Thermal Decomposition of (Pentamethylcyclopentadienyl)titanium(IV) Complexes Containing Dialkylamido Ligands – X-ray Structure of [{η^5 :η^2-$C_5Me_4CH_2CH_2N(Me)CN(C_6H_3Me_2)$}$TiCl_2$]

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The new organometallic binuclear complexes [{Cp* Ti(NEt_2)}$_2$(μ-NEt)$_2$] (**1**), [(Cp*Ti)$_2$(NMe_2)($NHMe_2$)(μ-NMe)(μ-NCH_2)] (**2**), and [(Cp*TiCl)$_2$(μ-NMe)$_2$] (**3**) have been obtained by heating the dialkylamido derivatives [Cp*Ti(NR_2)$_n$$Cl_{3-n}$] (R = Et, n = 3; R = Me, n = 2, 3) (Cp* = η^5-C_5Me_5) in solution and at different temperatures. The thermal decomposition of [Cp*Ti(NMe_2)Cl_2] at temperatures above 145 °C caused the activation of the pentamethylcyclo-pentadienyl ligand to give the new, geometrically constrained, complex [{η^5:η^1-$C_5Me_4CH_2CH_2N(Me)$}$TiCl_2$] (**5**). Addition of the isocyanide 2,6-$Me_2C_6H_3NC$ to the solution obtained in this last process led to the isolation of the complex [{η^5:η^2-$C_5Me_4CH_2CH_2N(Me)CN(C_6H_3Me_2)$}-$TiCl_2$] (**6**) by insertion of one isocyanide molecule into the titanium–nitrogen bond in **5**. The structure of **6** has been proved by an X-ray diffraction study which showed the organic ligand, $C_5Me_4CH_2CH_2N(Me)CN(C_6H_3Me_2)$, to be coordinated to the titanium atom via the cyclopentadienyl ring and a η^2-iminocarbamoyl fragment. Heating of the trinuclear oxo derivative [{Cp*Ti(NMe_2)}$_3$(μ-O)$_3$] at 110 °C gave the complex [{Cp*$_3$Ti$_3$(NMe_2)(μ-η^2-CH_2NMe)}(μ-O)$_3$] (**4**) where an imine ligand bridges two of the three metallic centres.

Studies on the decomposition of inorganic or organometallic complexes and polymers is currently a fast emerging area in chemistry. The preparation of ceramic materials from precursor complexes is a fascinating challenge for inorganic or solid-state chemists involved in the design of routes to new or improved refractory metal oxides, carbides, and nitrides.[1]

For instance, titanium nitride possesses a number of useful properties, including extreme hardness, excellent chemical resistance, desirable optical properties, and good electrical conductivity.[2] The current trend to obtain this material in low-temperature processes necessitates the use of inorganic precursors, and in particular amido complexes Ti(NR_2)$_4$ have been extensively used.[3] Their thermal decomposition in vapour-phase CVD processes has been shown to lead to the incorporation of carbon and hydrogen in the desired nitride.[4] These impurities can be reduced by reaction with ammonia[5] but in all cases, the carbon percentage is significant, and attributed to the formation of metallacycles, as has been described in solution.[6]

In our research into the stability of mono(pentamethylcyclopentadienyl)titanium derivatives, we have recently reported on the formation of alkylidyne complexes by the thermal decomposition of the alkyl precursors[7] and we were interested in expanding these studies to other ligands attached to the metal centre. Here we describe the synthesis and characterisation of several organometallic derivatives obtained by heating the dialkylamido complexes of titanium, [Cp*Ti(NR_2)$_n$$Cl_{3-n}$] and [{Cp*Ti($NMe_2$)}$_3$(μ-O)$_3$] in solution.[8]

Results and Discussion

A toluene solution of the complex [Cp*Ti(NEt_2)$_3$] was heated at 70°C for 20 d in a Carius tube (to guarantee the purity of the atmosphere); subsequent evacuation of the volatiles under vacuum and crystallisation from hexane allowed the isolation of [{Cp*Ti(NEt_2)}$_2$(μ-NEt)$_2$] (**1**) as a pure complex (see Scheme 1).

The spectroscopic and analytical data (Experimental Section) are consistent with a dimeric structure of **1**, with two bridging ethylimide ligands. According to the ^{1}H-NMR data, this complex is characterised by a *cis* arrangement[9] of both the terminal diethylamido and pentamethylcyclopentadienyl ligands with respect to the central Ti_2(μ-NEt)$_2$ core.

