A General Route to Sandwich and Half-sandwich Titanium Imido Complexes: X-Ray Structure of $[Ti(\eta^4-Me_8taa)(NBu^t)]$ (Me_4taa = tetramethyldibenzotetraaza[14]annulene)

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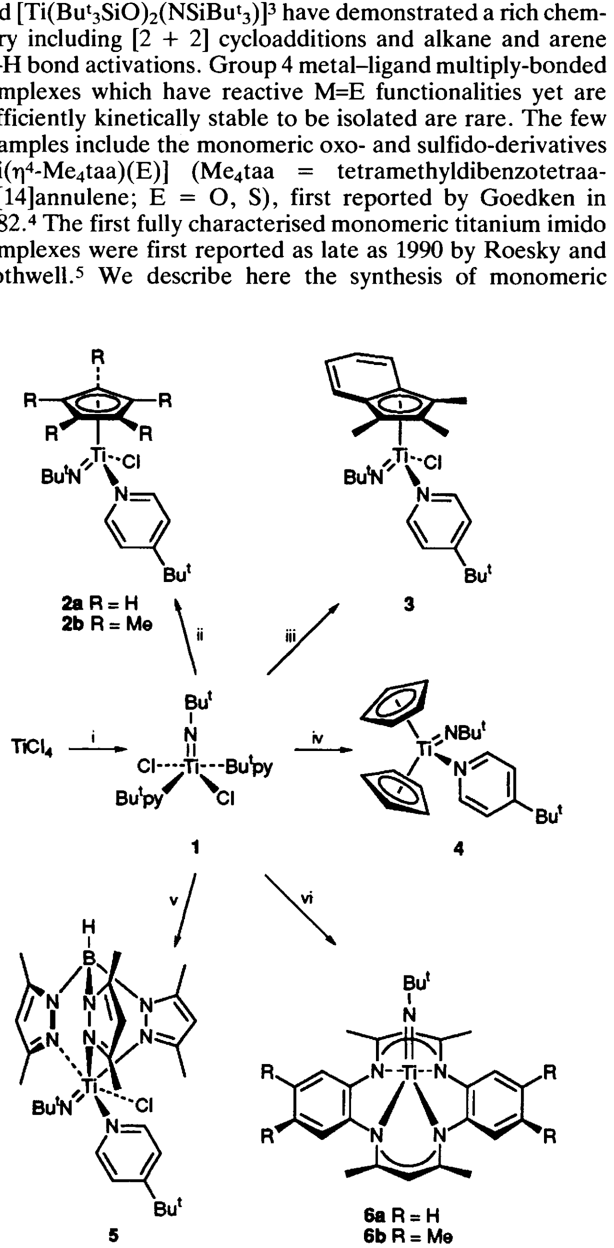
The readily available complex $[Ti(NBu^t)Cl_2(Bu^tpy)_2]$ (Bu^tpy = 4-*tert*-butylpyridine) is a useful precursor to a range of sandwich- and half-sandwich titanium imido derivatives including $[Ti(\eta-C_9H_4Me_3)(NBu^t)Cl(Bu^tpy)]$ ($C_9H_4Me_3$ = trimethylindenyl), $[Ti(\eta-C_5H_5)_2(NBu^t)(Bu^tpy)]$, $[Ti(dmbpz)(NBu^t)Cl(Bu^tpy)]$ [dmbpz = tris(3,5-dimethylpyrazolyl) borate] and $[Ti(\eta^4-Me_ntaa)(NBu^t)]$ {n = 4 or 8; $Me_{(4\ \mathrm{or}\ 8)}taa$ = (tetra- or octa-)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 $[Zr(\eta^5-C_5H_5)_2(NBu^t)]$,[2] and Wolczanski's $[Zr(Bu^t{}_3SiNH)_2(NSiBu^t{}_3)]$ and $[Ti(Bu^t{}_3SiO)_2(NSiBu^t{}_3)]$[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 $[Ti(\eta^4-Me_4taa)(E)]$ (Me_4taa = 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 {Ti(NR)} unit.



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, $Na[C_5H_5]$ **2a** or $Li[C_5Me_5]$ **2b**, thf, −40 °C, 1 h then room temp., 16 h, 30–50%; iii, $Li[C_9H_4Me_3]$, thf, −50 °C, 1 h then room temp., 12 h, 40%; iv 2 $Na[C_5H_5]$, thf, room temp., 16 h, *ca.* 50%; v, K(dmbpz), thf, room temp., 1.5 h, 55%; vi, $Li_2[Me_ntaa]$, thf, room temp., 16 h, 70%. All the yields and conditions are unoptimised except those for the synthesis of $[Ti(NBu^t)Cl_2(Bu^tpy)_2]$ **1**.

