

A General Route to Sandwich and Half-sandwich Titanium Imido Complexes: X-Ray Structure of $[\text{Ti}(\eta^4\text{-Me}_8\text{taa})(\text{NBu}^t)]$ ($\text{Me}_4\text{taa} = \text{tetramethyldibenzotetraaza[14]annulene}$)

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The readily available complex $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{Bu}^t\text{py})_2]$ ($\text{Bu}^t\text{py} = 4\text{-tert-butylpyridine}$) is a useful precursor to a range of sandwich- and half-sandwich titanium imido derivatives including $[\text{Ti}(\eta\text{-C}_9\text{H}_4\text{Me}_3)(\text{NBu}^t)\text{Cl}(\text{Bu}^t\text{py})]$ ($\text{C}_9\text{H}_4\text{Me}_3 = \text{trimethylindenyl}$), $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{NBu}^t)(\text{Bu}^t\text{py})]$, $[\text{Ti}(\text{dmbpz})(\text{NBu}^t)\text{Cl}(\text{Bu}^t\text{py})]$ [$\text{dmbpz} = \text{tris}(3,5\text{-dimethylpyrazolyl})\text{borate}$] and $[\text{Ti}(\eta^4\text{-Me}_n\text{taa})(\text{NBu}^t)]$ ($n = 4$ or 8 ; $\text{Me}_{(4 \text{ or } 8)}\text{taa} = (\text{tetra- or octa-})\text{methyl-dibenzotetraaza[14]annulene}$ respectively).

Much of the current interest in transition metal–ligand multiple bonds has focused on the early transition metals.^{1–5} Reactive group 4 imido transients such as Bergman's $[\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2(\text{NBu}^t)]$,² and Wolczanski's $[\text{Zr}(\text{Bu}^t_3\text{SiNH})_2(\text{NSiBu}^t_3)]$ and $[\text{Ti}(\text{Bu}^t_3\text{SiO})_2(\text{NSiBu}^t_3)]$ ³ have demonstrated a rich chemistry including $[2 + 2]$ cycloadditions and alkane and arene C–H bond activations. Group 4 metal–ligand multiply-bonded complexes which have reactive M=E functionalities yet are sufficiently kinetically stable to be isolated are rare. The few examples include the monomeric oxo- and sulfido-derivatives $[\text{Ti}(\eta^4\text{-Me}_4\text{taa})(\text{E})]$ ($\text{Me}_4\text{taa} = \text{tetramethyldibenzotetraaza[14]annulene}$; E = O, S), first reported by Goedken in 1982.⁴ The first fully characterised monomeric titanium imido complexes were first reported as late as 1990 by Roesky and Rothwell.⁵ We describe here the synthesis of monomeric

sandwich and half-sandwich titanium imido derivatives *via* a general route which should provide straightforward access to new chemistry of the $\{\text{Ti}(\text{NR})\}$ unit.

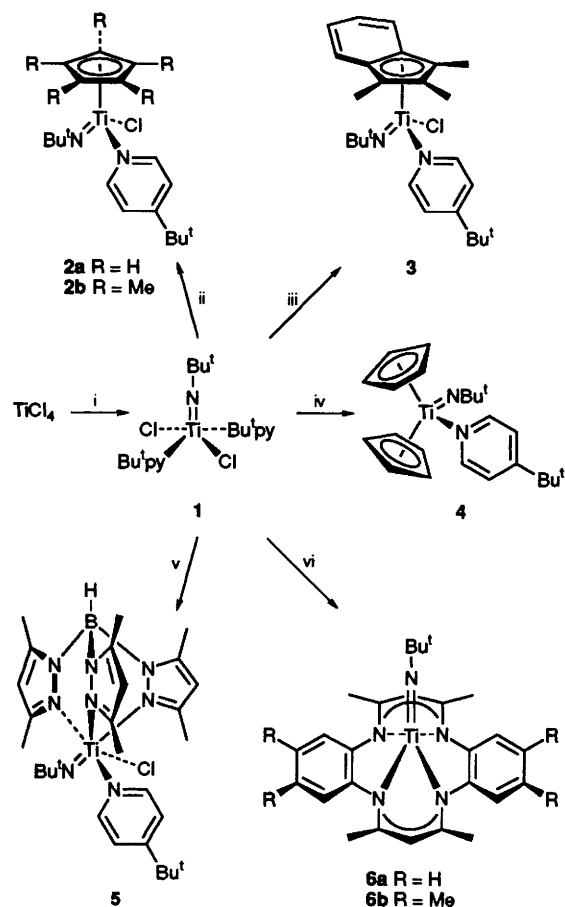
We have found that the $\text{Bu}^t\text{py}(\text{Bu}^t\text{py} = 4\text{-tert-butylpyridine})$ titanium *tert*-butylimido complex, $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{Bu}^t\text{py})_2]$ **1**† is a useful precursor to monomeric titanium imido complexes.‡ The new compound **1** is readily prepared in 25 g quantities and *ca.* 80% yield from TiCl_4 , Bu^tNH_2 and Bu^tpy (see Scheme 1). Other derivatives $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(4\text{-NC}_5\text{H}_4\text{R})_2]$ (R = H or Me) may be similarly prepared.⁶