Complex [Cp*Ti(NMe_2)$_3$] decomposed between 120 and 150°C with elimination of $NHMe_2$ and formation of the organometallic derivative {[Cp*Ti]$_2$(NMe_2)($NHMe_2$)(μ-NMe)(μ-N=CH_2)} (**2**) (see Scheme 1 and Experimental Section). Complex **2** was isolated in a yield of 64% as a dark-green crystalline solid. The ^{13}C-NMR spectrum of **2** shows one doublet of doublets at $\delta = 100.8$ ($^1J = 154.1$ Hz, $^1J = 159.6$ Hz) while its ^{1}H-NMR spectrum presents two signals at $\delta = 3.79$ (1 H) and 3.81 (1 H) ($^2J < 0.2$ Hz), corresponding to the existence of a bridging μ-N=CH_2 ligand.[10] Two broad signals for the methyl groups of the

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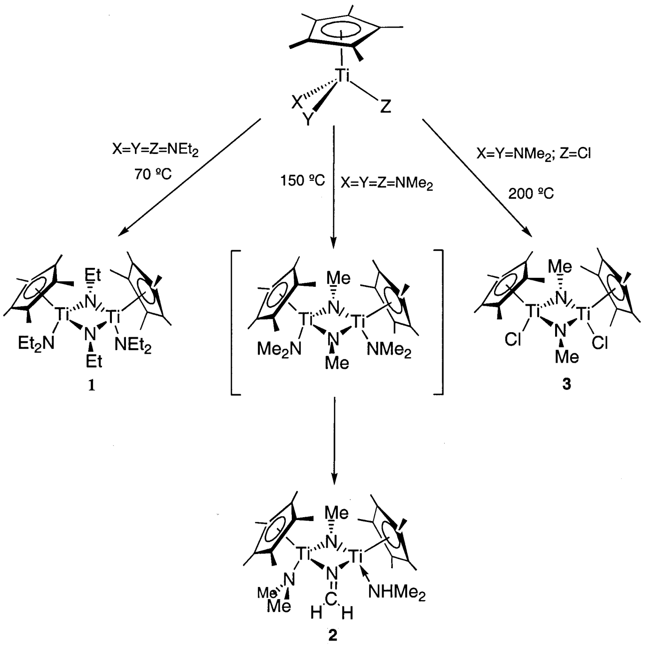
Scheme 1. Thermolyses of the complexes $[Cp^*Ti(NEt_2)_3]$, $[Cp^*Ti(NMe_2)_3]$ and $[Cp^*Ti(NMe_2)_2Cl]$



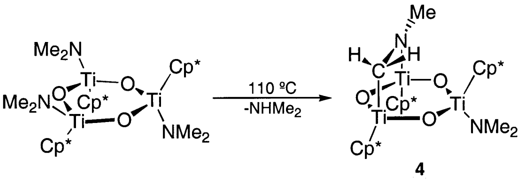
terminal NMe_2 ligands were also observed in the spectra at room temp., which collapsed together at 313 K ($\Delta G^{\#} \approx 63$ kJ/mol). This spectral behaviour is based on the slow rotation around the Ti−N bond, indicating π-donation of the nitrogen electron pair to the titanium centre. The value of the Gibbs free energy is similar to those reported for other dimethylamido complexes (46−100 kJ/mol).[11] Finally the ^1H-NMR spectrum exhibits two doublets at $\delta = 1.6$ ($^3J = 6.0$ Hz) and 1.7 ($^3J = 6.0$ Hz) for the diastereotopic methyl groups, and one septuplet at $\delta = 4.01$ for the amine proton of the coordinated $HNMe_2$ ligand. This ligand remains in the complex after several hours under vacuum (10^{-2} Torr) or even in THF solution. The formation of complex **2** might be explained by the activation of one C−H bond in a methylimide group[12] from a "$[\{Cp^*Ti(NMe_2)\}_2(\mu\text{-}NMe)_2]$" intermediate, similar to **1** (Scheme 1), and formation of one equivalent of $NHMe_2$ which is retained in the complex.

In an analogous procedure, heating a solution of $[Cp^*Ti(NMe_2)_2Cl]$ in toluene at 135−200°C afforded the compound $[(Cp^*TiCl)_2(\mu\text{-}NMe)_2]$ (**3**) in a yield of 63%. The analytical and spectroscopic data of **3** agree with a dimeric formulation where the Cp* rings appear in a *cis* arrangement, as proposed for **1** (Scheme 1).

