

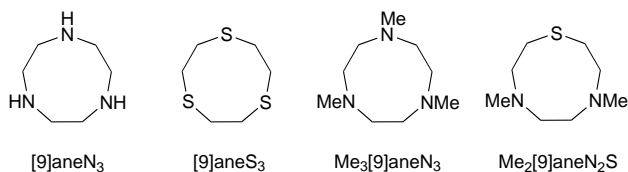
Syntheses and structures of a new class of aza- and thio-ether macrocyclic d⁰ imido complexes

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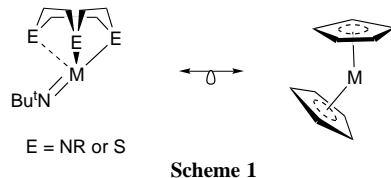
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The synthesis and structures of a family of macrocyclic, d⁰ titanium imido complexes [Ti(NBu^t)(L)Cl₂] (L = [9]aneN₃, Me₃[9]aneN₃, [9]aneS₃ or Me₂[9]aneN₂S) are reported; the new compounds are isolobal analogues of group 4 metallocene dichlorides.

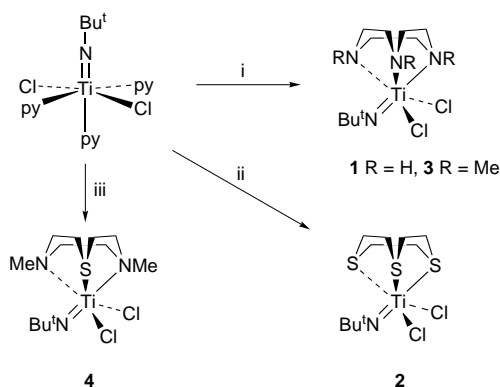
The triaza macrocycle R₃[9]aneN₃ (R = H or alkyl) and its thioether analogue, [9]aneS₃, are effective six-electron capping ligands for a range of transition metal centres.¹ As part of a study of early transition metal imido chemistry,² we were interested to determine whether these ligands might support imido chemistry at d⁰ centres. No R₃[9]aneN₃- or [9]aneS₃-supported imido complexes have been reported previously,³ and none of [9]aneS₃ with any group 4 element. Indeed, previous



examples of [9]aneS₃ transition metal complexes have been almost entirely restricted to later, low to mid-oxidation state transition metals,^{1b} presumably due to hard-soft acid-base considerations;⁴ the two exceptions are the d¹ V^{IV} vanadyl complex [V(O)([9]aneS₃)Cl₂]^{5a} and the trioxorhenium species [R(O)₃([9]aneS₃)]^{5b}. The [9]aneN₃ or [9]aneS₃ macrocycle-metal-imido fragment (Scheme 1) is isolobal and valence isoelectronic⁶ with the ubiquitous bis(η⁵-cyclopentadienyl)metal moiety. Consequently complexes containing this ligand set would clearly promise an interesting and extensive reaction chemistry that may have applications in alkene polymerisation and related catalysis.⁷ Additionally, both the ring and/or the imido ligand N-substituents in such complexes may be readily varied so as to control solubility and electronic and steric properties. We report herein a new class of macrocyclic, d⁰ imido complexes containing [9]aneN₃, [9]aneS₃, Me₃[9]aneN₃, and Me₂[9]aneN₂S.



The syntheses and structures of the new compounds are shown in Scheme 2.‡ Addition of [9]aneN₃ or [9]aneS₃ to a dichloromethane solution of [Ti(NBu^t)Cl₂(py)₃]^{2d} results in displacement of the pyridine ligands and formation of [Ti(NBu^t)([9]aneN₃)Cl₂] **1** and [Ti(NBu^t)([9]aneS₃)Cl₂] **2**, respectively. For comparative purposes and to establish the scope of the reactions, we also prepared the related complex [Ti(NBu^t)(Me₃[9]aneN₃)Cl₂] **3** and its mixed N₂S-donor homologue [Ti(NBu^t)(Me₂[9]aneN₂S)Cl₂] **4** in an analogous fashion.



