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# Reactions of Trimethylsilyl-heterocyclics with Ti(IV) and Fe(III) Chlorides

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Trimethylsilyldialkyamines, $Me_3SiNRR'$, are already known to undergo cleavage with titanium(IV) halides to form dialkylamido derivatives, $X_{4-n}Ti(NRR')_n$, where n = 1 or 2 [1]. As a part of our study on metal–nitrogen compounds, we report here the results of reactions of trimethylsilyl-heterocyclics with Ti(IV) and Fe(III) chlorides.

Equimolar reaction of $Me_3SiNEt_2$ with $TiCl_4$ in benzene provides titanium(IV)–amido derivative, $Cl_3TiNEt_2$ and no reduction occurs even under reflux for 12 h. However, 1:1 reactions of trimethylsilyl-heterocyclics, $Me_3Si$–NR where R = $(CH_2)_4$ or $(CH_2)_5$, with $TiCl_4$ and $FeCl_3$ under similar conditions, result in reduction of titanium to the 3+ and iron to 2+ oxidation states with the formation of precipitates of $3TiCl_3\cdot 2RNH$, (*1*) and $3FeCl_2\cdot 2RNH$, (*2*), respectively. Compound (*1*) is very sensitive to oxidation in air whereas (*2*) is comparatively more stable. Presence of Ti(III) in (*1*) and Fe(II) in (*2*) is supported by redox titration against Ce(IV), electronic spectra of (*1*) showing bands at 460 nm and 410 nm typical of Ti(III) and magnetic moment values of about 4.5 BM in case of (*2*). This value is lower than the normal value for mononuclear species (4.9 BM) and this arises perhaps because of antiferromagnetic coupling between iron atoms.

Simple cleavage of Si–N bond in case of $Me_3SiNEt_2$ but easy redox reaction with $Me_3SiNR$ excludes the possibility of steric factors playing any significant role because the steric effect of pyrrolidido or piperidido group is in no way greater than diethylamido group. Alternatively it may be supposed that $TiCl_4$ chlorinates heterocyclic base to give the chloro derivative of the base, $Me_3SiCl$ and $TiCl_3$. Had it been so, adducts of simple pyrrolidine or piperidine $3TiCl_3\cdot 2RNH$ would not have resulted from their silyl derivatives. Furthermore, the redox reaction would not be solvent dependent. In fact, it has been observed that the redox reaction in case of Ti takes place only in benzene, toluene or methylene chloride where a hydrogen radical can be abstracted. An equimolar mixture of $Me_3SiNR$ with $TiCl_4$ in an aprotic solvent $CCl_4$does not undergo redox reaction even at reflux temperature but provides an adduct, $3TiCl_4\cdot 2Me_3SiNR$ and a substitution derivative, $Cl_3Ti$–NR. Even an excess of base or longer refluxing times do not cause redox reaction and instead the adduct undergoes substitution to give, for example, $Ti_3Cl_{11}(NC_5H_{10})\cdot 2Me_3SiNC_5H_{10}$. This indicates that the solvent may play a role in providing hydrogen radicals in the system. It is expected that free radical RN• may be formed from $Me_3SiNR$ (by the loss of $Me_3Si$ group that may produce intermediates, $TiCl_3$ and $Me_3SiCl$) and then RN• interacts with benzene to form RNH (which adds on to $TiCl_3$ to give $TiCl_3\cdot 2/3RNH$) and phenyl radical which may dimerise or polymerise to give higher molecular weight organic polymers. However, $FeCl_3$ undergoes reduction even in $CCl_4$ but the product is not well defined and appears to be a mixture. Unlike $TiCl_4$, $FeCl_3$ may chlorinate heterocyclic base as it does with many aromatics [2].

