Structural Characterization of Titanium(III) Amide Complexes; a Planar Geometry at Nitrogen in the Absence of Ti–N Multiple Bonding

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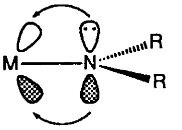
The titanium(III) complexes [Ti(η^5-C_5Me_5)$_2$(NMePh)] and [Ti(η^5-C_5Me_5)$_2$(NMePh)(CNBu^n)] have been characterized by X-ray crystallography.

The high M–N bond energies of early transition metal amide complexes have generally been attributed to metal–nitrogen multiple bonding. In addition, the observation of short metal–nitrogen bond distances, as well as trigonal-planar amide ligands, has been used as evidence supporting the existence of nitrogen to metal π-donation (as shown schematically in structure X).[1] We report here the structures of complexes **1** and **2**, the first titanocene amide complexes containing Ti^{III} to have been crystallographically characterized. Although both compounds contain planar amide ligands, a Ti–N π-bond is almost certainly *not* present in either case.

$[Ti(\eta^5\text{-}C_5Me_5)_2(NMeP\dot{h})]$
1
$[Ti(\eta^5\text{-}C_5Me_5)_2(NMePh)(CNBu^n)]$
2

The structure of **1** is shown in Fig. 1.† The plane defined by N(1), C(1) and C(2) of the *N*-methylanilido ligand is perpendicular to that defined by Ti and the C_5Me_5 ligand centroids, thus minimizing steric interactions between the ligands. This orientation of the amide ligand makes donation of the nitrogen lone pair of electrons to titanium unlikely, even though the latter is electronically unsaturated (15 e): the low-lying $1a_1$ and b_2 acceptor orbitals of bent metallocene complexes are in the plane perpendicular to the (C_5Me_5)–M–(C_5Me_5) plane.[2] A repulsive interaction between the nitrogen lone pair and the filled titanium $1b_1$ orbital[3] is possible, however (Fig. 2). The Ti–N bond distance is unusually long as a result [2.054 (2) Å].‡ Within experimental error, this distance is equal to the sum of the single-bond radii for titanium and nitrogen (2.06 Å);[4] it is longer, however, than that generally observed for Ti–N σ-bonds in other unsaturated complexes (1.85–1.98 Å).[5] The crowded coordination sphere in **1**, as indicated by the relatively small (C_5Me_5)–Ti–(C_5Me_5) angle (140.5°),[6] probably also contributes to the long Ti–N distance. The geometry about nitrogen is strictly trigonal planar [the sum of the three angles about N(1) is 359°]. We attribute this to steric interactions between the amide and C_5Me_5 ligands, and perhaps also conjugation of the nitrogen lone pair with the phenyl ring.§ A weak multiple bonding interaction between nitrogen and the titanium's high-lying, empty $2b_1$ orbital[2] cannot be entirely ruled out, however.[7]



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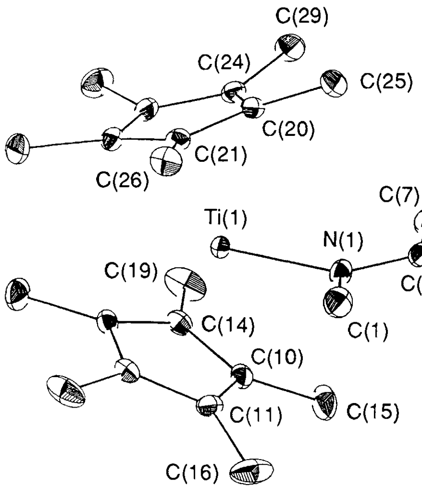

Fig. 1 Structure of complex **1**. Selected distances (Å) and angles (°): Ti(1)–N(1) 2.054(2), N(1)–C(1) 1.447(3), N(1)–C(2) 1.361(3), Ti(1)–N(1)–C(1) 110.8(2), Ti(1)–N(1)–C(2) 131.6(1), C(1)–N(1)–C(2) 116.7(2).