Reaction of $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{Bu}^t\text{py})_2]$ **1** with one equivalent of $\text{Na}[\text{C}_5\text{H}_5]$ or $\text{Li}[\text{C}_5\text{Me}_5]$ gave the monomeric half-sandwich cyclopentadienyl complexes $[\text{Ti}(\eta\text{-C}_5\text{R}_5)(\text{NBu}^t)\text{Cl}(\text{Bu}^t\text{py})]$ (R = H, **2a**; or Me, **2b**) (Scheme 1).§ The analogous reaction of **1** with $\text{Li}[\text{C}_9\text{H}_4\text{Me}_3]$ ($\text{C}_9\text{H}_4\text{Me}_3 = \text{trimethylindenyl}$) afforded the first group 4 indenyl–imido derivative $[\text{Ti}(\eta\text{-C}_9\text{H}_4\text{Me}_3)(\text{NBu}^t)\text{Cl}(\text{Bu}^t\text{py})]$ **3** in *ca.* 40% yield.

Treatment of **1** with two equivalents of $\text{Na}[\text{C}_5\text{H}_5]$ in thf followed by recrystallisation from pentane afforded the red air- and moisture-sensitive bis(η -cyclopentadienyl) derivative $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{NBu}^t)(\text{Bu}^t\text{py})]$ **4**. The oxo analogue of **4**, $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)(\text{O})(4\text{-NC}_5\text{H}_4\text{R})]$ (R = H, Ph), has only recently been reported.⁷ $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{NBu}^t)(\text{Bu}^t\text{py})]$ **4** is analogous to the Zr congeners $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\text{NBu}^t)(\text{L})]$ (L = thf, OPPh_3)² and thus promises an interesting reaction chemistry. The only titanium analogues of **4** are the vinylimido complexes $[\text{Ti}(\eta\text{-C}_3\text{H}_5)_2(\text{NC}(\text{CH}_2)\text{Bu}^t)(\text{L})]$ (L = PMe_3 , py, $4\text{-NC}_5\text{H}_4\text{NMe}_2$) prepared from Tebbe's reagent⁸ and the nitrile $\text{Bu}^t\text{C}\equiv\text{N}$.⁹

We were also interested in preparing N-donor half-sandwich derivatives of the $\{\text{Ti}(\text{NBu}^t)\}$ unit. $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{Bu}^t\text{py})_2]$ **1** reacted smoothly at room temperature with $\text{K}(\text{dmbpz})$ in thf to afford $[\text{Ti}(\text{dmbpz})(\text{NBu}^t)\text{Cl}(\text{py-Bu}^t)]$ **5** in 55% yield. The tris(3-isopropylpyrazolyl)borate and tris(3-isopropyl-4-bromopyrazolyl)borate analogues of **5** may be similarly prepared.⁶

Pyrazolylborato–imido complexes are relatively rare¹⁰ and $[\text{Ti}(\text{dmbpz})(\text{NBu}^t)\text{Cl}(\text{py-Bu}^t)]$ **5** is the first example of a group 4 pyrazolylborato–imido derivative.