In order to explain the formation of the complexes **1**−**3**, we suggest that the thermal decomposition of the compounds $[Cp^*Ti(NR_2)_nCl_{3-n}]$ (R = Et, $n = 3$; R = Me, $n = 2$, 3) produces azatitanacyclopropane or imine intermediates similar to those described in the literature for other dialkylamido derivatives.[6] The evolution of these intermediates at high temperatures would give rise to Ti=NR groups; processes which are well-documented for tantalum complexes.[6b][13] However, titanium derivatives with terminal imido ligands are only known in the presence of donor molecules,[14] and in their absence binuclear arrangements with $[Ti_2(\mu\text{-}NR)_2]$ cores are usually found.[15]

The proposed azatitanacyclopropane intermediates were not detected in the case of mononuclear precursors, but fortunately we could isolate and characterise the complex $[Cp^*_3Ti_3(NMe_2)(\mu\text{-}\eta^2\text{-}CH_2NMe)(\mu\text{-}O)_3]$ (**4**) with the imine group bridging two titanium centres, as mentioned above (see Scheme 2). This compound was obtained as a crystalline red solid (63% yield) by heating a toluene solution of the trinuclear oxo derivative $[Cp^*_3Ti_3(NMe_2)_3(\mu\text{-}O)_3]$.

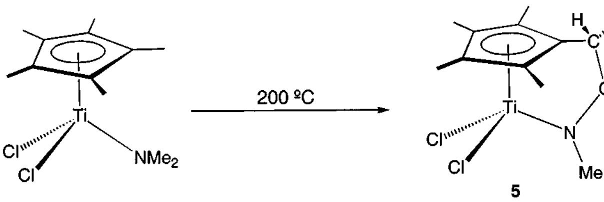
Scheme 2. Thermal evolution of the trinuclear oxo compound $[\{Cp^*Ti(NMe_2)\}_3(\mu\text{-}O)_3]$



The ^1H- and ^{13}C-NMR data of **4** show three resonances for the Cp* ligands and one signal for the terminal NMe_2 group, while the signal of the CH_2 moiety of the bridging imine fragment appears as a triplet of quadruplets ($\delta = 87.9$, $^1J = 149.5$ Hz, $^3J = 3.7$ Hz) in the ^{13}C-NMR spectrum and as an AB spin system ($\delta = 1.82$, 2.86; $J_{AB} = 5.9$ Hz) in the ^1H-NMR spectrum. The formation of this kind of bridging imine groups from an amido ligand has been already reported by Chisholm et al. for the complex $[W_2Cl_3(NMe_2)_2L_2(\mu\text{-}CHCH_2)(\mu\text{-}CH_2NMe)]$.[6e]

Different results than those described above were observed when a [D6]benzene solution of the $[Cp^*Ti(NMe_2)Cl_2]$ derivative was heated above 140°C. Not only did the activation of the amido group take place, but also the activation of the Cp* unit, yielding the compound $[\{\eta^5{:}\eta^1\text{-}C_5Me_4CH_2CH_2N(Me)\}TiCl_2]$ (**5**) (see Scheme 3).

Scheme 3. Thermal decomposition of the complex $[Cp^*Ti(NMe_2)Cl_2]$

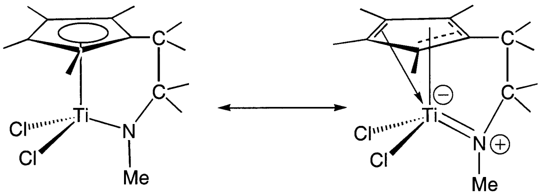


The ^1H-NMR spectrum of **5** in $CDCl_3$ shows two resonances for the α- and β-methyl groups of the C_5Me_4 ring [$\delta = 2.11$ (6 H), 2.17 (6 H)] and an AA′BB′K3 spin system [$\delta = 3.32$ (2 H), 4.54 (2 H) and 3.55 (3 H)] assigned to the CH_2CH_2NMe moiety, supporting the hypothesis of C−H activation giving rise to the chelating ligand $[C_5Me_4(CH_2)_2NMe]$. This ligand is linked to the titanium atom via the cyclopentadienyl ring and the amido group in a similar fashion to those reported for the $\{[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_nNR]MX_2\}$ (M = Ti, Zr) complexes.[16]

The most important features of the ^{13}C-NMR spectrum (see Experimental Section) are the downfield shift ($\Delta\delta$ =

11.3) of the $C_{ipso}CH_2$ resonance (δ = 139.7) with respect to the starting complex [Cp*Ti(NMe$_2$)Cl$_2$], and the observation of the CH$_2$NMe signal at δ = 79.4. These data are best accounted for if a high contribution of the constrained geometry resonance structure **II** depicted in Figure 1 is assumed.

