Inorganica Chimica Acta, 154 (1988) 177–182

Alkylimido Complexes of Titanium(IV)

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(Received April 14, 1988)

Abstract

$TiCl_4$ reacts with t-butylamine in benzene to give $[Ti(NCMe_3)Cl_2(NH_2CMe_3)_2]_x$ and t-butylamine hydrochloride. The IR spectrum indicates both *cis* and *trans* metal dichlorides (300; and 308, 208 cm^{-1}). In the ^{13}C NMR spectrum the t-butylimido quaternary carbon resonance occurs at 72.1 ppm. A dimeric structure incorporating symmetric t-butylimido bridges is proposed. $TiCl_4$ in benzene reacts under reflux with two equivalents of $Me_3SiNHCMe_3$ to give $[Ti(NCMe_3)Cl_2(NH_2CMe_3)]_x$ and with iso-propylamine and ethylamine to give complexes of the form $[Ti(NR)Cl_2(NH_2R)_2]_x$. Broad bands below 800 cm^{-1} in the IR spectra suggest polymeric M–N–M bridges. For $[Ti(NCHMe_2)Cl_2(NH_2CHMe_2)]_x$ the iso-propylimido CH resonance in the ^{13}C NMR spectrum occurs at 67 ppm. $[Ti(NCMe_3)Cl_2(NH_2CMe_3)_2]_2$ reacts with L = bipy or tmed to give $[Ti(NCMe_3)Cl_2(L)]_2$, and $TiCl_4$ reacts with two equivalents of $Me_3SiNHCMe_3$ in benzene and then tmed to give $[Ti(NCMe_3)Cl_2(tmed)]_2$. The ^{13}C NMR spectrum shows the t-butylimido quaternary carbon resonance at 73.5 ppm and the tmed resonances are chemically equivalent. A dimeric μ-$NCMe_3$ bridging structure is proposed for the complex.

Introduction

Few methods are known for the preparation of titanium complexes containing the alkylimido ligand (NR) [1]. Polymeric $[Ti(NR)_2]_x$ is formed when $[Ti(NMe_2)_4]$ or $[Ti(NEt)_4]$ are reacted with a variety of alkylamines while t-butylamine gives rise to dimers such as $[Ti(\mu\text{-}NCMe_3)(NMe_2)]_2$ and $[Ti(\mu\text{-}NCMe_3)(NHCMe_3)(NMe_2)]_2$ [2, 3]. Reaction of $[Ti_2(\mu\text{-}\eta^1\eta^5Cp)(\eta^5Cp)_3]$ with ethylamine results in the formation of $[Ti_2(Cp)_4(\mu\text{-}NCH_2Me)_2(\mu\text{-}H)]$ [4]. A recent development involves abstraction of HCl from the amido complexes $[Ti(Cp)(NHR)Cl_2]$ (R = Me, CH_2Me, $CHMe_2$, CMe_3) to give the imido complexes $[Ti(Cp)(\mu\text{-}NR)Cl]_2$ [5].

We have recently been interested in developing preparative routes to organoimido complexes of the earlier transition metals by reacting the high-valent metal chlorides with primary amines and silylamines. Reactions of WCl_6 with t-butylamine or $Me_3SiNHCMe_3$ led to the bis-t-butylimido complex $[W(NCMe_3)_2Cl_2(NH_2CMe_3)]_2$ [6] while the pentachlorides of molybdenum, niobium and tantalum gave the complexes $[M(NCMe_3)(NHCMe_3)Cl_2(NH_2CMe_3)]_2$ and $[M(NCMe_3)Cl_3(NH_2CMe_3)]_2$ [7–9]. Iso-propylamine and ethylamine also reacted with the pentachlorides to give the $[M(NR)(NHR)Cl_2(NH_2R)]_x$ complexes.