Scheme 1 Reagents and conditions: i, 6 Bu^tNH_2 , CH_2Cl_2 , 3 h followed by 2 Bu^tpy , CH_2Cl_2 , 2 h, *ca.* 80%; ii, $\text{Na}[\text{C}_5\text{H}_5]$ **2a** or $\text{Li}[\text{C}_5\text{Me}_5]$ **2b**, thf, -40°C , 1 h then room temp., 16 h, 30–50%; iii, $\text{Li}[\text{C}_9\text{H}_4\text{Me}_3]$, thf, -50°C , 1 h then room temp., 12 h, 40%; iv, 2 $\text{Na}[\text{C}_5\text{H}_5]$, thf, room temp., 16 h, *ca.* 50%; v, $\text{K}(\text{dmbpz})$, thf, room temp., 1.5 h, 55%; vi, $\text{Li}_2[\text{Me}_n\text{taa}]$, thf, room temp., 16 h, 70%. All the yields and conditions are unoptimised except those for the synthesis of $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{Bu}^t\text{py})_2]$ **1**.

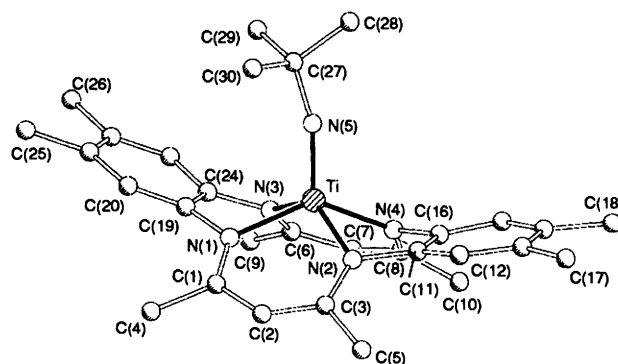


Fig. 1 Molecular structure of $[\text{Ti}(\text{Me}_8\text{taa})(\text{NBu}^t)]$ **6b**; hydrogen atoms omitted for clarity. Selected distances: $\text{Ti}-\text{N}(5)$ 1.724(4), $\text{N}(5)-\text{C}(27)$ 1.444(6), $\text{Ti}-\text{N}(1)$ 2.070(4), $\text{Ti}-\text{N}(2)$ 2.093(4), $\text{Ti}-\text{N}(3)$ 2.089(4), $\text{Ti}-\text{N}(4)$ 2.091(4), $\text{Ti}\cdots(\text{N}_4 \text{ plane})$ 0.76 Å; angle: $\text{Ti}-\text{N}(5)-\text{C}(27)$ $164.3(3)^\circ$. $\text{Ti}\cdots(\text{N}_4 \text{ plane})$ is the distance of the titanium atom from the least-squares plane defined by the atoms N(1), N(2), N(3) and N(4)

The aza-macrocyclic ligands, tetra- and octa-methyldibenzotetraaza[14]annulene (Me₄taa and Me₈taa respectively),¹¹ have been shown to stabilise metal–chalcogen multiple bonds in the complexes [Ti(Me_ntaa)(E)] (*n* = 4, 8; E = O, S)⁴ and [Ge(Me₈taa)(E)] (E = S, Se, Te).¹² In particular, the complexes [Ti(Me₄taa)(E)] have a rich addition and cycloaddition chemistry of the Ti=E multiple bond.^{4b} Reaction of **1** with one equivalent of the dilithium salts Li₂[Me₄taa]^{13a} or Li₂[Me₈taa]^{13b} in thf afforded the first group 4 macrocyclic imido derivatives [Ti(Me₄taa)(NBU^t)] **6a** and [Ti(Me₈taa)(NBU^t)] **6b** respectively.

The crystal structure of **6b** is shown in Fig. 1. The Ti atom lies 0.76 Å out of the macrocycle N₄ plane, and the Me₈taa ligand is saddle-shaped as expected. The Ti–N–Bu^t angle of 164.3(3)° is sufficiently close to linearity that we may infer that the Bu^tN ligand is acting as a four-electron donor. The Ti=NBU^t bond length [Ti–N(5) 1.724(4) Å] is quite long compared to titanium–imido linkages in general [range 1.672(7)–1.723(4) Å, seven examples; mean 1.710(1) Å]^{14a–c,5} and the longest found for a Ti=NBU^t linkage (the other values being 1.698(4) Å for [Ti(η-C₅Me₅)(NBU^t)Cl(py)]^{1b} and 1.672(7) Å for [Ti(NBU^t)Cl₂(OPPh₃)₂]^{1c}). The complexes **6** are formally fourteen-valence-electron species and promise an exciting reaction chemistry. Preliminary studies have shown that **6a** reacts with H₂O to afford the known yellow oxo complex [Ti(Me₄taa)-(O)]⁴ in 100% yield, and with CO₂ (1 atm pressure) to give an, as yet, unidentified product.