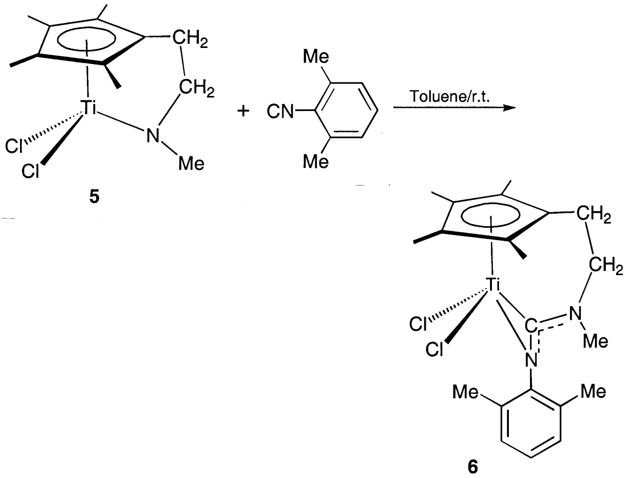
Figure 1. Resonance structures proposed for compound **5**



I **II**

The addition of excess of 2,6-dimethylphenyl isocyanide to a solution of **5** causes the insertion of one molecule of isocyanide into the Ti−N bond affording the iminocarbamoyl derivative [{η^5:η^2-C$_5$Me$_4$CH$_2$CH$_2$N(Me)CN(C$_6$H$_3$Me$_2$)}TiCl$_2$] (**6**) (Scheme 4).

Scheme 4. Insertion reaction of isocyanide in complex **5**



The complex **6** was obtained as an orange solid, insoluble in hexane, slightly soluble in benzene or toluene, and soluble in chloroform or dichloromethane. The most prominent band in the IR spectrum is the very intense ν_{CN} absorption at 1668 cm^{-1}, in agreement with the insertion of xylyl isocyanide.

In order to confirm the Cp* activation and assess its structural consequences, the molecular structure of this compound was determined by an X-ray diffraction study (see Figure 2). Selected bond lengths and angles of **6** can be found in Table 1. The compound is a monomer with the ligand [C$_5$Me$_4$CH$_2$CH$_2$N(Me)CN(C$_6$H$_3$Me$_2$)] linked to the metal centre through the cyclopentadienyl ring (η^5) and both the carbon and the nitrogen atoms (η^2) of the inserted isocyanide.

Figure 2. ORTEP drawing of [{η^5:η^2-C$_5$Me$_4$CH$_2$CH$_2$N(Me)CN(C$_6$H$_3$Me$_2$)}TiCl$_2$] (**6**); thermal ellipsoids at a 50% level are shown

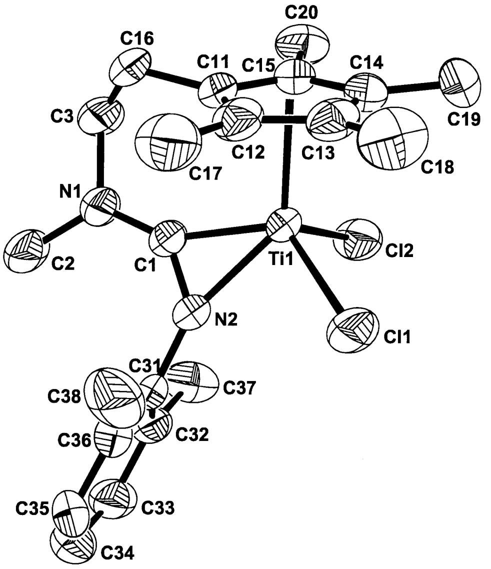


Table 1. Selected bond lengths [Å] and angles [°] for the compound [{η^5:η^2-C$_5$Me$_4$CH$_2$CH$_2$N(Me)CN(C$_6$H$_3$Me$_2$)}TiCl$_2$] (**6**); Cp* and E are the centroids of the cyclopentadienyl ring and the N(2)−C(1) bond, respectively

