Synthesis and molecular and electronic structure of monomeric $[Ti(\eta^8\text{-}C_8H_8)(NBu^t)]$

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Reaction of $[Ti(NBu^t)Cl_2(py)_3]$ with $K_2[C_8H_8]$ gave the monomeric, pseudo-two-coordinate complex $[Ti(\eta^8\text{-}C_8H_8)(NBu^t)]$ 1 which has been crystallographically characterised; the electronic structure of 1 has been investigated using density functional theory calculations and gas phase photoelectron spectroscopy.

As part of an ongoing programme in titanium–imido chemistry we found that the compound $[Ti(NBu^t)Cl_2(py)_3]$ provides a useful synthetic entry to a range of sandwich, half-sandwich and other new titanium imido compounds.[1] We noticed that although cyclopentadienyl and, to a lesser extent, arene coligands have been widely used in transition metal imido chemistry,[2] there has been only one report of imido complexes bearing cyclooctatetraenyl coligands, namely the dinuclear μ-arylimido derivatives $[M_2(\eta^8\text{-}C_8H_8)_2(\mu\text{-}NC_6H_3Pr^i{}_2\text{-}2,6)_2]$ (M = Zr, Hf).[3] We were therefore interested to see if using the smaller titanium congener would lead to a mononuclear derivative. Here we describe the synthesis and molecular and electronic structure of the cyclooctatetraenyltitanium imido complex $[Ti(\eta^8\text{-}C_8H_8)(NBu^t)]$ **1**.

Addition of 1 equiv. of $K_2[C_8H_8]$ to $[Ti(NBu^t)Cl_2(py)_3]$ in THF at −50 °C gave a dark red solution. Standard workup and crystallisation from pentane gave $[Ti(\eta^8\text{-}C_8H_8)(NBu^t)]$ **1** as a spectroscopically pure, dark yellow powder in 68% yield. Compound **1** is highly air- and moisture-sensitive, and its ^1H and ^{13}C NMR spectra contain signals attributable to a *tert*-butylimido ligand and an octahapto-coordinated C_8H_8 ring. Crystals of **1** suitable for X-ray diffraction analysis could be obtained by careful tube sublimation at 90–100 °C, 5×10^{-6} mbar.‡ The solid state structure of **1** is shown in Fig. 1. The $Ti{=}NBu^t$ and $Ti\cdots C_8H_8$ (ring centroid) distances of 1.699(6) and 1.369 Å are normal for terminal titanium-*tert*-butylimido and titanium(IV)-η^8-cyclooctatetraenyl complexes, respectively.[4] The near-linearity of the $Ti{=}N{-}Bu^t$ angle [Ti(1)–N(1)–C(1) 177.1(5)°] is consistent with the imido ligand acting as a four-electron donor to the titanium centre (*vide infra*), giving an overall metal valence-electron count of 16.

The pseudo-two-coordinate, 'one-legged piano stool' geometry for **1** is unique in early transition metal imido and cyclooctatetraenyl ligand chemistry.[2,5] A search of the Cambridge Structural Database[4] for complexes of the type $[Ti(\eta^8\text{-}C_8H_8(L)_n]$ showed that the formal value of *n* is at least three. As mentioned, there has been only one report of imido complexes bearing cyclooctatetraenyl coligands, these being dinuclear.[3] The molecular structure of $[Ti(\eta^8\text{-}C_8H_8)(NBu^t)]$ is apparently related to those of the 18 valence electron, later transition metal compounds $[Os(\eta^6\text{-}C_6Me_6)(NBu^t)]$,[6a] $[Ir(\eta^5\text{-}C_5Me_5)(NBu^t)]$,[6b] and $[Ni(\eta^5\text{-}C_5H_5)(NO)]$.[6c] The bonding in these compounds is analagous to that of mixed ring sandwich compounds[7] as we[8,9] and others[10] have previously analysed.

The gas phase He photoelectron (PE) spectrum§ of $[Ti(\eta^8\text{-}C_8H_8)(NBu^t)]$ **1** is shown in Fig. 2, and numerical data are summarised in Table 1. Its assignment is made relatively straightforward by comparison with related imido and cyclooctatetraenyl compounds.[7b,8] The apparent paucity of low ionisation energy (IE) bands for **1** is explained by the fact that the e_2 ionisation of the Ti–C_8H_8 ring δ bonding orbitals overlaps with the e_1 ionisation of the Ti–N π bonds producing a complex band centred at 8 eV. Band C at 10.91 eV may be assigned to an e_1 ionisation of the C_8H_8 ring π orbitals. An increase in the intensity of bands A and B relative to C in the He II spectrum indicated that the e_2 and $2e_1$ orbitals that give rise to bands A and B have significant metal character.