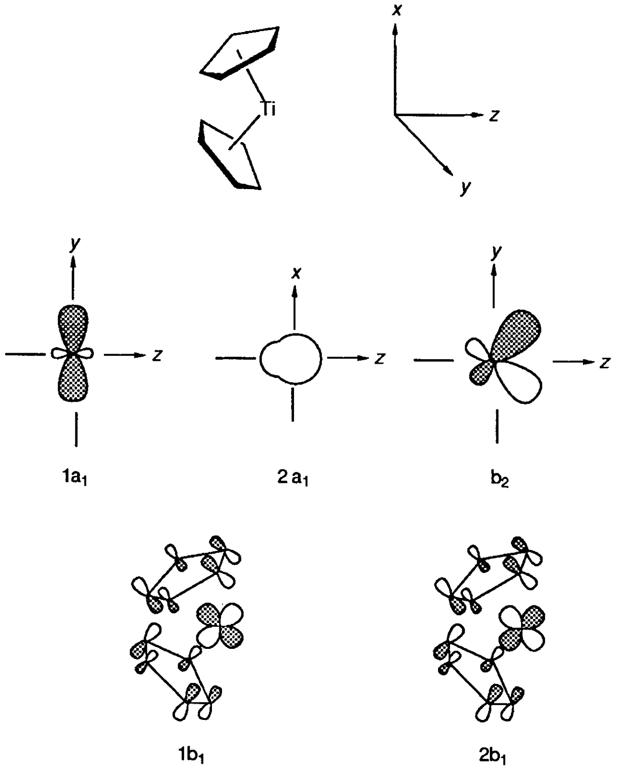

Fig. 2 $(C_5Me_5)_2Ti$ fragment orbitals (refs. 2 and 3)

Addition of *n*-butyl isocyanide to **1** gives complex **2**, the structure of which is shown in Fig. 3.† The Ti–N(1) bond distance of 2.157(5) Å in this compound is very long for a σ-bond between titanium and nitrogen, and in the range often observed for ≡N:→Ti dative bonds.[5a,8] The long Ti–N distance in **2** is undoubtedly due, in part, to the crowded coordination sphere in this molecule. It should also be noted that although the geometry about nitrogen is planar [the sum of the three angles about N(1) is 359°], there are no empty Ti orbitals of the correct symmetry to overlap with the nitrogen atom's lone electron pair.[2] Moreover, such an interaction would lead to a formal electron count of 19 e on titanium. Thus, despite the apparent sp^2 hybridization at N, we suggest that there is no

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† Compound **1** was prepared by addition of LiNMePh to $[Ti(C_5Me_5)_2Cl]$ (ref. 5) in tetrahydrofuran. *Crystal data* for **1**: $C_{27}H_{38}NTi$, monoclinic, $P2_1/c$ (No. 14), a = 11.891(6), b = 15.280(2), c = 12.985(6) Å, β = 94.26(2)°, from 25 reflections, T = −70 °C, V = 2352.8 $Å^3$, Z = 4, M_r = 424.51, D_c = 1.198 g cm^{-3}. A black irregular block, ~0.50 × 0.33 × 0.51 mm, obtained from pentane at −25 °C, was used for the data collection. 5792 Reflections were collected in the range $2.7° \leqslant 2\theta \leqslant 55.0°$ with scan width = 1.20–1.90 °ω and scan speed = 1.70–5.00 ° min^{-1}. Final R = 0.039, R_w = 0.036, error of fit = 1.32, max Δ/σ = 0.22.

Crystal data for **2**: $C_{32}H_{47}N_2Ti$, orthorhombic, *Pbca* (No. 61), a = 13.964(3), b = 26.053(3), c = 16.236(3) Å, from 25 reflections, T = −70 °C, V = 5906.7 $Å^3$, Z = 8, M_r = 507.64, D_c = 1.141 g cm^{-3}. A dark green, irregular block, ~0.54 × 0.33 × 0.58 mm, obtained from pentane at −25 °C, was used for the data collection. 7430 Reflections were collected in the range $1.6° \leqslant 2\theta \leqslant 55.0°$ with scan width = 1.20–1.90 °ω and scan speed = 1.50–5.00° min^{-1}. Final R = 0.067, R_w = 0.058, error of fit = 1.74, max Δ/σ = 0.02.