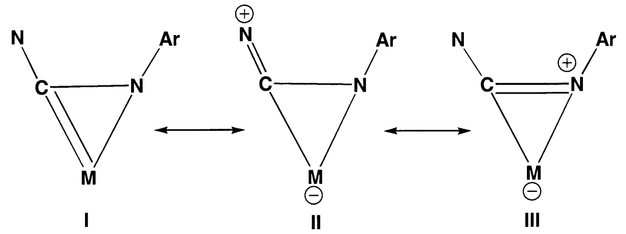
Ti(1)−C(1)	2.000(8)	N(2)−C(31)	1.421(10)
Ti(1)−N(2)	2.047(6)	N(1)−C(1)	1.316(10)
Ti(1)−Cl(1)	2.349(3)	N(1)−C(2)	1.457(11)
Ti(1)−Cl(2)	2.287(3)	N(1)−C(3)	1.476(11)
Ti(1)−C(11)	2.333(8)	C(3)−C(16)	1.513(14)
Ti(1)−C(12)	2.329(8)	C(16)−C(11)	1.504(12)
Ti(1)−C(13)	2.392(8)	C(11)−C(15)	1.399(11)
Ti(1)−C(14)	2.428(8)	C(11)−C(12)	1.420(12)
Ti(1)−C(15)	2.365(8)	C(12)−C(13)	1.403(13)
Ti(1)−Cp*	2.046	C(13)−C(14)	1.395(12)
Ti(1)−E	1.920	C(14)−C(15)	1.413(11)
N(2)−C(1)	1.284(9)		
C(1)−Ti(1)−N(2)	37.0(3)	N(2)−Ti(1)−Cl(1)	88.1(2)
C(1)−Ti(1)−Cl(2)	100.9(2)	Ti(1)−N(2)−C(31)	158.4(5)
C(1)−Ti(1)−Cl(1)	123.3(2)	Ti(1)−N(2)−C(1)	69.5(4)
Cl(1)−Ti(1)−Cl(2)	101.01(11)	C(1)−N(2)−C(31)	132.0(7)
E−Ti(1)−Cl(1)	105.6	Ti(1)−C(1)−N(1)	150.7(6)
E−Ti(1)−Cl(2)	100.7	Ti(1)−C(1)−N(2)	73.5(5)
Cp*−Ti(1)−Cl(1)	112.7	N(2)−C(1)−N(1)	135.5(8)
Cp*−Ti(1)−Cl(2)	112.5	C(1)−N(1)−C(2)	126.2(7)
Cp*−Ti(1)−N(2)	136.5	C(1)−N(1)−C(3)	115.5(7)
Cp*−Ti(1)−C(1)	105.7	C(2)−N(1)−C(3)	118.3(7)
Cp*−Ti(1)−E	121.8	N(1)−C(3)−C(16)	111.6(8)
N(2)−Ti(1)−Cl(2)	99.3(2)	C(3)−C(16)−C(11)	117.3(8)

The molecule exhibits a four-legged stool geometry for the titanium atom [Cl(1), Cl(2), C(1), N(2)] where the N(2) atom lies down from, and C(1) is shifted up to, the cyclopentadienyl ring due to the side chain [N(1), C(3), C(16)]; this shows a zigzag disposition similar to those found in the complexes [{η^5:η^1-C$_5$Me$_4$CH$_2$CH$_2$NMe$_2$}CoI$_2$],[17] [{η^5:η^1-C$_5$H$_4$CH$_2$CH$_2$NMe$_2$}Mo(CO)$_2$I],[18] and [{η^5:η^2-C$_5$H$_4$CH$_2$CH$_2$N(Me)CO]Re(CO)SePh].[19] The carbon−carbon bond lengths in the cyclopentadienyl ring are in the normal range [1.395(12)−1.420(12) Å]. The methyl groups in the C$_5$Me$_4$ fragment are displaced with respect to the metal centre, in particular C(16), which is placed 0.23 Å above the cyclopentadienyl ring plane.

The inserted isocyanide has an N(2)−C(1) bond length of 1.284(9) Å, which is consistent with a double bond,[20] while Ti(1)−N(2) [2.047(6) Å] is in agreement with the Ti−N distances found in η^2-iminoacyltitanium complexes,[20b][21] and is very similar to those of [$Cp^*{}_2Ti^{III}(NMePh)$] [2.054(2) Å][22] and [$(CO_5)W\{C(NMe_2)O\}TiCp^*(NMe_2)_2$] (av. 2.058 Å)[23] where a single bond with absence of multiple bonding is suggested. The Ti(1)−C(1) [2.000(8) Å] distance is not significantly different to that found in the comparable acyl complex [$Cp^*Ti(\eta^2\text{-}COMe)Cl_2$] [2.021(6) Å].[24]

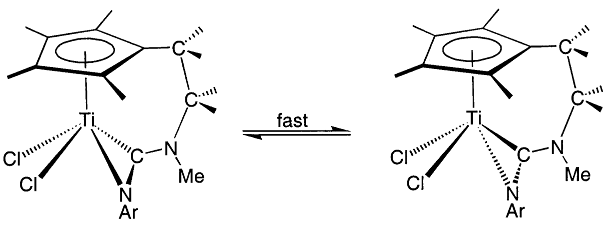
On the other hand, N(1)(sp^2) has a planar environment and its bond length with C(1)(sp^2) [1.316(10) Å] is only slightly longer than the double bond N(2)(sp^2)−C(1)(sp^2) and 0.1 Å shorter than the single bond N(2)(sp^2)−C(31)(sp^2) [1.421(10) Å]. All these data, together with the planarity of the C(3)C(2)N(1)C(1)N(2)C(31)Ti(1) system, are indicative of an extensive π delocalisation along the N(1)C(1)N(2) fragment, while the xylyl group is twisted 80.5(4)° with respect to this fragment. Analogous structural features have been reported in the literature for other η^2-iminocarbamoyl complexes, and are explained by the contribution of the three resonance forms shown in Figure 3.[25]

Figure 3. Resonance forms for the η^2-iminocarbamoyl group in complex **6**



The ^{1}H-NMR spectrum indicates two signals for methyl groups of the C_5Me_4 ring and an AA′BB′K$_3$ spin system for the CH_2CH_2NMe fragment. The C_s symmetry observed in solution is due to a very fast exchange, on the NMR time scale and even at low temperature, between the two enantiomers present (Figure 4).