The complexes prepared are not particularly useful for further synthetic work as they contain the primary amine ligand. Attempts to obtain phosphine derivatives have been unsuccessful but nitrogen donor ligands appear to have the required donor properties. In particular, *N,N,N',N'*-tetramethylethylenediamine (tmed) and 2,2'-bipyridyl (bipy) readily displace the primary amine ligands to give the derivatives $[W(NCMe_3)_2Cl_2(L)]$, $[M(NR)Cl_3(L)]$ and $[M(NR)(NHR)Cl_2(L)]$ [7].

The present work details the preparation and characterisation of the titanium(IV) alkylimido complexes $[Ti(NR)Cl_2(NH_2R)]_x$ (R = CMe_3, $CHMe_2$, CH_2Me) and the derivatives $[Ti(NCMe_3)Cl_2(tmed)]_2$ and $[Ti(NCMe_3)Cl_2(bipy)]_2$.

Results and Discussion

Previous studies have suggested that bis-amido complexes, $[Ti(NHR)_2Cl_2]$, result when $TiCl_4$ is treated with methyl, ethyl or n-propylamine [10]. In the present work it was found that when eight equivalents of t-butylamine were reacted with $TiCl_4$ in benzene an orange solid analysing as $[Ti(NCMe_3)Cl_2(NH_2CMe_3)_2]\cdot\frac{1}{6}C_6H_6$ was formed (see Table I).

t-Butylamine hydrochloride precipitated during the reaction but less than the amount expected for replacement of two chloro ligands. However, when solvent was removed from the reaction mixture, further amine hydrochloride was produced and after extracting the complex away the residue was found to make up that required for complete substitution of two chloro ligands (eqn. (1)).

$$TiCl_4 + 5Me_3CNH_2 \longrightarrow [Ti(NCMe_3)Cl_2(NH_2CMe_3)_2] + 2Me_3CNH_3Cl \qquad (1)$$

0020-1693/88/$3.50

TABLE I. Physical Data

Complex	Colour	Melting point[a] (°C)	Analytical data[b]		
			C	H	N
1 $[Ti(NCMe_3)Cl_2(NH_2CMe_3)_2]_x$[c]	pale orange	>140 d	44.1 (43.8)	9.2 (9.3)	12.2 (12.5)
2 $[Ti(NCMe_3)Cl_2(NH_2CMe_3)]_x$	orange	>160 d	36.4 (36.5)	7.9 (7.6)	10.8 (10.7)
3 $[Ti(NCHMe_2)Cl_2(NH_2CHMe_2)_2]_x$	orange	60	35.5 (36.7)	9.4 (8.6)	13.6 (14.3)
4 $[Ti(NCH_2Me)Cl_2(NH_2CH_2Me)_2]_x$	orange	>105 d	28.2 (28.6)	7.9 (7.6)	16.0 (16.6)
5 $[Ti(NCMe_3)Cl_2(bipy)]_2$	pale yellow	>190 d	47.4 (48.6)	5.3 (5.0)	12.1 (12.1)
6 $[Ti(NCMe_3)Cl_2(tmed)]_2$	yellow	133–135	38.9 (39.2)	8.3 (8.2)	13.8 (13.7)
7 $[Ti(N(SiMe_3)PhMe)Cl_3(tmed)]$	yellow	136 d	44.3 (44.2)	7.3 (7.2)	9.3 (9.1)

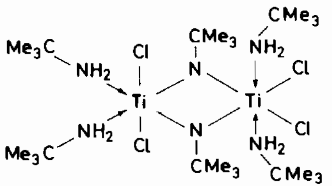
[a] d = decomposition. [b] Calculated figures in parentheses. [c] Calculated analytical figures contain $\frac{1}{6}C_6H_6$ solvent. Benzene verified by NMR spectra.

$\{[Ti(NCMe_3)Cl_2(NH_2CMe_3)_2]\cdot\frac{1}{6}C_6H_6\}_x$ is an orange crystalline solid which is soluble in hydrocarbon solvents including petroleum ether or hexane. The IR spectrum shows amine ligand NH absorbances at 3250 and 3200 cm^{-1} while in the far IR a strong band occurs at 300 cm^{-1} indicating *trans* metal dichloro ligands [11]. There are also shoulders at 308 and 280 cm^{-1} which suggest a *cis* dichloro species may also be present [11].

