Crystal structure of {2-[2-(1*H*-inden-3-yl)-2-phenylethyl]-1*H*-imidazolyl-κ*N*^{1}}-*tris*[*N*,*N*-diethylamido-κ*N*]titanium(IV), $C_{32}H_{47}N_5Ti$

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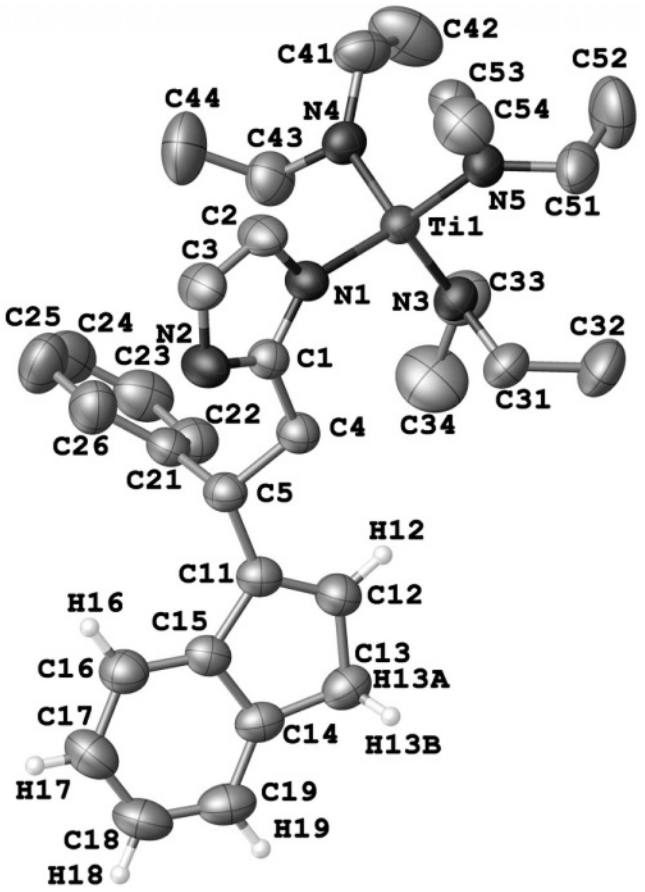

Abstract

$C_{32}H_{47}N_5Ti$, orthorhombic, *Pbca* (no. 61), a = 16.100(2) Å, b = 19.904(2) Å, c = 20.196(2) Å, V = 6472.3 Å^3, Z = 8, $R_{gt}(F)$ = 0.0405, $wR_{ref}(F^2)$ = 0.1178, T = 293 K.

Table 1. Data collection and handling.

Crystal:	yellow blocks, size 0.14×0.26×0.33 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.91 cm^{-1}
Diffractometer, scan mode:	BRUKER SMART APEXII, φ and ω
$2\theta_{max}$:	52.56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	33580, 6533
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3958
$N(param)_{refined}$:	349
Programs:	SAINT [6], SADABS [7], SHELX [8], OLEX2 [9]

Source of material

Initial ligand, 2-[2-(1*H*-inden-3-yl)-2-phenylethyl]-1*H*-imidazole, (II): 1-diethoxylmethyl-2-methyl-1*H*-imidazole (2.84 g, 0.01 mol) was metallated with *n*-BuLi (4.5 mL of a 2.2 M solution in hexane, 0.01 mol) in THF (50 mL) at 233 K. The mixture was kept at the same temperature for 30 min and treated with a solution of 1-phenylmethylidene-1*H*-indene (2.04 g, 0.01 mol) in THF (30 mL). After keeping overnight at 293 K, the dark brown solution was quenched with excess of aqueous HCl (0.5 M solution), the water phase was washed by diethyl ether (3 times 100 mL), neutralized, extracted with CH_2Cl_2 (3 times 100 mL), and the extract was concentrated till dryness under reduced pressure. Recrystallization of the crude product (brown oil) from diethyl ether gave (II) as a light-yellow powder (1.40 g, 31.7%). Complex (I) was prepared by a direct treatment of (II) (1.086 g, 3.0 mmol) with $Ti(NEt_2)_4$ (1.504 g, 3.0 mmol) in toluene (35 mL) at 353 K during 12 h. On removal of all of the volatiles under vacuum, the residue (brown oil) was extracted with hexane several times and the hexane extracts were stored at 250 K for several hours that gave (I) as yellow crystalline material (1.25 g, 72%). A single crystal of (I) suitable for the X-ray diffraction analysis was picked up directly from the isolated material, mounted into a Lindemann glass capillary (an N_2-filled glove box) and sealed off.

