0.6062(1)	0.8381(1)	–0.06816(4)	0.0427(6)	0.0491(7)	0.0186(5)	0.0040(5)	0.0106(4)	0.0071(5)
F(4)	4*e*	0.7661(1)	0.7146(1)	–0.00394(4)	0.0289(5)	0.0510(8)	0.0340(6)	0.0106(5)	0.0146(4)	0.0065(6)
F(5)	4*e*	0.6792(1)	0.6853(1)	0.08987(4)	0.0265(5)	0.0433(7)	0.0302(6)	0.0105(4)	0.0034(4)	0.0142(5)
F(6)	4*e*	0.2824(1)	0.42774(9)	0.23664(4)	0.0355(5)	0.0312(6)	0.0310(6)	–0.0020(4)	–0.0067(4)	0.0035(5)
F(7)	4*e*	0.3457(1)	0.2185(1)	0.23098(5)	0.0357(5)	0.0338(7)	0.0579(8)	0.0055(5)	0.0043(5)	0.0212(6)
F(8)	4*e*	0.2337(1)	0.10042(9)	0.15526(6)	0.0540(7)	0.0165(6)	0.080(1)	0.0004(5)	0.0279(7)	0.0002(6)
F(9)	4*e*	0.0560(1)	0.1908(1)	0.08408(5)	0.0574(7)	0.0315(7)	0.0494(8)	–0.0173(6)	0.0153(6)	–0.0208(6)
F(10)	4*e*	–0.0077(1)	0.3989(1)	0.08896(4)	0.0443(6)	0.0339(7)	0.0296(6)	–0.0085(5)	–0.0083(5)	–0.0031(5)

Acknowledgments. We thank the Deutsche Forschungsgemeinschaft (DFG) for financial support of our research.

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