Figure 4. The two enantiomers of complex **6**



In the ^{13}C-NMR spectrum we observed a signal at δ = 197.2 associated with the (η^2-iminocarbamoyl)Ti entity and a considerable higher field displacement for the carbon resonances of $C_{ipso}CH_2$ [δ = 123.4, Δδ = δ(**5**) − δ(**6**) = 16.3], NCH_2 (δ = 56.3, Δδ = 23.1) and CH_2NCH_3 (δ = 35.9, Δδ = 9.8). This spectral behaviour is attributable to the isocyanide insertion into the titanium−nitrogen bond of **5**, the consequent backbone expansion and the π delocalisation proposed for the iminocarbamoyl fragment (structures **I** and **III** in Figure 3).

Conclusions

In our exploration of the thermal decomposition of the titanium complexes [$Cp^*Ti(NR_2)_nCl_{3-n}$] we have observed the formation of binuclear derivatives with [$Ti_2(\mu\text{-}NEt)_2$] and [$Ti(\mu\text{-}NMe)(\mu\text{-}N{=}CH_2)Ti$] cores, and a mononuclear compound with the interesting methyl activation of the pentamethylcyclopentadienyl ligand. This last observation was definitely confirmed by the characterisation of the complex [$\{\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2N(Me)CN(C_6H_3Me_2)\}TiCl_2$], which is one of few examples known of isocyanide insertion into metal−nitrogen bonds. The thermal evolution of the trinuclear oxo compound [$\{Cp^*Ti(NMe_2)\}_3(\mu\text{-}O)_3$] seems to be facilitated by a cooperative effect between the metallic centres to form a bridging imine group [$-CH_2-N(Me)-$] supported on a TiO_2-like arrangement.

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Experimental Section

All reactions were carried out under argon by Schlenk techniques or in an M. Braun glovebox.[26] Hexane was refluxed over Na/K amalgam, toluene over sodium, and both distilled under argon prior to use. NMR solvents were dried with P_2O_5 ($CDCl_3$) or Na/K amalgam (C_6D_6) and vacuum-distilled from 4 Å molecular sieves. Oven-dried glassware was repeatedly evacuated with a pumping system (ca. 1×10^{-3} Torr) and subsequently filled with inert gas. 2,6-$Me_2C_6H_3NC$ (FLUKA) was used as received. [$Cp^*Ti(NR_2)_nCl_{3-n}$] and [$\{Cp^*Ti(NMe_2)\}_3(\mu\text{-}O)_3$] were prepared by known procedures.[8] − IR (KBr): Perkin-Elmer 883 spectrophotometer. − ^{1}H and ^{13}C NMR: Varian Unity-300 and/or 500-Plus spectrometer, trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to TMS. − EI MS: 70 eV with a Hewlett-Packard 5988 spectrometer. − Elemental analyses: Heraeus CHN-O-Rapid microanalyzer. − Thermolyses: Roth autoclave model III (300 ml), with heater model 30S (20−300°C) and temperature regulator model DR 500.

*Synthesis of [{Cp*Ti(NEt$_2$)}$_2$(μ-NEt)$_2$]* (**1**): A solution of [$Cp^*Ti(NEt_2)_3$] (0.55 g, 1.38 mmol) in toluene (20 ml) was transferred via cannula into a Carius tube (40 ml capacity) ready to be sealed by flame in vacuum. This solution was heated at 70°C for 20 d. The Carius tube was opened in a glovebox and the volatiles were removed under vacuum. The oily red solid obtained was dissolved in 15 ml of hexane and cooled overnight at −40°C to afford a red solid which, after several hours under vacuum, was characterised as the complex **1** (0.14 g, 37%). − IR (KBr): $\tilde{\nu}$ = 1439 cm^{-1} s, 1372 s, 1322 m, 1142 m, 1118 s, 1000 s, 875 m, 787 s, 584 s, 508 s, 419 m. − ^{1}H NMR (C_6D_6, 20°C): δ = 3.85 [q, ^3J = 7.2 Hz, 8 H, $N(CH_2CH_3)_2$], 3.66 [q, ^3J = 7.2 Hz, 4 H, μ-$N(CH_2CH_3)$], 2.04 (s, 30 H, C_5Me_5), 1.15 [t, 12 H, $N(CH_2CH_3)_2$], 1.11 [t, 6 H, μ-$N(CH_2CH_3)$]. − $^{13}C\{^1H\}$ NMR (C_6D_6, 20°C): δ = 118.3 (C_5Me_5), 55.6 [μ-$N(CH_2CH_3)$], 50.5 [$N(CH_2CH_3)_2$], 20.3 [(μ-$N(CH_2CH_3)$], 16.1 [$N(CH_2CH_3)_2$], 12.3 (C_5Me_5). − EI MS (70 eV); *m/z* (%): 523 (3) [M$^+$ − $NHEt_2$], 448 (17) [M$^+$ − 2$NHEt_2$], 313 (7) [M$^+$ − 2 $NHEt_2$ − Cp*]. − $C_{32}H_{60}N_4Ti_2$ (596.65): calcd. C 64.42, H 10.14, N 9.39; found: C 64.00, H 10.24, N 8.42.