Experimental details

Non-H atoms were refined anisotropically. H atoms were treated as riding atoms with distances C–H = 0.96 (CH3), 0.97 (CH2), 0.98 (CH), 0.93 Å (CArH), and U_{iso}(H) = 1.5 U_{eq}(C), 1.2 U_{eq}(C), 1.2 U_{eq}(C), 1.2 U_{eq}(C), respectively.

Discussion

The title compound, $C_{32}H_{47}N_5Ti$, (I), presents a Ti(IV) tetrakis-amido type mixed-ligated complex with three identical diethylamido ligands and one imidazolido-type ligand [for the asymmetric unit of (I), see the Figure]. Analysis of the Cambridge Structural Database (CSD; version 5.32, release February 2011 [1]) reveals only 5 entries (5 fragments) for the Group 4 transition metal complexes in which the tetrahedral central atom is linked to three aliphatic and one hetaryl-type amido-groups (for three Ti complexes, see [2-4]; for two Zr complexes, see [2]). In complex (I), the Ti1–N1 [2.0682(17) Å] and Ti1–N3 to Ti1–N5 distances [1.8773(16), 1.8574(18), and 1.8785(17) Å, respectively] nearly match the related ranges observed earlier [2.000 to 2.052 Å for Ti–N(pyrollido) and 1.876 to 1.898 Å for Ti–NMe_2 distances]. The N–Ti–N angles in (I) vary in a range of 106.41(8) to 115.41(7)° that is rather close to the tetrahedral angle. The Ti1 atom only slightly deviates from the imidazolido-group r. m. s.

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plane [0.146(4) Å]. The 1*H*-indenyl moiety is planar within 0.014 Å. The diethylamido-groups at atoms N3 through N5 are planar [sums of the valent angles at the N-atoms 359.9(5), 359.9(5), and 359.8(5)°, respectively] that is indicative of an additional $2e^-$ $p\pi-d\pi$ donation from each NEt_2 group towards the metal centre and, thus, of the $14e^-$ nature of the complex (or of its $16e^-$ nature, if an analogous additional donation from the imidazolido-group to the Ti-atom is considered; for the discussion of related cases, see [5]).