We have found that the Bu^tpy(Bu^tpy = 4-*tert*-butylpyridine) titanium *tert*-butylimido complex, $[Ti(NBu^t)Cl_2(Bu^tpy)_2]$ **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 $[Ti(NBu^t)Cl_2(4-NC_5H_4R)_2]$ (R = H or Me) may be similarly prepared.[6]

Reaction of $[Ti(NBu^t)Cl_2(Bu^tpy)_2]$ **1** with one equivalent of $Na[C_5H_5]$ or $Li[C_5Me_5]$ gave the monomeric half-sandwich cyclopentadienyl complexes $[Ti(\eta-C_5R_5)(NBu^t)Cl(Bu^tpy)]$ (R = H, **2a**; or Me, **2b**) (Scheme 1).§ The analogous reaction of **1** with $Li[C_9H_4Me_3]$ ($C_9H_4Me_3$ = trimethylindenyl) afforded the first group 4 indenyl–imido derivative $[Ti(\eta-C_9H_4Me_3)(NBu^t)Cl(Bu^tpy)]$ **3** in *ca.* 40% yield.

Treatment of **1** with two equivalents of $Na[C_5H_5]$ in thf followed by recrystallisation from pentane afforded the red air- and moisture-sensitive bis(η-cyclopentadienyl) derivative $[Ti(\eta-C_5H_5)_2(NBu^t)(Bu^tpy)]$ **4**. The oxo analogue of **4**, $[Ti(\eta-C_5Me_5)(O)(4-NC_5H_4R)]$ (R = H, Ph), has only recently been reported.[7] $[Ti(\eta-C_5H_5)_2(NBu^t)(Bu^tpy)]$ **4** is analogous to the Zr congeners $[Zr(\eta-C_5H_5)_2(NBu^t)(L)]$ (L = thf, $OPPh_3$)[2] and thus promises an interesting reaction chemistry. The only titanium analogues of **4** are the vinylimido complexes $[Ti(\eta-C_5H_5)_2\{NC(CH_2)Bu^t\}(L)]$ (L = PMe_3, py, $4-NC_5H_4NMe_2$) prepared from Tebbe's reagent[8] and the nitrile $Bu^tC{\equiv}N$.[9]

We were also interested in preparing N-donor half-sandwich derivatives of the {$Ti(NBu^t)$} unit. $[Ti(NBu^t)Cl_2(Bu^tpy)_2]$ **1** reacted smoothly at room temperature with K(dmbpz) in thf to afford $[Ti(dmbpz)(NBu^t)Cl(py-Bu^t)]$ **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 rare[10] and $[Ti(dmbpz)(NBu^t)Cl(py-Bu^t)]$ **5** is the first example of a group 4 pyrazolylborato–imido derivative.