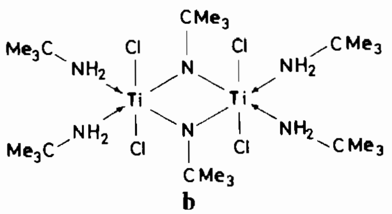
The ^1H NMR spectrum shows two t-butylamine and two t-butylimido methyl group proton resonances (ratio 2:1) consistent with two different environments for these ligands while the NH_2 protons appear as several resonances in the vicinity of 5.0 ppm and as a broad resonance centred at 8.2 ppm. A similar non-equivalence of NH protons has been observed in $[W(NCMe_3)(\mu\text{-}NPh)Cl_2(NH_2CMe_3)]_2$ where NH....Cl hydrogen bonding is present [12].

The ^{13}C NMR spectrum consists of three t-butyl methyl group resonances and three t-butyl quaternary carbon resonances. The two t-butylamine ligand methyl resonances are approximately equal in intensity as are the quaternaries which may arise from equal amounts of *cis* and *trans* dichloro species. The t-butylimido quaternary appears at 72.1 ppm which is to lower field than that observed in $[Ti(\mu\text{-}NCMe_3)(NMe_2)_2]_2$ [13]. The ^{13}C NMR spectrum clearly shows that formulation as the imido complex $[Ti(NCMe_3)Cl_2(NH_2CMe_3)_2]_x$ (1) is correct, rather than the amido alternative $[Ti(NHCMe_3)_2Cl_2]_x$ as quaternary carbon resonances characterisatic of the $NHCMe_3$ ligand (*ca.* 64 ppm [14]) are absent.

Attempts to recrystallise the complex have led to polymeric material and molecular weight determinations have been inconclusive so that the degree of association in the complex remains unknown. However a dimeric structure containing a symmetric bridge is likely, similar to that found by X-ray crystallography for $[Ti(\mu\text{-}NCMe_3)(NMe_2)_2]_2$ [3] and $[Ti(Cp)(\mu\text{-}NPh)Cl]_2$ [5]. Thus structure **a** is proposed on the basis of the physical data but a mixture containing **b** and **c** could also be present.



a



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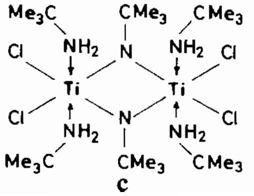


c

Reaction of $TiCl_4$ with two equivalents of $Me_3SiNHCMe_3$ in benzene led to an orange solid but ^1H and ^{13}C NMR spectra showed the presence of the trimethylsilyl group indicating the reaction was incomplete. On refluxing, an orange complex analysing as $[Ti(NCMe_3)Cl_2(NH_2CMe_3)]_x$ (2) was obtained for which an IR spectrum showed NH bands at 3275 and 3200 cm^{-1}, consistent with the formation of a t-butylamine ligand. In the far IR there was a strong M–Cl stretch at 290 cm^{-1} with associated side bands at 310 and 270 cm^{-1}. Low solubility of the complex has precluded NMR spectral verification of the imido and amine ligands but the reaction most likely involves proton transfer from *cis* coordinated t-butylamido ligands to give t-butylimido and amine ligands (eqns. (2) and (3)).

$$TiCl_4 + 2Me_3SiNHCMe_3 \longrightarrow Ti(NHCMe_3)_2Cl_2 + 2Me_3SiCl \qquad (2)$$

$$[Ti(NHCMe_3)_2Cl_2]_x \longrightarrow [Ti(NCMe_3)Cl_2(NH_2CMe_3)]_x \qquad (3)$$

Isopropylamine and ethylamine also react with $TiCl_4$ to give orange solutions from which complexes consistent with the formulation $[Ti(NR)Cl_2(NH_2R)_2]_x$ ($R = CHMe_2$ (3), $R = CH_2Me$ (4)), can be obtained. The non-crystalline solids invariably redissolved with difficulty and on attempted crystallisation insoluble polymeric materials formed.