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2)	8*c*	0.9176	–0.0193	0.4878	0.071
H(3)	8*c*	0.8601	–0.0555	0.5922	0.072
H(4A)	8*c*	0.6221	0.0253	0.4751	0.059
H(4B)	8*c*	0.6663	0.0944	0.4634	0.059
H(5)	8*c*	0.6138	0.0543	0.5908	0.057
H(12)	8*c*	0.5142	0.1099	0.4415	0.070
H(13B)	8*c*	0.3791	0.1674	0.4710	0.071
H(13A)	8*c*	0.3624	0.0894	0.4644	0.071
H(16)	8*c*	0.5123	0.0930	0.6803	0.070
H(17)	8*c*	0.3913	0.1021	0.7424	0.085
H(18)	8*c*	0.2662	0.1210	0.6913	0.088
H(19)	8*c*	0.2580	0.1314	0.5775	0.080
H(22)	8*c*	0.6101	0.2163	0.5166	0.076
H(23)	8*c*	0.6849	0.3092	0.5515	0.094
H(24)	8*c*	0.7757	0.2994	0.6389	0.103
H(25)	8*c*	0.7916	0.1984	0.6910	0.109
H(26)	8*c*	0.7201	0.1055	0.6549	0.088
H(31A)	8*c*	0.6240	0.0858	0.3489	0.073
H(31B)	8*c*	0.6895	0.0300	0.3329	0.073
H(32C)	8*c*	0.6988	0.0775	0.2230	0.132
H(32B)	8*c*	0.6204	0.1204	0.2410	0.132
H(32A)	8*c*	0.6143	0.0418	0.2386	0.132
H(33A)	8*c*	0.7232	0.1960	0.2781	0.090
H(33B)	8*c*	0.7762	0.2172	0.3396	0.090
H(34B)	8*c*	0.6468	0.2692	0.3411	0.163
H(34C)	8*c*	0.6576	0.2236	0.4038	0.163
H(34A)	8*c*	0.6035	0.1987	0.3441	0.163
H(41A)	8*c*	1.0090	0.1202	0.3450	0.083
H(41B)	8*c*	1.0289	0.1687	0.4039	0.083
H(42A)	8*c*	0.9464	0.2078	0.2882	0.157
H(42C)	8*c*	1.0387	0.2259	0.3053	0.157
H(42B)	8*c*	0.9660	0.2564	0.3473	0.157
H(43A)	8*c*	0.8257	0.1786	0.4644	0.082
H(43B)	8*c*	0.8907	0.2323	0.4413	0.082
H(44C)	8*c*	0.9916	0.1815	0.5093	0.152
H(44A)	8*c*	0.9251	0.1295	0.5335	0.152
H(44B)	8*c*	0.9156	0.2058	0.5515	0.152
H(51A)	8*c*	0.7968	0.0100	0.2434	0.081
H(51B)	8*c*	0.8764	–0.0342	0.2340	0.081
H(52A)	8*c*	0.8757	0.0538	0.1590	0.156
H(52C)	8*c*	0.9524	0.0603	0.2063	0.156
H(52B)	8*c*	0.8739	0.1055	0.2174	0.156
H(53B)	8*c*	0.9719	0.0001	0.3799	0.069
H(53A)	8*c*	0.9954	–0.0106	0.3054	0.069
H(54A)	8*c*	0.9187	–0.1109	0.3050	0.123
H(54B)	8*c*	0.8987	–0.1004	0.3802	0.123
H(54C)	8*c*	0.9903	–0.1137	0.3575	0.123