Compounds (*1*) and (*2*) may be given empirical formulations $TiCl_3\cdot 2/3RNH$ and $FeCl_2\cdot 2/3RNH$ or $3TiCl_3\cdot 2RNH$ and $3FeCl_2\cdot 2RNH$, respectively. These have been mentioned in the latter form as trinuclear species because $Ti_3Cl_9\cdot 2RNH$ and $Fe_3Cl_6\cdot 2RNH$ units appear to persist as stable entities in all the reaction products. This is supported by 1:2 reactions of $TiCl_4$ or $FeCl_3$ with $Me_3SiNR$. One of the chloro groups in the trinuclear entity is substituted by the silyl-base to form $Ti_3Cl_8(NR)\cdot 2RNH$ and $Fe_3Cl_5(NR)\cdot 2RNH$.

The infrared spectra of the compounds contain bands arising from $\nu$NH, $\delta$NH and others typical of bonded amine and amido groups. Bands attributable to $\nu$Ti–N, $\nu$Ti ← N and $\nu$Ti–Cl in the far i.r. region are listed in Table I.

All the compounds of Ti(III) and Fe(II) are less volatile, insoluble in nonpolar solvents and only very slightly soluble in nitrobenzene, nitromethane and THF and are thus likely to be polymerised in solid, probably through chlorine–chorine bridging. Their molar conductance values in nitrobenzene indicate their nonelectrolytic behaviour, whereas in DMF iron(II) compounds behave as 1:1 electrolytes and titanium(III) compounds as 1:2 electrolytes. In a basic solvent like DMF, bridging can be broken to give solvated ionic species. With alcohols, they react to form alkoxy derivatives.

On heating *in vacuo*, all titanium(III) compounds liberate a little free base up to about $100°/10^{-3}$ torr and then decompose to give a green sublimate $Cl_3Ti$–NR at about $120°/10^{-3}$ torr. The black residue, thus left behind, contains titanium in lower

TABLE I. Some Physical Properties and Analytical Data of Compounds of Ti and Fe Chlorides with Trimethylsilyl-Heterocyclics.

| Compound | Colour | M.P. (°C) | νTi–Cl | νTi ← N | Analytical Data: Found (Calcd.) % | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | M | Cl | N | C | H | Amine |
| $3TiCl_3 \cdot 2C_4H_8NH$ | Greyish black | 140d[a] | 380s, 322s | 270s | 23.9(23.8) | 53.4(52.8) | 4.9(4.6) | 15.4(15.8) | 3.5(3.0) | 21.8(23.4) |
| $3TiCl_3 \cdot 2C_5H_{10}NH$ | Pinkish brown | 130d | 380sb, 360s | 260s | 22.8(22.7) | 50.2(50.4) | 4.7(4.4) | 20.7(18.9) | 3.9(3.5) | 27.4(26.8) |
| $3FeCl_2 \cdot 2C_4H_8NH$ | Black | 122 | 385s, 365m | 270m | 31.7(32.0) | 40.7(40.8) | 5.4(5.4) | 17.3(18.4) | 3.6(3.4) | – |
| $3FeCl_2 \cdot 2C_5H_{10}NH$ | Dark brown | 113 | 380s, 310mb | 270mb | 30.7(30.4) | 40.2(38.7) | 4.9(5.1) | 20.6(21.8) | 3.6(4.0) | – |
| $3TiCl_4 \cdot 2C_4H_8NSiMe_3$ | Greyish black | 180d | 350–330vsb | 285w | 16.4(16.8) | 50.0(49.8) | 3.2(3.3) | 19.1(19.6) | 3.8(4.0) | 32.2(33.1) |
| $Ti_3Cl_{11}(NC_5H_{10}) \cdot 2C_5H_{10}NSiMe_3$ | Brown | 175d | 380sb, 330sb | 280w, 620w* | 15.8(15.4) | 42.1(41.9) | 4.2(4.5) | 26.4(27.0) | 5.0(5.2) | 42.5(42.7) |
| $Ti_3Cl_8(NC_4H_8) \cdot 2C_4H_8NH$ | Dirty green | 155d | 335sb, 320s | 290w, 620w* | 22.7(22.5) | 44.5(44.4) | 6.5(6.6) | 22.1(22.5) | 4.0(4.1) | 33.3(33.3) |
| $Ti_3Cl_8(NC_5H_{10}) \cdot 2C_5H_{10}NH$ | Dirty green | 208d | 375s, 330s | 285m, 630m* | 20.9(21.1) | 41.0(41.6) | 5.9(6.2) | 26.1(26.4) | 4.3(4.7) | 38.0(37.4) |
| $Fe_3Cl_5(NC_4H_8) \cdot 2C_4H_8NH$ | Light grey | 115 | 380s, 360m | 275m, 610m* | 30.1(30.1) | 32.2(31.9) | 6.9(7.5) | 25.1(25.9) | 4.6(4.7) | – |