The IR spectrum of $[Ti(NCHMe_2)Cl_2(NH_2CHMe_2)]_x$ (3) showed similar NH absorptions to those of the t-butyl complex (**1**) but below 800 cm^{-1} the bands were broad suggesting polymeric M–N–M bridges [11] while there were several weak M–Cl stretches in the vicinity of 200 cm^{-1}. The ^1H NMR spectrum showed several overlapping doublets for the isopropyl methyl groups indicating structural assymmetry [7, 15] and the NH protons were non-equivalent (resonances at 4.2 and 7.8 ppm) suggesting possible NH- - -Cl hydrogen bonding. In the ^{13}C NMR spectrum there were several isopropyl methyl group resonances as well as isopropylamine ligand CH resonances while the formation of the isopropylimido ligand was confirmed by resonances in the vicinity of 67 ppm. Lack of resonances attributable to an amido species (56.9 ppm in $[Ti(Cp)(NHCHMe_2)Cl_2]$ [14] indicates that while the product may be polymeric, the reaction still proceeds through to the imido stage even with the smaller steric requirements of an isopropyl group.

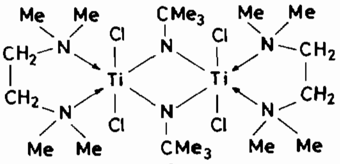
Attempts to prepare $[Ti(NEt)Cl_2(NH_2Et)_2]_x$ from $TiCl_4$ and ethylamine in benzene led to insoluble material, but the complex **4** was obtained using dichloromethane as solvent. However, once the complex is isolated it becomes insoluble, the IR spectrum showing broad absorptions below 800 cm^{-1} and several poorly defined M–Cl stretches in the vicinity of 200 cm^{-1}.

The t-butylimido complex (**1**) can be used to prepare derivatives of the type $[Ti(NCMe_3)Cl_2(L)]_2$ by replacement of the amine ligands. As found for group V and VI organoimido complexes the more successful preparations involve the chelating nitrogen donors tmed and bipy while phosphines produce ill-defined products [7]. For example when $[Ti(NCMe_3)Cl_2(NH_2CMe_3)_2]_2$ (**1**) was treated with PMe_3 in benzene NMR spectral analysis of the product obtained showed little of the amine ligand had been replaced.

Reaction of bipy with $[Ti(NCMe_3)Cl_2(NH_2CMe_3)_2]_2$ (**1**), in benzene (or with $[Ti(NCMe_3)Cl_2(NH_2CMe_3)]_x$ (**2**), solubilised in benzene by addition of Me_3CNH_2) gave microcrystals of $[Ti(NCMe_3)Cl_2(bipy)]_2$ (**5**). The complex is insoluble in organic solvents which precluded NMR spectral characterisation but the IR spectrum showed no absorptions attributable to amine ligands while there were new bands attributable to the bipy aromatic ring. In the far IR there was a strong band at 325 cm^{-1} suggesting *trans*-dichloro ligands and medium intensity shoulders at 370 and 345 cm^{-1} possibly due to *cis*-dichloro ligands. However, titanium(IV)–bipy complexes also exhibit two medium intensity Ti–N bands in this region [11] which complicates the assignment.

When $[Ti(NCMe_3)Cl_2(NH_2CMe_3)_2]_2$ (**1**) was reacted with tmed the more soluble complex $[Ti(NCMe_3)Cl_2(tmed)]_2$ (**6**) was formed. In both the ^1H and ^{13}C NMR spectra there was a single resonance for the t-butyl methyl groups as well as the tmed ligand methyl and methylene groups, the latter indicating chemical equivalence [7]. The t-butylimido quaternary carbon resonance appeared at 73.5 ppm.