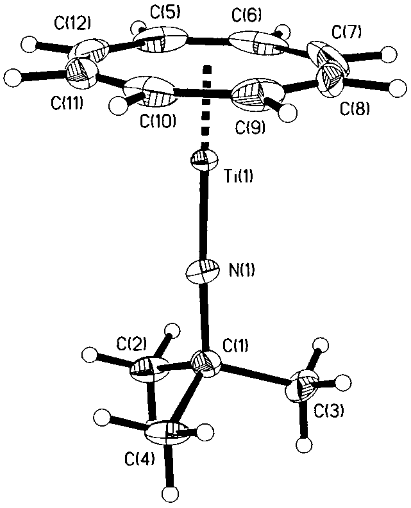

Fig. 1 Displacement ellipsoid plot of $[Ti(\eta^8\text{-}C_8H_8)(NBu^t)]$ **1**. Hydrogen atoms are drawn as spheres of arbitrary radius. Displacement ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (°): Ti(1)–N(1) 1.699(6), Ti(1)–$C_{average}$ 2.280 [range 2.267(8) to 2.290(8)], Ti(1)···C_8(centroid) 1.369; Ti(1)–N(1)–C(1) 177.1(5), C_8(centroid)–Ti(1)–N(1) 179.3.

An interesting comparison may be made with the 17 valence electron, d^1 compound $[Ti(\eta^8\text{-}C_8H_8)(\eta^5\text{-}C_5Me_5)]$.[7b] In the PE spectrum of this compound there is an additional low-lying ionisation band of the extra d electron at 5.28 eV, but the e_2 and $2e_1$ bands are also found to be coincident with a maximum at

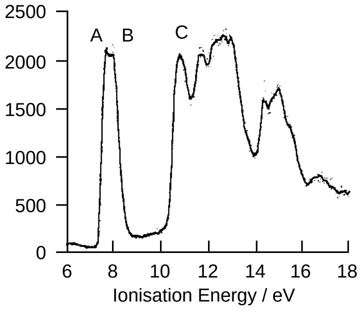

Fig. 2 He I full range PE spectrum of **1** [see http://www.rsc.org/suppdata/cc/1998/1235 for PE spectrum of **1**: (*a*) He I full range, (*b*) He I short range, (*c*) He II short range]

Table 1 Comparison of calculated ionisation energies (eV) and bond lengths (Å) for **1** and [Ti(η^8-C_8H_8)(NH)], **2**, with experimental values for **1**

	1 (exptl.)	**1** (calc.)	**2** (calc.)
Ionisation energies			
$1e_2$	7.78 (A)	7.70	8.16
$2e_1$	8.05 (B)	7.88	8.91
$1e_1$	10.91 (C)	[a]	10.83
Bond lengths			
Ti–C	2.267(8)–2.290(8)	2.282	2.275
Ti–N	1.699(6)	1.689	1.683
C–C ring	1.37(2)–1.44(2)	1.409	1.408
Bu^t	1.51(1)–1.52(1)	1.519	

[a] SCF convergence not achieved for this ion state.

7.54 eV. Furthermore, the $1e_1$ band lies at 10.5 eV, which is of a very similar energy to that for **1**. Thus we may conclude that the cyclopentadienyl–imido analogy[8] holds for these compounds and that *tert*-butylimido is electronically similar to the pentamethylcyclopentadienyl ligand though it provides one less electron.

Density functional calculations[11] were used to optimise the geometry of **1**.¶ C_s symmetry was assumed but in addition parameters were fixed so that the Ti-ring fragment had C_{8v} symmetry and the N–Bu^t fragment C_{3v} symmetry. Calculated bond lengths and angles are compared with the experimental ones in Table 1 which shows that the agreement is very good. Calculation of IEs‖ for **1** proved difficult because of the low symmetry and the proximity of ion states of identical symmetry. IE calculations were therefore also carried out on [Ti(η^8-C_8H_8)(NH)] **2** as a model for **1**. C_{8v} symmetry was assumed throughout these calculations. The calculated IEs for both **1** and **2** are given in Table 1 along with experimental values for **1**. The *tert*-butyl substituent has a bigger effect on the Ze_1 IE than the e_2 EI. The closeness of the two ion states means that their exact assignment is uncertain.

