A New Class of Five-co-ordinate Titanium Complexes containing a Polyfunctional Amido Ligand. Crystal Structure of $[TiBr_2\{CH(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2\}]$

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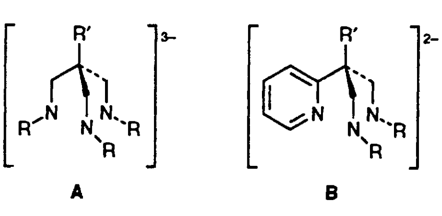
A new class of titanium amido halides containing a tripodal ligand with two amido and one pyridyl-N function, which are potential building blocks for the synthesis of oligonuclear complexes, has been prepared; a single-crystal X-ray structure analysis of $[TiBr_2\{CH(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2\}]$ has established its five-co-ordinate molecular geometry.

The design of reactive centres in co-ordination compounds of early-transition metals has recently created considerable interest. Polyfunctional amido ligands, in particular, have been studied in this context, since they offer an efficient kinetic stabilisation of these complexes through steric shielding of a large (and easily modified) sector of their co-ordination sphere.[1,2] The remaining reactive position is normally occupied by a halide ligand which is readily substituted by nucleophiles or removed by reduction of the compound.[3]

In order to extend the use of tripodal amido ligands to tetravalent transition-metal compounds containing two halide ligands which may then be removed in subsequent conversions, it was necessary to replace an amido function (as in **A**) by a tertiary (and thus neutral) amino function. This may be conveniently achieved by incorporation of a pyridine ring into the ligand framework (as in **B**).

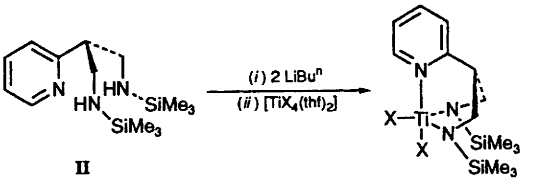


A **B**

The target amido ligand may be readily obtained by functionalisation of the known 2-(2-pyridyl)propane-1,3-diamine **I**.[4] Trimethylsilylation of **I** affords the corresponding secondary amine **II** [equation (1)]. Dilithiation of **II** and subsequent

$$\underset{\mathbf{I}}{\mathrm{CH(2\text{-}C_5H_4N)(CH_2NH_2)_2}} \xrightarrow{\mathrm{SiClMe_3\text{-}NEt_3}} \underset{\mathbf{II}}{\mathrm{CH(2\text{-}C_5H_4N)(CH_2NHSiMe_3)_2}} \quad (1)$$

reaction with 1 molar equivalent of $[TiX_4(thf)_2]$ (X = Cl or Br, thf = tetrahydrofuran) yielded the titanium complexes $[TiX_2\{CH(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2\}]$ (X = Cl **1a** or Br **1b**) as air- and moisture-sensitive orange microcrystalline solids, equation (2).† The formulation of **1a** and **1b** was established by microanalysis while the resonance patterns in the ^1H NMR spectra indicated a molecular C_s symmetry and thus probably a five-co-ordinate structure. That the pyridine ring co-ordinates to the titanium is inferred from the significant co-ordination shifts of the ring protons, in particular in the *ortho* position (H^6) relative to the N atom (δ 9.60 for **1b** compared to δ 8.45 in the free ligand).



II (2)

X = Cl **1a**
Br **1b**

In order to establish the details of the monomeric, five-co-ordinate structure and thereby assess the suitability of the