In the IR spectrum there were four absorptions between 390 and 320 cm^{-1} which is also the region in which the M–N stretching vibration occurs in ethylene diamine complexes of titanium(IV) [11], so that *cis* or *trans* dichloro ligands could not be distinguished. However, based on the chemical equivalence of the tmed ligand in the NMR spectra, structure **d** is likely.



d

The tmed chelate ring clearly confers stability on the complex as it was formed in good yield when tmed was added to a mixture containing $TiCl_4$ and two equivalents of $Me_3SiNHCMe_3$, a reaction which previously produced a t-butylimido ligand only when the reactants were refluxed.

The $[Ti(NR)Cl_2(NH_2R)_2]_x$ complexes 3 and 4 also react with bipy or tmed in benzene but the products appear to be mixtures and pure $[Ti(NR)Cl_2(bipy)]$ and $[Ti(NR)Cl_2(tmed)]$ complexes have not been obtained so far. Attempts to prepare arylimido complexes by the methods outlined have also failed to give characterisable products. For example, reaction of $TiCl_4$ with $MePhN(SiMe_3)_2$ followed by tmed gave the arylamido complex $[Ti(NSiMe_3PhMe)Cl_3(tmed)]$ (7) which produced gummy materials on further attempts to abstract Me_3SiCl.

Conclusions

The results presented here indicate that alkylimido complexes of titanium(IV) can be prepared by a simple reaction between $TiCl_4$ and t-butyl, isopropyl or ethylamine and that bipy and tmed derivatives are readily formed from the t-butylimido complex. The complexes containing smaller alkyl groups appear to be polymeric and as such are expected to contain M—N—M bridges. For the reaction of $TiCl_4$ with $Me_3SiNHCMe_3$ a bis-alkylamido species is likely to form initially followed by interligand proton transfer to give a symmetrical μ-imido bridge and an amine ligand. With the primary amines, abstraction of HCl from an amido species $[Ti(NHR)Cl_3]_x$ is also possible.

In passing, it is noted that alkylimido complexes can now be prepared from alkylamines and d^0 metal chlorides of groups IV, V, VI and VII [6–9,16]. In all cases the reactions proceed forming imido complexes which contain two residual chloro ligands. Attempts to further substitute these groups by amido ligands using LiNHR reagents have so far proved unsuccessful.

Experimental

t-Butylamine, isopropylamine, ethylamine and *N,N,N',N'*-tetramethylethylenediamine were dried over and distilled from finely ground calcium hydride. *N*(Trimethylsilyl)t-butylamine was prepared by treating trimethylsilyl chloride with two equivalents of t-butylamine and distilling the product [17]. Titanium tetrachloride was distilled prior to use. Petroleum ether (boiling point 40–60 °C) and benzene were distilled over sodium wire and dichloromethane over finely ground calcium hydride. All distillations and bench-top manipulations were carried out under N_2 treated to remove oxygen and water [18]. IR spectra were recorded on a Perkin-Elmer 597 spectrometer, ^1H NMR spectra on a Varian T60 Model spectrometer and ^{13}C NMR spectra on a Jeol FX60 spectrometer. Analytical data were obtained by Prof. A. D. Campbell and his associates, University of Otago, New Zealand. Melting points were determined in sealed tubes under N_2 on an Electrothermal melting point apparatus and are uncorrected.

Tetra-t-butylaminebis(μ-t-butylimido)tetrachlorodititanium(IV) (1)

t-Butylamine (9.5 cm^3, 90.6 mmol) in benzene (40 cm^3) was added very slowly to titanium tetrachloride (2.4 g, 12.7 mmol) in benzene (120 cm^3) cooled to ice-water temperature and the mixture was stirred with the ice-bath removed for 18 h. The solution was filtered from the precipitated t-butylamine hydrochloride (1.8 g, 64%), the solvent removed and the orange solid extracted with warm petroleum ether until the extracts were no longer coloured orange. The combined extracts were filtered and the volume reduced giving the complex as light orange crystals which lost crystallinity on drying *in vacuo*. Tield 3.9 g (88%).