Scheme 2 Reagents and conditions: i, R₃[9]aneN₃, CH₂Cl₂, room temp., 2 h, 71% (for **1**) or 92% (for **3**); ii, [9]aneS₃, CH₂Cl₂, room temp., 2 h, 21%; iii, Me₂[9]aneN₂S, CH₂Cl₂, room temp., 24 h, 68%

Compound **4** crystallises exclusively as the isomer shown in Scheme 2 (*i.e.* with S *cis* to the *tert*-butylimido group). The yellow–orange compounds **1–4** are all mildly air- and moisture-sensitive.

Recrystallisation from cold dichloromethane solutions yielded crystals suitable for X-ray diffraction analysis.§ The molecular structures of **1** and **2** are shown in Figs. 1 and 2 respectively, and selected bond lengths and angles for all four compounds **1–4** are summarised in Table 1 for ease of comparison. The solid state structures are fully consistent with solution ¹H and ¹³C NMR data in CDCl₃.

All four monomeric complexes feature an approximately octahedral titanium(IV) coordination sphere that is comprised of a *fac*-coordinated macrocycle, a multiply-bonded *tert*-butylimido ligand and two mutually *cis* chloride ligands. The Ti–N_{macrocycle} or Ti–S bonds *trans* to NBU^t are significantly lengthened relative to their *cis* Ti–N_{macrocycle} or Ti–S counterparts, reflecting the well known *trans* influence of the imido ligand.^{3b} The angles subtended at the imido nitrogen lie in the

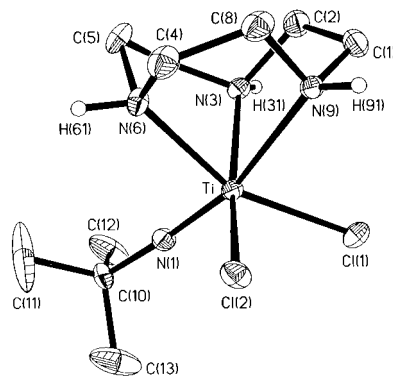


Fig. 1 Displacement ellipsoid (40% probability) plot for [Ti(NBu^t)([9]aneN₃)Cl₂] **1**. Hydrogen atoms are excluded except for those bonded to N; these are drawn as spheres of arbitrary radius. The CH₂Cl₂ solvent molecule is also excluded.

Table 1 Comparison of selected distances (Å) and angles (°) for **1–4**; *cis* and *trans* refer to coordination sites with respect to NBU^t

Compound	Ti–N _{cis}	Ti–N _{trans}	Ti–S _{cis}	Ti–S _{trans}	Ti–Cl	Ti–N _{imide}	Cl–Ti–Cl	C–N _{imide} –Ti
1	2.213(3) 2.227(3)	2.359(3)	—	—	2.407(1) 2.403(1)	1.703(3)	97.23(4)	174.3(2)
2	—	—	2.575(1) 2.591(1)	2.750(1)	2.370(1) 2.379(1)	1.694(3)	103.02(4)	178.3(3)
3	2.265(3) 2.270(3)	2.437(3)	—	—	2.394(1) 2.392(1)	1.694(2)	95.75(4)	171.0(2)
4	2.285(9)	2.498(8)	2.561(4)	—	2.379(4) ^a 2.397(4) ^b	1.708(8)	98.0(2)	166.4(6)

^a *Trans* to S_{cis}. ^b *Trans* to N_{cis}.

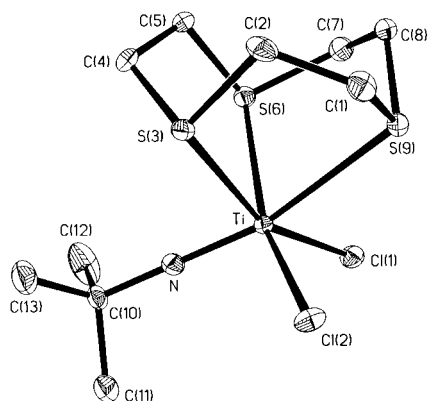


Fig. 2 Displacement ellipsoid (40% probability) plot for [Ti(NBU^t)([9]aneS₃)Cl₂] **2**. Hydrogen atoms and the CH₂Cl₂ solvent molecule are excluded.