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)	8*c*	0.83024(2)	0.07636(2)	0.38156(2)	0.0384(2)	0.0459(2)	0.0416(2)	0.0010(2)	–0.0013(2)	–0.0008(2)
N(1)	8*c*	0.8051(1)	0.02810(9)	0.47000(8)	0.042(1)	0.056(1)	0.047(1)	0.0054(8)	0.0013(8)	0.0058(9)
N(2)	8*c*	0.7523(1)	–0.0070(1)	0.56698(9)	0.052(1)	0.069(1)	0.055(1)	0.008(1)	0.0045(9)	0.014(1)
N(3)	8*c*	0.7399(1)	0.12118(9)	0.34280(8)	0.049(1)	0.052(1)	0.051(1)	0.0018(9)	–0.0070(8)	0.0037(9)
N(4)	8*c*	0.9093(1)	0.14166(9)	0.40020(9)	0.049(1)	0.049(1)	0.055(1)	–0.0004(8)	–0.0014(8)	–0.0059(9)
N(5)	8*c*	0.8778(1)	0.01925(9)	0.31797(8)	0.049(1)	0.053(1)	0.047(1)	0.0032(9)	–0.0009(8)	–0.0052(9)
C(1)	8*c*	0.7392(1)	0.0275(1)	0.5120(1)	0.043(1)	0.044(1)	0.046(1)	0.001(1)	0.0020(9)	–0.001(1)
C(2)	8*c*	0.8644(1)	–0.0097(1)	0.5031(1)	0.044(1)	0.074(2)	0.060(2)	0.016(1)	0.002(1)	0.012(1)
C(3)	8*c*	0.8323(1)	–0.0298(1)	0.5608(1)	0.056(1)	0.067(2)	0.057(1)	0.013(1)	–0.006(1)	0.015(1)
C(4)	8*c*	0.6574(1)	0.0589(1)	0.4955(1)	0.045(1)	0.053(1)	0.049(1)	0.004(1)	0.0017(9)	0.001(1)
C(5)	8*c*	0.6121(1)	0.0883(1)	0.5557(1)	0.041(1)	0.051(1)	0.049(1)	0.0040(9)	0.002(1)	0.004(1)
C(11)	8*c*	0.5219(1)	0.1020(1)	0.5406(1)	0.043(1)	0.047(1)	0.056(1)	0.001(1)	0.003(1)	0.000(1)
C(12)	8*c*	0.4858(1)	0.1111(1)	0.4816(1)	0.049(1)	0.071(2)	0.055(1)	0.004(1)	0.004(1)	0.000(1)
C(13)	8*c*	0.3941(1)	0.1234(1)	0.4878(1)	0.049(1)	0.060(2)	0.070(2)	0.002(1)	–0.009(1)	–0.001(1)
C(14)	8*c*	0.3808(1)	0.1189(1)	0.5606(1)	0.042(1)	0.045(1)	0.066(2)	0.001(1)	–0.000(1)	–0.000(1)
C(15)	8*c*	0.4572(1)	0.1068(1)	0.5916(1)	0.046(1)	0.040(1)	0.055(1)	0.001(1)	0.005(1)	–0.000(1)
C(16)	8*c*	0.4616(1)	0.1007(1)	0.6596(1)	0.051(1)	0.061(2)	0.064(2)	0.006(1)	0.002(1)	0.003(1)
C(17)	8*c*	0.3891(2)	0.1062(1)	0.6965(1)	0.073(2)	0.074(2)	0.066(2)	0.008(1)	0.020(1)	0.005(1)
C(18)	8*c*	0.3141(2)	0.1175(1)	0.6658(2)	0.054(2)	0.080(2)	0.086(2)	0.005(1)	0.022(1)	0.005(2)
C(19)	8*c*	0.3090(2)	0.1239(1)	0.5979(1)	0.044(1)	0.063(2)	0.093(2)	0.004(1)	0.002(1)	0.000(2)
C(21)	8*c*	0.6571(1)	0.1505(1)	0.5816(1)	0.043(1)	0.060(2)	0.049(1)	0.003(1)	0.007(1)	–0.002(1)
C(22)	8*c*	0.6472(2)	0.2120(1)	0.5516(1)	0.058(2)	0.062(2)	0.072(2)	0.004(1)	0.003(1)	–0.003(1)
C(23)	8*c*	0.6918(2)	0.2681(1)	0.5726(2)	0.078(2)	0.062(2)	0.094(2)	–0.000(2)	0.017(2)	–0.007(2)
C(24)	8*c*	0.7457(2)	0.2622(2)	0.6246(2)	0.084(2)	0.090(2)	0.085(2)	–0.027(2)	0.015(2)	–0.029(2)
C(25)	8*c*	0.7555(2)	0.2021(2)	0.6553(2)	0.094(2)	0.102(3)	0.075(2)	–0.028(2)	–0.018(2)	–0.008(2)
C(26)	8*c*	0.7121(2)	0.1465(2)	0.6338(1)	0.077(2)	0.082(2)	0.061(2)	–0.007(2)	–0.004(1)	0.003(1)
C(31)	8*c*	0.6729(1)	0.0757(1)	0.3227(1)	0.049(1)	0.073(2)	0.060(1)	–0.001(1)	–0.010(1)	–0.002(1)
C(32)	8*c*	0.6494(2)	0.0792(2)	0.2496(1)	0.075(2)	0.118(3)	0.072(2)	0.004(2)	–0.029(2)	–0.007(2)
C(33)	8*c*	0.7275(2)	0.1921(1)	0.3258(1)	0.074(2)	0.065(2)	0.085(2)	0.009(1)	–0.011(2)	0.013(2)
C(34)	8*c*	0.6521(2)	0.2238(2)	0.3565(2)	0.115(3)	0.081(2)	0.130(3)	0.038(2)	0.007(2)	0.009(2)
C(41)	8*c*	0.9888(1)	0.1589(1)	0.3693(1)	0.053(1)	0.066(2)	0.089(2)	–0.012(1)	0.007(1)	–0.007(2)
C(42)	8*c*	0.9846(2)	0.2175(2)	0.3235(2)	0.117(3)	0.072(2)	0.125(3)	–0.015(2)	0.043(2)	0.013(2)
C(43)	8*c*	0.8841(2)	0.1859(1)	0.4551(1)	0.077(2)	0.059(2)	0.069(2)	0.003(1)	–0.002(1)	–0.012(1)
C(44)	8*c*	0.9337(2)	0.1746(2)	0.5182(1)	0.134(3)	0.103(3)	0.068(2)	0.000(2)	–0.023(2)	–0.024(2)