IR (Nujol) bands at 3250w, 3200m, 2700m, 2580m, 2480w, 2075w, 1604m, 1575m, 1504m, 1470m, 1395s, 1350m, 1335w, 1295s, 1280w, 1220s, 1150m, 1140m, 1105m, 1022m, 925w, 902m, 804w, 750w, 720w, 658m, 604m, 530m, 518m, 445s, 420w, 375w, 350w, 335w, 308m, 300s and 280m cm^{-1}.

^1H NMR (C_6D_6) 1.34 and 1.42 (2s, 36H, CH_3t-butylamine); 2.74 and 2.83 (2s, 18H, CH_3t-butylimido); 4.8 and 8.32 (b, 8H, NH_2). ^{13}C NMR (C_6D_6) 28.3, 30.9 and 31.5 (Me_3); 52.2 and 52.5 (NH_2C); 72.1 (NC). ^{13}C NMR ($CDCl_3$) 28.3, 30.9 and 31.5 (Me_3s); 52.2 and 52.5 (NH_2C); 72.1 (NC).

[t-Butylamine-t-butylimidodichlorotitanium(IV)]$_x$ (2)

N(Trimethylsilyl)t-butylamine (2.1 cm^3, 10.9 mmol) in benzene (30 cm^3) was added to titanium tetrachloride (1.0 g, 5.3 mmol) in benzene (60 cm^3). The solution immediately turned yellow then more slowly became dark red and then back to orange after approximately 10 min. The mixture was refluxed for 3 h, the solution filtered and the solvent removed to give the complex as an orange solid which was washed with petroleum ether (2 X 100 cm^3) and dried *in vacuo*. Yield 1.25 g (90%).

IR (Nujol) 3275m, 3200s, 2700m, 2570w, 2480w, 2050w, 1600w, 1555m, 1500w, 1395m, 1345m, 1290w, 1260m, 1230s, 1208s, 1135s, 1018m, 965w, 924m, 904m, 840m, 805m, 745m, 720m, 672w, 615s, 520s, 425w, 410w, 365m, 310m, 290s and 270m cm^{-1}.

[Dichlorobisisopropylamine(isopropylimido) titanium(IV)]$_x$ (3)

Isopropylamine (6.3 cm^3, 74.0 mmol) in benzene (50 cm^3) was added to titanium tetrachloride (2.0 g, 10.5 mmol) in benzene (100 cm^3) cooled to ice-water temperature and the mixture was stirred for 10 h with the ice bath removed. The solution was filtered and the solvent removed to give an orange non-crystalline solid which was extracted with warm petroleum ether (120 cm^3). The solution was filtered and the solvent removed to give the complex as a non-crystalline orange solid.

IR (Nujol) bands at 3175m, 3075m, 2700m, 2600m, 2510m, 2025w, 1590m, 1500m, 1340m, 1295w, 1210m, 1155m, 1060w, 1005w, 935w, 885w, 800m, 765w, 720s, 640m, 518w, 465m, 410m, 370w, and 320w cm^{-1}.

^1H NMR ($CDCl_3$), 0.94 and 0.98 (d, Me_2); 1.09–1.62 (several d, Me_2); 3.20–3.80 (broad sept, 3H, CHs); 3.99–4.58 and 7.60–8.2 ratio 1:4, (broad, 4H, $2NH_2$). ^{13}C NMR ($CDCl_3$) 21.0, 24.0, 24.7 and 25.2 (Me_2); 44.8, 47.6, 48.5 and 49.6 (NH_2CH); 67.7 and 68.5 (NCH).

[Dichlorobisethylamine(ethylimido)titaniumIV)]$_x$ (4)

Ethylamine (4.3 cm^3, 76.1 mmol) in dichloromethane (100 cm^3) was added to titanium tetrachloride (2.0 g, 10.5 mmol) in dichloromethane (120 cm^3) cooled to ice-water temperature and the mixture was stirred for 18 h with the ice bath removed. The solution was filtered and the solvent removed to give an orange solid which was extracted with dichloromethane (100 cm^3). The solution was filtered and the solvent removed to give the complex as an orange non-crystalline material which was washed with petroleum ether (50 cm^3) and dried *in vacuo*. Yield 1.95 g (74%).