range 166.4(6)–178.3(3)°, consistent with the NBU^t ligand acting as four-electron donor to Ti^{IV} and forming a Ti≡N_{imide} triple bond (pseudo-σ²π⁴ configuration).^{3a} Table 1 shows that the Ti–Cl bond lengths in **1** and **3** (*i.e.* both *trans* to N) are significantly longer than those in **2** (*i.e.* *trans* to S). Consistent with these observations, compound **4** has a Ti–Cl bond *trans* to N [2.397(4) Å] that is significantly longer than that *trans* to S [2.379(4) Å]. In addition, the ligand R₃[9]aneN₃ in **1** and **3** produces Cl–Ti–Cl angles of 97.23(4) and 95.75(4)°, respectively, while [9]aneS₃ gives a substantially increased angle of 103.02(4)° in **2**. These data demonstrate clearly the importance of the different macrocycles in tuning and varying structural parameters of **1–4**, which, in other systems, have been shown⁷ to be important features in catalyst design.

The complexes [Ti(NBU^t)([9]aneS₃)Cl₂] **2** and [Ti(NBU^t)(Me₂[9]aneN₂S)Cl₂] **4** are the first group 4 derivatives of [9]aneS₃ or R₂[9]aneN₂S.⁸ Furthermore, the four complexes **1–4** represent the first such macrocycle–imido derivatives, and are related to oxo complexes of Me₃[9]aneN₃.⁹ Preliminary studies have demonstrated that the chloride ligands in **3** may be substituted to give [Ti(NBU^t)(Me₃[9]aneN₃)(R)₂] (R = CH₂SiMe₃ or CH₂Ph), and we have also prepared the cationic group 5 complexes [Nb(NBU^t)(Me₃[9]aneN₃)Cl₂]X (X = Cl or PF₆) which are valence isoelectronic with **1–4**. Reactivity studies of all the new complexes are underway.

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Notes and References

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‡ Satisfactory spectroscopic and analytical data for **1–4** have been obtained.

§ *Crystal data* for **1–4**. Crystals were mounted in a film of RS3000 perfluoropolyether oil (Hoechst) on a glass fibre and transferred to a Stöe Stadi-4 four-circle diffractometer and data were collected at 150(2) [220(2) for **4**] K. **1**: C₁₀H₂₄Cl₂N₄Ti·CH₂Cl₂, *M* = 404.07, monoclinic, space group *P*2₁/*c*, *a* = 10.677(3), *b* = 11.371(3), *c* = 15.752(3) Å, β = 104.20(3)°, *U* = 1854.1(7) Å³, *Z* = 4, μ = 1.04 mm⁻¹, all 3096 independent reflections (*R*_{merge} = 0.03) used in refinement, no. of parameters refined 182, final *R* indices: *R* = 0.039, *wR*₂ = 0.059. **2**: C₁₀H₂₁Cl₂NS₃Ti·CH₂Cl₂, *M* = 455.20, monoclinic, space group *P*2₁/*n*, *a* = 12.035(3), *b* = 12.368(3), *c* = 13.925(3) Å; β = 108.47(2)°, *U* = 1965.9(6) Å³, *Z* = 4, μ = 1.28 mm⁻¹, 3471 independent reflections (*R*_{merge} = 0.03), no. of parameters refined 182, final *R* indices: *R* = 0.039, *R*_w = 0.040. **3**: C₁₃H₃₀Cl₂N₄Ti·CH₂Cl₂, *M* = 446.15, orthorhombic, space group *Pbca*, *a* = 15.104(6), *b* = 14.515(6), *c* = 19.933(7) Å, *U* = 4370(3) Å³, *Z* = 8, μ = 0.88 mm⁻¹, 3597 independent reflections (*R*_{merge} = 0.02) used in refinement, no. of parameters refined 209, final *R* indices: *R* = 0.047, *wR*₂ = 0.0584. **4**: C₁₂H₂₇Cl₂N₃STi·CH₂Cl₂, *M* = 449.17, monoclinic, space group *P*2₁/*n*, *a* = 10.114(3), *b* = 14.445(6), *c* = 15.207(4) Å, β = 107.24(3)°, *U* = 2121.8(10) Å³, *Z* = 4, μ = 1.00 mm⁻¹, 2759 independent reflections (*R*_{merge} = 0.12), 2152 reflections with *I* > 0 used in refinement, no. of parameters refined 200, final *R* indices: *R* = 0.102, *wR*₂ = 0.130. CCDC 182/820.

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