Isosurfaces for these two orbitals (e_2 and $2e_1$) together with those for the $1e_1$ and the a_1 N–Ti σ-bonding orbital are shown in Fig. 3. Mulliken population analysis of the ground state structure of **1** gives the Ti contribution to the $2e_1$ and e_2 orbitals as 26% and 21%, while that of $1e_1$ is estimated as 8%. This is consistent with the intensity increase of bands A + B relative to C as the photon energy is increased. The most striking aspect of the metal ligand bonding orbitals is that binding to the imido group is through σ and π orbitals whereas that to the C_8H_8 ring is virtually exclusively through δ symmetry orbitals. This is in contrast to bis-cyclopentadienyl metal complexes where both rings compete for the metal π symmetry orbitals.

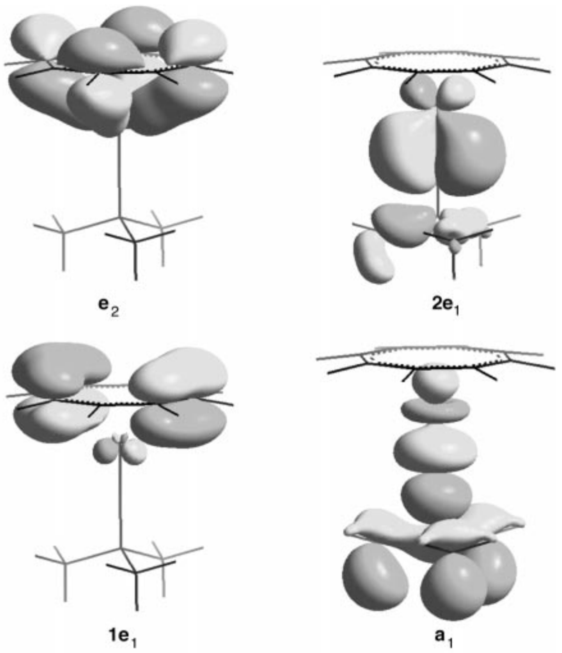

Fig. 3 Isosurfaces for the e_2, $2e_1$, $1e_1$ and M–N a_1 orbitals of **1** (see http://www.rsc.org/suppdata/cc/1998/1235 for a full colour version of this figure)

In conclusion, we have firmly established a new class of early transition metal cyclooctatetraenyl and imido complexes through structural, spectroscopic and theoretical studies. Recent preliminary studies suggest that the Ti=NBu^t linkage in **1** is reactive towards a range of organic substrates. Our work in this area and syntheses of other early transition metal cyclooctatetraenyl–imido complexes are continuing.

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Notes and References

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‡ *Crystal data* for **1**: $C_{12}H_{17}NTi$, M = 223.17, triclinic, space group $P\bar{1}$ (no. 2), a = 6.255(3), b = 8.980(4), c = 11.144(6) Å, α = 82.58(6), β = 89.74(4), γ = 70.51(6)°, U = 584.7(8) Å^3, Z = 2, T = 150(2) K, μ = 0.69 mm^{-1}, no. of $I > 3\sigma(I)$ data used in refinement 1204, no. of parameters refined 129, full-matrix least squares on F with Chebychev polynomial weighting scheme, final R indices: R = 0.094, R_w = 0.097 for 4774 data, GOF = 1.14 (on F), final $(\Delta/\sigma)_{max}$ 0.001, largest residual peaks 1.12 and −1.09 e Å^{-3}. CCDC 182/841.

§ PE spectra were measured using a PES Laboratories 0078 spectrometer and were calibrated with N_2, Xe and He.

¶ Calculations were performed using the density functional methods of the Amsterdam Density Functional (ADF) code Version 2.3.0.[11] The basis set used triple-ζ accuracy sets of Slater orbitals with a single polarisation function added to main group atoms, 2p on H, 3p on C and N. Cores of the atoms were frozen, (C 1s, N 1s and Ti 3p). Vosko, Wilk and Nusair's local exchange correlation potential[12] was employed with non-local exchange corrections by Becke[13] and non-local correlation corrections by Perdew.[14] Vertical ionisation energies were estimated by calculating the energy of the molecular ion, with identical geometry to the optimised structure for the molecule, in its ground and low lying excited states and subtracting the energy of the molecular ground state.

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