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Footnotes

† Selected ¹H NMR data: **1** (250 MHz, CDCl₃, room temp.) 9.18 (4 H, d, *J* = 6.6 Hz, 2,6-NC₅H₄Bu^t), 7.42 (4 H, d, *J* = 6.6 Hz, 3,5-NC₅H₄Bu^t), 1.36 (18 H, s, NC₅H₄Bu^t) 0.99 (9 H, s, NBU^t).

2a (250 MHz, CDCl₃, room temp.) δ 8.63 (2 H, d, *J* = 6.7 Hz, 2,6-NC₅H₄Bu^t), 7.42 (2 H, d, *J* = 6.7 Hz, 3,5-NC₅H₄Bu^t), 6.34 (5 H, s, C₅H₅), 1.35 (9 H, s, NC₅H₄Bu^t), 1.08 (9 H, s, NBU^t).

3 (250 MHz, CD₂Cl₂, 213 K) δ 7.85 (2 H, d, *J* = 6.6 Hz, 2,6-NC₅H₄Bu^t), 7.41 (1 H, d, *J* = 8.3 Hz, 4- or 7-C₉H₄Me₃), 7.30 (2 H, d, *J* = 6.6 Hz, 3,5-NC₅H₄Bu^t), 6.99 [1 H, d of d, *J* = 8.0, 8.3 Hz, 5- or 6-C₉H₄Me₃], 6.82 (1 H, d of d, *J* = 8.0, 8.3 Hz, 6- or 5-C₉H₄Me₃), 6.60 (1 H, d, *J* = 8.3 Hz, 7- or 4-C₉H₄Me₃), 2.80 (3 H, s, 2-C₉H₄Me₃), 2.46, 2.20 (2 × 3 H, 2 × s, 1- and 3-C₉H₄Me₃), 1.28 (9 H, s, NC₅H₄Bu^t), 0.99 (9 H, s, NBU^t).

5 (500 MHz, CD₂Cl₂, 223 K) δ 9.74 (1 H, d, *J* = 6.0 Hz, 2- or 6-NC₅H₄Bu^t), 7.55 (1 H, d of d, *J* = 6.0, 2.1 Hz, 3- or 5-NC₅H₄Bu^t), 7.28 (1 H, d, *J* = 6.0 Hz, 6- or 2-NC₅H₄Bu^t), 7.19 (1 H, d of d, *J* = 6.0, 2.1 Hz, 5- or 3-NC₅H₄Bu^t), 5.90, 5.88, 5.39 (3 × 1 H, 3 × s, N₂C₃Me₂H), 4.7 (1 H, br s, BH), 2.75, 2.41, 2.37, 2.24, 2.19 (5 × 3 H, 5 × s, N₂C₃Me₂H), 1.28 (9 H, s, NC₅H₄Bu^t), 1.16 (3 H, s, N₂C₃Me₂H), 1.10 (9 H, s, NBU^t).

6a (250 MHz, CDCl₃, room temp.) δ 7.32–7.36, 7.18–7.24 (2 × 4 H, 2 × m, C₆H₄ of Me₄taa ring), 5.13 (2 H, s, MeNCHNMe), 2.40 (12 H, s, 4 × NMe), 0.26 (9 H, s, NBU^t).

§ Two pyridine analogues of **2** have recently been described by Roesky {31–45% overall yield from Bu^tNH₂ and [Ti(η-C₅R₅)Cl₃], C₅R₅ = C₅Me₅ or C₅H₄(SiMe₃)}.^{1b}