For both structures, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ The bond distances in $[Ti(\eta^5\text{-}C_5H_5)_2(NC_4H_4)_2]$ [2.070(5), 2.100(4) Å] are comparable (R. V. Bynum, W. E. Hunter, R. D. Rogers and J. L. Atwood, *Inorg. Chem.*, 1980, **19**, 2368). Although these authors invoke a Ti–N d_π–p_π interaction in this complex, we interpret their results very differently: the planar geometries at nitrogen, nearly equidistant C–C bonds in the pyrrolyl rings, and long Ti–N bonds suggest aromatic pyrrolyl ligands and minimal N→Ti π-donation.

§ The N–Ph distances in **1** and **2** are slightly shorter than in aniline (1.401 Å), which has a pyramidal geometry. However, the N–Me distances are also slightly shorter than expected (N–C 1.474 Å in methylamine), so it is questionable whether conjugation alone accounts for the observed N–Ph distances (see D. G. Lister, J. K. Tyler, J. H. Høg and N. W. Larsen, *J. Mol. Structure*, 1974, **23**, 253).

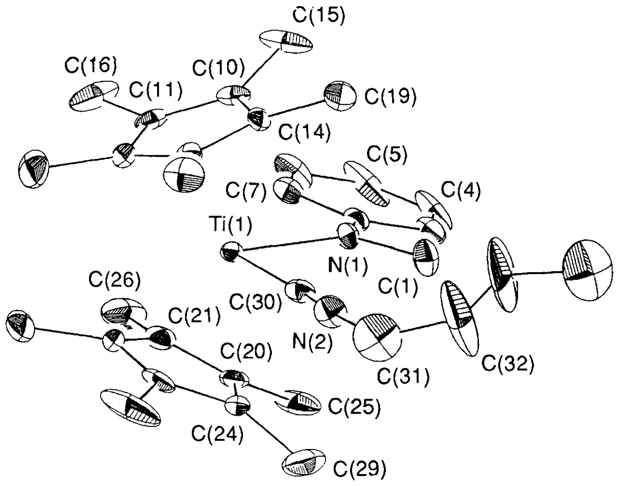

Fig. 3 Structure of complex **2**. Selected distances (Å) and angles (°): Ti(1)-N(1) 2.157(5), Ti(1)-C(30) 2.139(8), N(1)-C(1) 1.459(7), N(1)-C(2) 1.369(7), N(2)-C(30) 1.160(8), N(2)-C(31) 1.466(9), Ti(1)-N(1)-C(1) 121.2(4), Ti(1)-N(1)-C(2) 125.6(4), C(1)-N(1)-C(2) 112.2(5), N(1)-Ti(1)-C(30) 88.9(2), Ti(1)-C(30)-N(2) 174.4 (7), C(30)-N(2)-C(31) 174.2(9).

d_π–p_π interaction between Ti and N in **2**, and that the Ti–N bond order is one. It is also interesting to note that, within experimental error, the Ti–N(1) and Ti–C(30) bonds in **2** are of equal length.

We conclude that a trigonal-planar geometry at nitrogen in early transition metal amide complexes is not necessarily an indication of multiple bonding.[9] The long Ti–N bonds in compounds **1** and **2** suggest that they may be more reactive than high oxidation state analogues; we are currently exploring this possibility.

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7 An interaction of this type has been suggested for $[Y(C_5Me_5)_2\{N(SiMe_3)_2\}]$, in which the Y–N distance (2.26 Å) is 0.1 Å shorter than the sum of the covalent radii for Y and N (ref. 4): K. H. den Haan, J. L. de Boer, J. H. Teuben, A. L. Spek and B. Kojic-Prodic, *Organometallics*, 1986, **5**, 1726.

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