Synthesis of $[\{Cp^*Ti\}_2(NMe_2)(NHMe_2)(\mu\text{-}NMe)(\mu\text{-}N{=}CH_2)]$ (**2**): As for compound **1**, a hexane solution (40 ml) of 1.00 g (3.17 mmol) of $[Cp^*Ti(NMe_2)_3]$ was heated in an autoclave at 150°C for 8 d. The solution was cooled at −40°C for 1 d to yield dark-green crystals of **2**. After washing with hexane (20 ml) and drying under vacuum, 0.52 g (64%) of the complex **2** was isolated. − IR (KBr): $\tilde{\nu}$ = 1437 cm^{-1}s, 1373 s, 1304 m, 1233 m, 1131 s, 1023 m, 930 s, 902 m, 787 s, 638 m, 595 s, 518 s, 460 m, 350 m. − ^1H NMR (C_6D_6, 20°C): δ = 4.54 (s, 3 H, μ-N*Me*), 4.01 (spt, 1 H, N*H*Me$_2$), 3.81 (s, 1 H, NC*H*H), 3.79 (s, 1 H, NCH*H*), 2.22 (br., 3 H, N*Me*Me), 2.05 (br., 3 H, NMe*Me*), 2.04 (s, 15 H, C_5Me_5), 1.94 (s, 15 H, C_5Me_5), 1.70 (d, ^3J = 6.0 Hz, 3 H, NH*Me*Me), 1.61 (d, ^3J = 6.0 Hz, 3 H, NHMe*Me*). − $^{13}C\{^1H\}$ NMR (C_6D_6, 20°C): δ = 115.4 and 114.8 (C_5Me$_5$), 100.8 (N=*C*H$_2$), 50.6 (μ-N*Me*), 44.6 and 42.0 (br. s, N*Me$_2$*), 39.0 and 38.9 (NH*Me$_2$*), 11.5 and 11.3 (C_5Me_5). − EI MS (70 eV); *m/z* (%): 467 (51) [M^+ − NHMe$_2$], 448 (29) [M^+ − 2 NHMe$_2$]. − $C_{26}H_{48}N_4Ti_2$ (512.49): calcd. C 60.94, H 9.44, N 10.93; found C 61.18, H 9.34, N 10.87.

Synthesis of $[\{Cp^*TiCl\}_2(\mu\text{-}NMe)_2]$ (**3**): After heating 1.06 g (3.46 mmol) of $[Cp^*Ti(NMe_2)_2Cl]$ in toluene (25 ml) at 200°C for 6 d, the resulting solution was left at room temp. affording a first portion of red crystals of **3**, which were collected by filtration. A second portion of crystals was obtained from the filtrate after cooling at −40°C. The combined yield of the imido complex **3** was 0.54 g (63%). − IR (KBr): $\tilde{\nu}$ = 1488 cm^{-1} m, 1427 s, 1377 s, 1107 vs, 1024 m, 785 vs, 730 m, 581 vs, 521 m, 444 s, 407 m, 357 m, 314 m. − ^1H NMR (C_6D_6, 20°C): δ = 3.41 (s, 6 H, μ-N*Me*), 1.98 (s, 30 H, C_5Me_5). − $^{13}C\{^1H\}$ NMR (C_6D_6, 20°C): δ = 124.1 (C_5Me$_5$), 48.6 (μ-N*Me*), 11.4 (C_5Me_5). − EI MS (70 eV); *m/z* (%): 495 (19) [M^+], 465 (100) [M^+ − 2 Me], 360 (37) [M^+ − Cp*], 330 (52) [M^+ − 2 Me − Cp*]. − $C_{22}H_{36}Cl_2N_2Ti_2$ (495.25): calcd. C 53.36, H 7.33, N 5.66; found C 53.10, H 7.42, N 5.71.