*Refers to νTi–N. [a] d = decomposed, s = strong, m = medium, w = weak, b = broad, v = very.

oxidation states. However, iron(II) compounds decompose differently and no amido derivative sublimes out. The compound loses free base in the beginning but then around 160°/$10^{-3}$ torr it sublimes out base hydrochloride leaving behind a brown residue containing iron(II).

Dichlorobis(cyclopentadienido)titanium(IV) does not react even with an excess of $Me_3SiNR$ at reflux temperature in toluene. Tin(IV) chloride forms simple adducts at room temperature but undergoes reduction at higher temperature. Such reactions and characterisation of reaction products are in progress.

## Experimental

All manipulations were done on vacuum line or under dry nitrogen.

Trimethylsilyl amines, prepared by 1:2 reaction of $Me_3SiCl$ with the amine, were purified by fractionation: $Me_3SiNEt_2$ 70°/120 mm; $Me_3SiN(CH_2)_4$ 75°/80 mm; $Me_3SiN(CH_2)_5$ 89°/80 mm.

### *Preparation of Compounds*

Trimethylsilyl-pyrrolidine (20 mmol) in 20 ml solvent (benzene or toluene) was added dropwise with stirring to $TiCl_4$ (20 mmol) in 50 ml of solvent. The colour changed from yellow to brown to greenish black and contained a greyish black precipitate of a Ti(III) compound. If the precipitate is separated after stirring at room temperature, the yield of $3TiCl_3 \cdot 2C_4H_8NH$ is low. Normally the mixture was heated for 2 h at 80 °C. The precipitate was isolated, washed with solvent and dried *in vacuo*. The filtrate was evaporated and the greenish black residue either crystallised from benzene or toluene or sublimed at 80°/$10^{-3}$ torr, $Cl_3TiNC_4H_8$ (Found: Ti 21.3, Cl 47.2, $NC_4H_8$ 32.0. Calcd: Ti 21.4, Cl 47.4, $NC_4H_8$ 31.2%).

Reaction of silyl-piperidine with $TiCl_4$ under similar conditions shows colour changes from yellow to brown to reddish brown and gives a precipitate of $3TiCl_3 \cdot 2C_5H_{10}NH$ and the reddish brown filtrate on crystallisation or sublimation gives a green compound $Cl_3TiNC_5H_{10}$ (Found: Ti 20.0, Cl 44.1, $NC_5H_{10}$ 36.0. Calcd: Ti 20.1, Cl 44.7, $NC_5H_{10}$ 35.2%).

These reactions if carried out in $CCl_4$ at reflux temperature for 2 h provide a precipitate of the Ti(IV) compound, $Cl_4Ti \cdot 2C_4H_8NSiMe_3$ and the filtrate yields $Cl_3TiNC_4H_8$. A slight excess of base over a molar ratio of 1:1 or longer refluxing time (12 h) give a precipitate of $Ti_3Cl_{11}(NC_5H_{10}) \cdot 2C_5H_{10}NSiMe_3$ and the filtrate yields $Cl_3TiNC_5H_{10}$.

Reaction of silyl-heterocyclic: $TiCl_4$ in a molar ratio of 2:1 in benzene at reflux temperature for 4 h yields a precipitate corresponding to $Ti_3Cl_8(NR) \cdot 2RNH$.

A suspension of $FeCl_3$ in toluene was treated with 1 or 2 mol of $Me_3SiNR$ and the mixture heated in a bath at 80 °C for 4–6 h. A precipitate of $3FeCl_2 \cdot 2RNH$ or $Fe_3Cl_5(NR) \cdot 2RNH$ was isolated.

## References

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