IR (Nujol) bands at 3200s, 3050s, 2700s, 2580m, 2475m, 2350w, 2040w, 1595s, 1508w, 1385m, 1330w, 1215m, 1190m, 1040s, 995w, 975m, 962m, 880w, 790s, 720s, 640s, 500s, 418s, 320s and 300s cm^{-1}.

Bis(2,2′-bipyridyl)bis(μ-t-butylimido)tetrachlorodititanium(IV) (5)

N(Trimethylsilyl)t-butylamine (1.3 cm^3, 6.7 mmol) in benzene (40 cm^3) was added to titanium tetrachloride (0.6 g, 3.2 mmol) in benzene and the mixture was stirred for 5 h. The solution was filtered, 2,2′-bipyridyl (0.5 g, 3.2 mmol) in benzene (30 cm^3) added and the mixture stirred for 2 h. The solid was filtered, washed with benzene (30 cm^3), followed by petroleum ether (30 cm^3) and dried *in vacuo* to give the complex as a light yellow powder. Yield 0.92 g (84%).

IR (Nujol) bands at 1595m, 1570w, 1555w, 1490w, 1350m, 1317w, 1300w, 1282w, 1250s, 1208m, 1164m, 1155m, 1105w, 1058w, 1040w, 1020m, 805w, 800w, 770s, 742w, 730m, 718w, 650m, 635w, 590w, 530m, 450w, 418w, 370m, 345m, and 325s cm^{-1}.

Bis(μ-t-butylimido)tetrachlorobis(N,N,N′,N′-tetramethylethylenediamine)dititanium(IV) (6)

(a) *N*(Trimethylsilyl)t-butylamine (2.0 cm^3, 10.6 mmol) in benzene (30 cm^3) was added slowly to titanium tetrachloride (1.0 g, 5.3 mmol) in benzene (100 cm^3) and the mixture was stirred for 2 h. *N,N,N′,N′*-Tetramethylethylenediamine (0.65 cm^3, 5.6 mmol) in benzene (20 cm^3) was added and the mixture was refluxed for 20 min. Benzene (50 cm^3) was added and the solution heated until the yellow solid dissolved. The solution was filtered while hot and the volume reduced to *ca.* 30 cm^3 giving the complex as yellow crystals. On drying *in vacuo* crystallinity was lost giving a yellow powder. Yield 1.3 g (81%).

IR (Nujol) bands at 2690m, 2580m, 2500m, 2350w, 2060w, 1605w, 1510w, 1400m, 1350m, 1290w, 1280w, 1236s, 1204m, 1164w, 1130w, 1119w, 1095w, 1062w, 1044m, 995w, 985w, 942m, 924w, 835w, 795s, 765m, 720w, 600w, 504s, 445w, 382m, 370m, 346s, and 325m cm^{-1}.

^1H NMR ($CDCl_3$) 1.04 (s, 9H, Me_3); 2.82 (s, 12H, $2NMe_2$); 3.11 (s, 4H, $2NCH_2$). ^{13}C NMR ($CDCl_3$) 30.8 (Me_3); 51.2 (NMe_2); 58.7 (NCH_2); 73.5 (NC).

(b) t-Butylamine (8 cm^3, 76.3 mmol) in benzene (40 cm^3) was added slowly to titanium tetrachloride (2 g, 10.5 mmol) in benzene (120 cm^3) and the mixture was stirred for 18 h. The solution was filtered and *N,N,N′,N′*-tetramethylethylenediamine (1.3 g, 11.2 mmol) in benzene (30 cm^3) added. The mixture was refluxed for 1 h, filtered while hot and the volume reduced to *ca.* 20 cm^3 giving the complex as yellow crystals and a yellow powder after drying *in vacuo*. Yield 2.8 g (88%). The complex had identical IR, ^1H and ^{13}C NMR spectra to the sample prepared under (a).