Table 3. continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(51)	8*c*	0.8567(2)	0.0096(1)	0.2481(1)	0.067(2)	0.077(2)	0.058(2)	0.013(1)	–0.009(1)	–0.020(1)
C(52)	8*c*	0.8929(2)	0.0620(2)	0.2037(1)	0.141(3)	0.119(3)	0.053(2)	–0.010(2)	–0.010(2)	0.011(2)
C(53)	8*c*	0.9522(1)	–0.0179(1)	0.3381(1)	0.050(1)	0.066(2)	0.057(1)	0.000(1)	0.005(1)	–0.001(1)
C(54)	8*c*	0.9388(2)	–0.0925(1)	0.3459(2)	0.091(2)	0.065(2)	0.091(2)	0.016(2)	0.004(2)	0.008(2)

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References

1. Allen, F. H.: The Cambridge Structural Database: a quarter of a million crystal structures and rising. Acta Crystallogr. **B58** (2002) 380-388.
2. Tanski, J. M.; Parkin, G.: Synthesis and Structures of Zirconium-Pyrrolyl Complexes: Computational Analysis of the Factors That Influence the Coordination Modes of Pyrrolyl Ligands. Organometallics **21** (2002) 587-589.
3. Black, K.; Jones, A. C.; Bacsa, J.; Chalker, P. R.; Marshall, P. A.; Davies, H. O.; Heys, P. N.; O'Brien, P.; Afzaal, M.; Raftery, J.; Critchlow, G. W.: Investigation of New 2,5-Dimethylpyrrolyl Titanium Alkylamide and Alkoxide Complexes as Precursors for the Liquid Injection MOCVD of TiO_2. Chemical Vapor Deposition **16** (2010) 93-99.
4. Ferreira da Silva, J. L.; Galvão, A. C.; Ferreira, A. P.; Galvão, A. M.; Dias, A. R.; Gomes, P. T.; Salema, M. S.: Effect of ancillary ligands in the hapticity of the pyrrolyl ligand in $[Ti(pyrrolyl)(NMe_2)_xCl_{3-x}]$ (x=0, 1, 2, 3) complexes. J. Organomet. Chem. **695** (2010) 1533-1540.
5. Wang, X.; Nie, W.; Ge, F.; Borzov, M. V.: Two 18e$^-$ Ti IV η^5-Cp-tris(sec-amido)- type complexes derived from 1*H*-imidazol-2-yl side-chain functionalized cyclopentadienes. Acta Crystallogr. **C65** (2009) m255-m259.
6. Bruker: *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA (2007).
7. Sheldrick, G. M.: *SADABS*. University of Göttingen, Germany (1996).
8. Sheldrick, G. M.: A short history of *SHELX*. Acta Crystallogr. **A64** (2008) 112-122.
9. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.: *OLEX2*: a complete structure solution, refinement and analysis program. J. Appl. Cryst. **42** (2009) 339-341.