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† Preparation of complexes **1a**, **1b** and **2**. To a stirred solution of **II** (740 mg, 2.5 mmol) in pentane (50 cm^3), which was cooled to −40 °C, was added *n*-butyllithium (2 cm^3 of a 2.5 mol dm^{-3} solution in hexane, 5.00 mmol). The reaction mixture was warmed to room temperature and then briefly heated under reflux, whereupon the initially colourless solution turned bright red. Solid $[TiX_4(thf)_2]$ (X = Cl or Br) (2.75 mmol) was added to the solution of the amide at −50 °C. The reaction mixture was warmed to room temperature over a period of 15 h, filtered, and the filtrate concentrated to *ca.* 5 cm^3 and stored at −60 °C. The complex $[Ti\{CH(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2\}_2]$ **2** precipitated as a microcrystalline orange solid. Yield: 151 mg (19%) (Found: C, 53.20; H, 9.10; N, 13.15. $C_{28}H_{54}N_6Si_4Ti$ requires C, 53.00; H, 8.60; N, 13.25%). ^1H NMR (200 MHz, C_6D_6, 295 K): δ 0.30, 0.37 [s, $Si(CH_3)_3$], 3.71 (m, 3 H), 4.48 (m, 2 H), 6.59 [ddd, H^5 of pyridyl, $^3J(H^5H^4)$ 7.4, $^3J(H^5H^6)$ 4.8, $^4J(H^5H^3)$ 1.4], 6.92 [ddd, H^3 of pyridyl, $^3J(H^3H^4)$ 7.7, $^5J(H^3H^6)$ 0.9], 7.04 [dt, H^4 of pyridyl, $^4J(H^4H^6)$ 1.9 Hz], 8.47 (ddd, H^6 of pyridyl). The residue of the filtration was extracted with toluene (4 × 30 cm^3), the extract evaporated to dryness and the remaining solid recrystallised from thf (15 cm^3). Yield: **1a** 432 mg (42%), **1b** 702 mg (56%). Complex **1a** (Found: C, 40.75; H, 6.65; N, 9.85. $C_{14}H_{27}Cl_2N_3Si_2Ti$ requires C, 40.80; H, 6.60; N, 10.20%). ^1H NMR (200 MHz, C_6D_6, 295 K): δ 0.24 [s, $Si(CH_3)_3$], 3.07 [m, $C\mathit{H}(CH_2NSiMe_3)$], 3.23 [dd, $CH(C\mathit{H}HNSiMe_3)$, $^2J(HH)$ 13.0, $^3J(HH)$ 3.4], 4.18 [dd, $CH(CH\mathit{H}NSiMe_3)$, $^3J(HH)$ 2.1], 6.38 [ddd, H^5 of pyridyl, $^3J(H^5H^4)$ 7.5, $^3J(H^5H^6)$ 5.5, $^4J(H^5H^3)$ 1.4], 6.56 [ddd, H^3 of pyridyl, $^3J(H^3H^4)$ 7.5, $^5J(H^3H^6)$ 0.9], 6.87 [dt, H^4 of pyridyl, $^4J(H^4H^6)$ 1.7 Hz] and 9.45 (ddd, H^6 of pyridyl). Complex **1b** (Found: C, 33.50; H, 5.50; N, 8.10. $C_{14}H_{27}Br_2N_3Si_2Ti$ requires C, 33.55; H, 5.45; N, 8.40%). ^1H NMR (200 MHz, C_6D_6, 295 K): δ 0.28 [s, $Si(CH_3)_3$], 3.06 [m, $C\mathit{H}(CH_2NSiMe_3)$], 3.19 [dd, $CH(C\mathit{H}HNSiMe_3)$, $^2J(HH)$ 13.1, $^3J(HH)$ 3.4], 4.16 [dd, $CH(CH\mathit{H}NSiMe_3)$, $^3J(HH)$ 2.0], 6.41 [ddd, H^5 of pyridyl, $^3J(H^5H^4)$ 7.6, $^3J(H^5H^6)$ 5.6, $^4J(H^5H^3)$ 1.4], 6.53 [ddd, H^3 of pyridyl, $^3J(H^3H^4)$ 7.6, $^5J(H^3H^6)$ 0.9], 6.89 [dt, H^4 of pyridyl, $^4J(H^4H^6)$ 1.7 Hz] and 9.60 (ddd, H^6 of pyridyl).

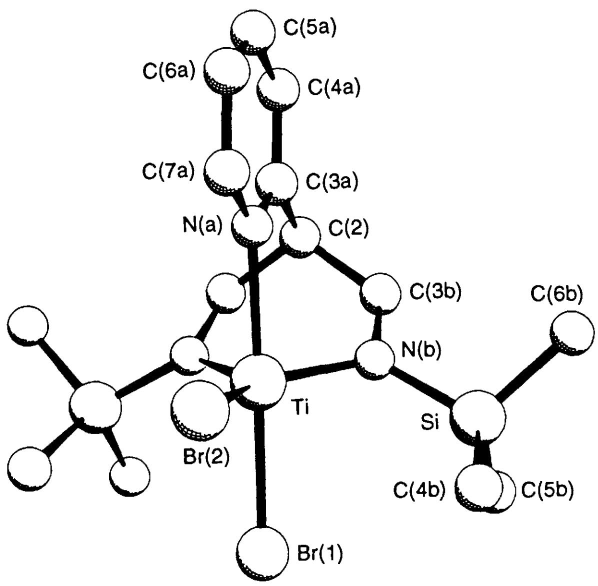
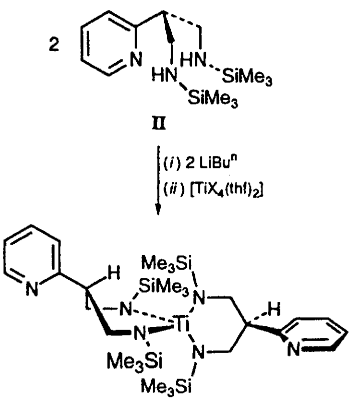