Trichloro(N,N,N′,N′-tetramethylethylenediamine)N-tolyltrimethylsilylamidotitanium(IV) (7)

N(Tolylbistrimethylsilyl)amine (1.5 cm^3, 5.4 mmol) in benzene (30 cm^3) was added to $TiCl_4$ (1 g, 5.3 mmol) in benzene (80 cm^3) and the mixture was stirred for 4 h. *N,N,N′,N′*-Tetramethylethylenediamine (0.8 cm^3, 5.4 mmol) in benzene (25 cm^3) was added and the mixture stirred for 18 h. The solution was filtered and the yellow crystalline solid washed with benzene (2×20 cm^3), petroleum ether (2×50 cm^3) and dried *in vacuo*. Yield 1.8 g (74%).

IR (Nujol) 1620w, 1520m, 1508s, 1385w, 1335m, 1302m, 1290m, 1172m, 1155w, 1118w, 1082w, 1058w, 1022m, 1002m, 990w, 968w, 850w, 830s, 818s, 780w, 738m, 658m, 620m, 520m, 460w, 425w, 398w, 344w and 322m cm^{-1}.

^1H NMR ($CDCl_3$) 0.02 (s, 9H, $SiMe_3$); 2.18 (s, 3H, Me); 2.89 (s, 12H, NMes); 3.00 (s, 4H, $2CH_2$); 2.75 (s, 4H, aromatic Hs). ^{13}C NMR ($CDCl_3$) 0.0 ($SiMe_3$); 20.9 (Me); 51.5 (NMes); 58.7 (NCH_2s);

123.2 (*o*-CHs); 128.6 (*m*-CHs); 131.1 (*p*-C); 157.8 (*ipso*-C).

References

1 W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, *31*, 123 (1980).

2 D. C. Bradley and E. G. Torrible, *Can. J. Chem.*, *41*, 134 (1963).

3 W. A. Nugent and R. L. Harlow, *Inorg. Chem.*, *18*, 2030 (1979).

4 J. N. Armor, *Inorg. Chem.*, *17*, 203 (1978).

5 C. T. Vroegop, J. H. Teuben, F. van Bolhuis and J. G. M. van der Linden, *J. Chem. Soc., Chem. Commun.*, 550 (1983).

6 A. J. Nielson, *Polyhedron*, *6*, 1657 (1987).

7 A. J. Nielson, *Polyhedron*, *7*, 67 (1988).

8 T. C. Jones, A. J. Nielson and C. E. F. Rickard, *J. Chem. Soc., Chem. Commun.*, 206 (1984).

9 P. A. Bates, A. J. Nielson and J. M. Waters, *Polyhedron*, *4*, 1391 (1985).

10 R. T. Cowdell and G. W. A. Fowles, *J. Chem. Soc.*, 2522 (1960).

11 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds', 4th edn., Wiley, New York, 1986.

12 D. C. Bradley, R. J. Errington, M. B. Hursthouse, A. J. Nielson and R. L. Short, *Polyhedron*, *2*, 843 (1983).

13 W. A. Nugent, R. J. McKinney, R. U. Kasowski and F. A. van-Catledge, *Inorg. Chim. Acta*, *65*, L91 (1982).

14 C. T. Jekel-Vroegop and J. H. Teuben, *J. Organomet. Chem.*, *286*, 309 (1985).

15 D. C. Bradley, R. C. Mehrotra and D. P. Gaur, 'Metal Alkoxides', Academic Press, London, 1978, p. 125.

16 G. R. Clark, A. J. Nielson and C. E. F. Rickard, *Polyhedron*, *7*, 117 (1988).

17 R. M. Pike, *J. Org. Chem.*, *26*, 232 (1961).

18 A. J. Nielson, *Chem. In N.Z.*, *49*, 11 (1986).