¶ Crystal data for **6b**: C₃₀H₃₉N₅Ti, *M* = 517.6, triclinic, space group P $\bar{1}$, *T* = 150 K, *a* = 9.920(9), *b* = 12.181(8), *c* = 13.305(14) Å, α = 77.16(7), β = 71.83(7), γ = 68.25(6)°, *U* = 1408(2) Å³, *Z* = 2, *D_c* = 1.22 g cm⁻³, *F*(000) = 552, graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å, μ = 3.3 cm⁻¹. The intensities of 5204 reflections (4953 independent) were measured on a Rigaku AFC6S diffractometer (Lehmann–Larsen scan, θ < 25°) at 150 K. The structure was solved by direct methods (SHELXS-86) and refined in anisotropic approximation (H atoms isotropic in riding model) by full-matrix least-squares (SHELXL-93) against *F*² for all reflections to *wR*₂ = 0.174 [to *R*₁ = 0.069 for 3014 reflections with *I* > 2σ(*I*)]. Large displacement parameters of the methyl carbon atoms in the NBU^t ligand probably indicate static (rotational) disorder of the NBU^t group. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

- (a) J. E. Hill, P. E. Fanwick and I. P. Rothwell, *Inorg. Chem.*, 1991, **30**, 1143; R. Duchateau, A. J. Williams, S. Gambarotta and M. Y. Chang, *Inorg. Chem.*, 1991, **30**, 4863; C. H. Zambrano, R. D. Profflet, J. E. Hill, P. E. Fanwick and I. P. Rothwell, *Polyhedron*, 1993, **12**, 689; (b) Y. Bai, M. Noltemeyer and H. W. Roesky, *Z. Naturforsch., Teil B*, 1992, **46**, 1357; (c) C. H. Winter, P. H. Sheridan, T. S. Lekebandova, M. J. Heeg and J. W. Proscia, *J. Am. Chem. Soc.*, 1992, **114**, 1095; (d) W. A. Howard and G. Parkin, *J. Am. Chem. Soc.*, 1994, **116**, 606; P. L. McGrane, M. Jensen and T. Livinghouse, *J. Am. Chem. Soc.*, 1992, **114**, 5459; P. L. McGrane and T. Livinghouse, *J. Am. Chem. Soc.*, 1993, **115**, 11485.
- A. M. Baranger and R. G. Bergman, *J. Am. Chem. Soc.*, 1994, **116**, 3822; K. E. Meyer, P. J. Walsh and R. G. Bergman, *J. Am. Chem. Soc.*, 1994, **116**, 2669; P. J. Walsh, F. J. Hollander and R. G. Bergman, *Organometallics*, 1993, **12**, 3705.
- C. P. Schaller, J. B. Bonanno and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1994, **116**, 4133; J. L. Bennet and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1994, **116**, 2179.
- (a) V. L. Goedken and J. A. Ladd, *J. Chem. Soc., Chem. Commun.*, 1982, 142; (b) C. E. Housmekerides, D. L. Ramage, C. M. Kretz, J. T. Schontz, R. S. Pilato, G. L. Geoffroy, A. L. Rheingold and B. S. Haggerty, *Inorg. Chem.*, 1992, **31**, 4453.
- H. W. Roesky, H. Voelker, M. Witt and M. Noltemeyer, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 669; J. E. Hill, R. D. Profflet, P. Fanwick and I. P. Rothwell, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 664.
- S. C. Dunn, K. A. Butakoff and P. Mountford, unpublished results.
- M. R. Smith, P. T. Matsunaga and R. A. Andersen, *J. Am. Chem. Soc.*, 1993, **115**, 7049.
- F. N. Tebbe, G. W. Parshall and G. S. Reddy, *J. Am. Chem. Soc.*, 1978, **100**, 3611.
- K. M. Doxsee and J. B. Farahi, *J. Chem. Soc., Chem. Commun.*, 1990, 1452; K. M. Doxsee, J. B. Farahi and H. Hope, *J. Am. Chem. Soc.*, 1991, **113**, 8889.
- L. Luan, P. S. White, M. Brookhart and J. L. Templeton, *J. Am. Chem. Soc.*, 1990, **112**, 8190; L. Luan, M. Brookhart and J. L. Templeton, *Organometallics*, 1992, **11**, 1433; J. Sundermeyer, J. Putterlik, M. Foth, J. S. Fied and N. Rawnesas, *Chem. Ber.*, 1994, **127**, 1201.
- F. A. Cotton and J. Czuchajowska, *Polyhedron*, 1990, **9**, 2553.
- M. C. Kuchta and G. Parkin, *J. Chem. Soc., Chem. Commun.*, 1994, 1351.
- (a) S. De Angelis, E. Solari, E. Gallo, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Inorg. Chem.*, 1992, **31**, 2520; (b) R. F. Jordan, personal communication.