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Preliminary communication

The synthesis of 1,3,5,7-tetrakis(trimethylsilyl)-2,2,4,4,6,6,8,8-octachlorocyclotetratitan(IV)azane

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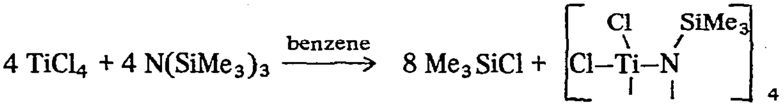
SUMMARY

$(Me_3Si)_3N$ reacts with $TiCl_4$ to yield the novel heterocycle $(TiCl_2NSiMe_3)_4$.

Tris(trimethylsilyl)amine $N(SiMe_3)_3$ (I) with an almost total lack of valence electron density at the nitrogen centre[1] is extremely unlikely to support normal Lewis base (σ-donor) activity. A 1/1 adduct involving aluminium(III) chloride is known, but the anomalous dissociation and decomposition behaviour reported for this complex[2] is not surprising since reactions of (I) with reference Lewis acids invariably involve (Si–N) bond cleavage[3]. We have found that interaction with titanium(IV) chloride occurs, albeit grudgingly, to give the novel titanium–nitrogen heterocyclic compound 1,3,5,7-tetrakis(trimethylsilyl)-2,2,4,4,6,6,8,8-octachlorocyclotetratitan(IV)azane (II) according to Eqn. (1):



$$4\,TiCl_4 + 4\,N(SiMe_3)_3 \xrightarrow{\text{benzene}} 8\,Me_3SiCl + [Cl_2Ti{-}N(SiMe_3)]_4 \qquad (1)$$

To our knowledge $[Ti(N\text{-}t\text{-}Bu)(NMe_2)_2]_2$ and $[Ti(N\text{-}t\text{-}Bu)(HN\text{-}t\text{-}Bu)(NMe_2)]_2$, for which dimeric bridge structures are proposed, provide the only previous examples of this kind of ring compound[4].

A mixture of (I) (1 mol) and excess titanium(IV) chloride (3 mol) in benzene solution was sealed in an evacuated glass vessel to give an orange solution. On leaving the vessel in a water bath at 323K for several weeks, a matte of orange crystals and dark brown solid material separated from the now red solution. Careful work-up under strict anhydrous conditions gave the expected trimethylchlorosilane (2 mol) and the title product (II) as orange needle crystals (65% yield). (Found: C, 17.2; H, 4.5; Cl, 34.0; N, 6.6; Ti, 23.6. $C_3H_9Cl_2NSiTi$ calcd.: C, 17.3; H, 4.4; Cl, 34.1; N, 6.7; Si, 13.5; Ti, 24.0%.) Confirmation of (II) as a cyclic tetramer is based on preliminary results of an X-ray analysis[*].

The orange crystals are extremely sensitive to air-moisture hydrolysis, decompose without melting at $T > 415$K to a brown-black mass and show limited solubility in benzene, cyclohexane, chloroform and dichloromethane. The proton NMR spectrum (60 MHz; CH_2Cl_2) indicates equivalent Me_3Si-protons, the sharp singlet at τ 9.46 having been shifted 0.26 ppm downfield relative to pure (I). The IR spectrum (CH_2Cl_2) contains bands at 2965 m ($\nu_{as}(CH_3)$), 2910 s ($\nu_s(CH_3)$), 1410 s ($\delta_{as}(CH_3)$), 1265 (sh), 1252 s ($\delta_s(CH_3)$), 1150 w, 1070 w, 985 w, 896 s ($\nu_{as}(SiN)$), 847 s ($\rho_{as}(CH_3)$), 826 m, 759 s ($\rho_s(CH_3)$), 698 m, 670 s ($\nu_{as}(SiC_3)$), 641 m, 624 s ($\nu_s(SiC_3)$), 468 s ($\nu(TiCl)$) and 358 m cm^{-1} respectively, tentative assignments being based on previously reported data for reactants[5,6]. The electronic absorption spectrum (cyclohexane, λ_{max} (cm^{-1}) (ϵ); 45 660 (4100); ~44 250 (sh); ~40 800 (sh); ~33 500 (sh); 25 510 (995)) shows a bathochromic shift of 4 240 cm^{-1} for the UV absorption maximum as compared to (I), consistent with the skeletal change $NSi_3 \rightarrow NSiTi_2$ involving a departure from essentially planar towards tetrahedral geometry as a result of less delocalisation of the nitrogen lone pair[7]. The absence of d–d bands in the visible region and the presence of a strong band at 468 cm^{-1} ($\nu(TiCl)$) in the IR spectrum are consistent with the formulation of (II) as a four coordinate titanium(IV) d^0 species.

The nature of (II) clearly indicates that two chlorine atoms per titanium have been removed from titanium(IV) chloride as volatile trimethylchlorosilane, but exactly how this loss occurs is open to conjecture. We consider replacement of one or both chlorine atoms through solvolysis, *e.g.*, $Cl_3Ti{-}N(SiMe_3)_2$ and $Cl_2Ti[N(SiMe_3)_2]_2$ followed by intramolecular and intermolecular (with titanium(IV) chloride) elimination of trimethylchlorosilane respectively to be equally attractive[**].

Treatment of (II) by heating at reflux in high boiling solvents and by vacuum sublimation experiments gave no further controlled release of trimethylchlorosilane, but under drastic conditions, *e.g.*, heating in vacuo at 600K, thermal decomposition to an almost black polymeric solid approximating to $(ClTiN)_x$ does occur. Further studies of the molecular structure and chemical properties of (II) are in progress.

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[*] Crystallographic investigation gives space group $P2_1/c$ and a density determination indicates mol. wt. 840 for $Z = 4$ corresponding to a ring $(C_3H_9SiNTiCl_2)_4$ mol. wt. 824.02. This tetrameric assignment is strongly supported by non-systematic extinctions in the $h0l$ plane which correspond to a sub-cell one quarter the size of the actual cell.

[**] Although the reaction has been halted at various time intervals in repeated experiments, we have as yet been unable to isolate either of these titanium amides from the initial orange solution; $Cl_3Ti{-}N(SiMe_3)_2$ has been reported in the literature[8].

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