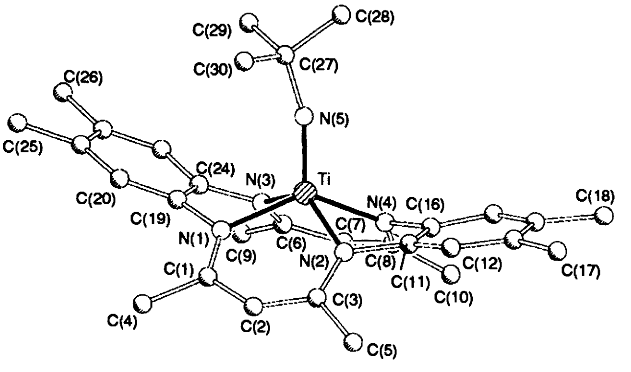


Fig. 1 Molecular structure of $[Ti(Me_8taa)(NBu^t)]$ **6b**; hydrogen atoms omitted for clarity. Selected distances: Ti–N(5) 1.724(4), N(5)–C(27) 1.444(6), Ti–N(1) 2.070(4), Ti–N(2) 2.093(4), Ti–N(3) 2.089(4), Ti–N(4) 2.091(4), Ti···(N_4 plane) 0.76 Å; angle: Ti–N(5)–C(27) 164.3(3)°. Ti···(N_4 plane) 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 (Me_4taa and Me_8taa 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(Me_8taa)(E)] (E = S, Se, Te).[12] In particular, the complexes [Ti(Me_4taa)(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 Li_2[Me_4taa][13a] or Li_2[Me_8taa][13b] in thf afforded the first group 4 macrocyclic imido derivatives [Ti(Me_4taa)(NBu^t)] **6a** and [Ti(Me_8taa)(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 N_4 plane, and the Me_8taa 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][1a–c,5] and the longest found for a Ti=NBu^t linkage {the other values being 1.698(4) Å for [Ti(η-C_5Me_5)(NBu^t)Cl(py)][1b] and 1.672(7) Å for [Ti(NBu^t)Cl_2($OPPh_3$)$_2$][1c]}. The complexes **6** are formally fourteen-valence-electron species and promise an exciting reaction chemistry. Preliminary studies have shown that **6a** reacts with H_2O to afford the known yellow oxo complex [Ti(Me_4taa)-(O)][4] in 100% yield, and with CO_2 (1 atm pressure) to give an, as yet, unidentified product.

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Footnotes

† Selected ^1H NMR data: **1** (250 MHz, $CDCl_3$, room temp.) 9.18 (4 H, d, J = 6.6 Hz, 2,6-$NC_5H_4Bu^t$), 7.42 (4 H, d, J = 6.6 Hz, 3,5-$NC_5H_4Bu^t$)], 1.36 (18 H, s, $NC_5H_4Bu^t$) 0.99 (9 H, s, NBu^t).

2a (250 MHz, $CDCl_3$, room temp.) δ 8.63 (2 H, d, J = 6.7 Hz 2,6-$NC_5H_4Bu^t$), 7.42 (2 H, d, J = 6.7 Hz, 3,5-$NC_5H_4Bu^t$), 6.34 (5 H, s, C_5H_5), 1.35 (9 H, s, $NC_5H_4Bu^t$), 1.08 (9 H, s, NBu^t).

3 (250 MHz, CD_2Cl_2, 213 K) δ 7.85 (2 H, d, J = 6.6 Hz, 2,6-$NC_5H_4Bu^t$), 7.41 (1 H, d, J = 8.3 Hz, 4- or 7-$C_9H_4Me_3$), 7.30 (2 H, d, J = 6.6 Hz, 3,5-$NC_5H_4Bu^t$), 6.99 [1 H, d of d, J = 8.0, 8.3 Hz, 5- or 6-$C_9H_4Me_3$], 6.82 (1 H, d of d, J = 8.0, 8.3 Hz, 6- or 5-$C_9H_4Me_3$), 6.60 (1 H, d, J 8.3 Hz, 7- or 4-$C_9H_4Me_3$), 2.80 (3 H, s, 2-$C_9H_4Me_3$), 2.46, 2.20 (2 × 3 H, 2 × s, 1- and 3-$C_9H_4Me_3$), 1.28 (9H, s, $NC_5H_4Bu^t$), 0.99 (9 H, s, NBu^t).

5 (500 MHz, CD_2Cl_2, 223 K) δ 9.74 (1 H, d, J 6.0 Hz, 2- or 6-$NC_5H_4Bu^t$), 7.55 (1 H, d of d, J = 6.0, 2.1 Hz, 3- or 5-$NC_5H_4Bu^t$), 7.28 (1 H, d, J = 6.0 Hz, 6- or 2-$NC_5H_4Bu^t$), 7.19 (1 H, d of d, J 6.0, 2.1 Hz, 5- or 3-$NC_5H_4Bu^t$), 5.90, 5.88, 5.39 (3 × 1 H, 3 × s, $N_2C_3Me_2H$), 4.7 (1 H, br s, BH), 2.75, 2.41, 2.37, 2.24, 2.19 (5 × 3 H, 5 × s, $N_2C_3Me_2H$), 1.28 (9 H, s, $NC_5H_4Bu^t$), 1.16 (3 H, s, $N_2C_3Me_2H$), 1.10 (9 H, s, NBu^t).

6a (250 MHz, $CDCl_3$, room temp.) δ 7.32–7.36, 7.18–7.24 (2 × 4 H, 2 × m, C_6H_4 of Me_4taa 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^tNH_2 and [Ti(η-C_5R_5)Cl_3], C_5R_5 = C_5Me_5 or $C_5H_4(SiMe_3)$}.[1b]

¶ *Crystal data* for **6b**: $C_{30}H_{39}N_5Ti$, 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) Å^3, Z = 2, D_c = 1.22 g cm^{-3}, $F(000)$ = 552, grapite-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, $\theta < 25°$) 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 (SHELXTL-93) against F^2 for all reflections to wR_2 = 0.174 [to R_1 = 0.069 for 3014 reflections with $I > 2\sigma(I)$]. 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.

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