Fig. 1 The molecular structure of **1b**. Selected bond distances (Å) and angles (°): Ti–N(a) 2.262(12), Ti–N(b) 1.842(9), Ti–Br(1) 2.508(3), Ti–Br(2) 2.494(4), N(b)–Si 1.750(9); Br(1)–Ti–Br(2) 90.6(1), N(a)–Ti–Br(1) 176.9(3), N(a)–Ti–Br(2) 86.3(3), N(b)–Ti–Br(1) 96.4(3), N(b)–Ti–Br(2) 125.7(3), N(b)–Ti–N(b′) 107.1(5), N(a)–Ti–N(b) 85.4(3)

ligand system with regard the general concept outlined above, a single-crystal X-ray structure analysis of **1b** was carried out.* The molecular structure shown in Fig. 1 has exact C_s symmetry, with the pyridine ring, C(2), Br(1), Br(2) and Ti lying on a crystallographic mirror plane. The ligand arrangement around the titanium(IV) centre is slightly distorted trigonal bipyramidal, with two amido-N atoms and Br(2) lying in the equatorial plane while Br(1) and the pyridyl-N atom occupy the axial positions [N(a)–Ti–Br(1) 176.9(3)°]. The pyridine ring is slightly tilted with respect to the Ti–N(a) vector as a consequence of the geometrical constraints imposed by the ligand framework, a situation which is reminiscent of the geometry which oligopyridines co-ordinated to transition metals frequently adopt.[8] The Ti–N distance involving the equatorial amido nitrogen is 1.842(9) Å which is somewhat shorter than that observed ($\geqslant$1.90 Å[9]) in most other chelating titanium silylamides. The amido-N atoms possess a planar geometry, as has been found for almost all structurally characterised transition-metal amides. As expected, the pyridyl nitrogen–titanium bond, at 2.262(12) Å is considerably longer than that of the amido nitrogen–titanium bond and lies within the usual range.[10] The Ti–Br distances are unexceptional.

A by-product in the synthesis of **1a** and **1b** is the symmetrical species [Ti{CH(2-C_5H_4N)(CH_2NSiMe_3)$_2$}$_2$] **2** [equation (3)].



2 (3)

The orange microcrystalline solid **2** is soluble in saturated hydrocarbons and may be separated from **1a**, **1b** by extracting the solid residue of the crude reaction mixture with hexane. The structure of **2** as deduced from the spectroscopic data is probably similar to that reported previously for a number of spirocyclic titanum compounds.[11]

The availability of complexes such as **1a** and **1b** has now opened up the possibility for their use in the synthesis of more complex oligonuclear systems. Such work is currently in progress.

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* Crystal data for **1b**. $C_{14}H_{27}Br_2N_3Si_2Ti$, $M = 501.27$, orthorhombic, *Pnma*, $a = 13.900(3)$, $b = 14.649(3)$, $c = 10.523(2)$ Å, $U = 2142.70$ Å^3, $Z = 4$, $D_c = 1.55$ g cm^{-3}, μ(Mo-Kα) = 41.9 cm^{-1}, $F(000) = 1008$. An orange crystal of dimensions 0.30 × 0.35 × 0.45 mm was used in the data collection. Data were collected on a Philips PW1100 four-circle diffractometer using Mo-Kα radiation (λ = 0.710 69 Å) from a graphite monochromator by the method described previously.[5] Equivalent reflections were merged to give 749 unique reflections with $I/\sigma(I) > 3$. An absorption correction was applied to the data after initial refinement with isotropic thermal parameters for all atoms.[6] The positions of the titanium and two bromine atoms were deduced from a Patterson synthesis assuming the centrosymmetric space group *Pnma*.[7] The remaining non-hydrogen atoms to which they were bonded were located in subsequent Fourier difference syntheses. The thermal parameters of the H atoms were tied to two 'free variables' which refined to final U values of 0.11 (aliphatic) and 0.12 Å^2 (aromatic). Anisotropic parameters were assigned to the titanium, bromine, silicon, nitrogen and methyl carbon atoms in the final cycles of the full-matrix least-squares refinement which converged at $R = 0.0479$ and $R' = 0.0454$ with weights of $1/\sigma^2(F)$ assigned to individual reflections. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

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