Synthesis of $[\{Cp^*_3Ti_3(NMe_2)(\mu\text{-}\eta^2\text{-}CH_2NMe)\}(\mu\text{-}O)_3]$ (**4**): In a similar procedure, 1.04 g (1.43 mmol) of $[\{Cp^*Ti(NMe_2)\}_3(\mu\text{-}O)_3]$ in 70 ml of toluene was heated at 110°C for 17 d to give a dark solution. Red crystals of complex **4** were obtained when the solution was allowed to cool to room temp. Other fractions of the product were collected by concentration to half of the initial volume and cooling at −40°C for 5 d. The combined yield was 0.62 g (63%). − IR (KBr): $\tilde{\nu}$ = 1438 cm^{-1} s, 1372 s, 1235 s, 1172 m, 1074 m, 956 s, 717 vs, 681 s, 645 s, 617 s, 567 m, 402 vs. − ^1H NMR (C_6D_6, 20°C): δ = 2.97 (s, 6 H, N*Me$_2$*), 2.86 and 1.82 (AB spin system, ^2J = 5.9 Hz, 2 H, C*H$_2$*NMe), 2.71 (s, 3 H, CH$_2$N*Me*), 2.01 (s, 15 H, C_5Me_5), 1.98 (s, 15 H, C_5Me_5), 1.91 (s, 15 H, C_5Me_5). − $^{13}C\{^1H\}$ NMR (C_6D_6, 20°C): δ = 120.1, 118.7 and 118.5 (C_5Me$_5$), 87.9 (*C*H$_2$NMe), 48.5 (N*Me$_2$*), 48.2 (CH$_2$N*Me*), 11.7, 11.4 and 11.1 (C_5Me_5). − EI MS (70 eV); *m/z* (%): 639 (9) [M^+ − NHMe$_2$], 625 (67) [M^+ − NMe$_3$], 611 (90) [M^+ − NMe$_2$ − C_2H_5], 596 (76) [M^+ − NHMe$_2$ − NC$_2$H$_5$], 477 (84) [M^+ − NMe$_2$ − C_2H_4 − Cp*], 341 (63) [M^+ − NMe$_2$ − C_2H_4 − 2 Cp*], 206 (58) [M^+ − NMe$_2$ − C_2H_4 − 3 Cp*]. − $C_{34}H_{56}N_2O_3Ti_3$ (684.53): calcd. C 59.66, H 8.25, N 4.09; found C 58.83, H 8.19, N 4.09.

Synthesis of $[\{\eta^5{:}\eta^1\text{-}C_5Me_4CH_2CH_2NMe\}TiCl_2]$ (**5**): Heating for 15 d at 200°C 2.06 g (6.91 mmol) of $[Cp^*Ti(NMe_2)Cl_2]$ in 50 ml of toluene afforded a dark-red solution. The volatiles were removed under vacuum to give a dark red solid. All attempts to obtain a pure fraction of **5** failed and it could be characterised only by NMR spectroscopy. − ^1H NMR (C_6D_6, 20°C): δ = 3.88 (m, 2 H, NC*H$_2$*), 3.37 (m, 3 H, N*Me*), 2.66 (m, 2 H, C$_5$Me$_4$C*H$_2$*), 1.97 (s, 6 H, C$_5$*Me$_4$*), 1.82 (s, 6 H, C$_5$*Me$_4$*). − $^{13}C\{^1H\}$ NMR (C_6D_6, 20°C): δ = 139.7, 133.9 and 125.6 (C_5Me$_4$), 79.4 (N*C*H$_2$), 45.7 (N*Me*), 24.4 (C$_5$Me$_4$*C*H$_2$), 12.9 and 12.6 (C$_5$*Me$_4$*).

Synthesis of $[\{\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2N(Me)CN(C_6H_3Me_2)\}TiCl_2]$ (**6**): 0.45 g (3.43 mmol) of 2,6-$Me_2C_6H_3NC$ was added to the solution obtained in the thermal decomposition of 1.00 g (3.35 mmol) of $[Cp^*Ti(NMe_2)Cl_2]$ in 40 ml of toluene. Strong magnetic stirring overnight at room temp., followed by slow deposition during 1 d, afforded an orange powder and a red solution. After filtration, the orange solid was washed with hexane (2 × 20 ml) and dried under vacuum to yield 0.40 g (28% with respect to the initial $[Cp^*Ti(NMe_2)Cl_2]$) of compound **6**. − IR (KBr): $\tilde{\nu}$ = 3065 cm^{-1} w, 2952 m, 2917 s, 1668 vs, 1587 m, 1467 s, 1422 s, 1378 s, 1326 m, 1238 m, 1206 m, 814 m, 771 s, 679 m, 447 m, 405 m, 379 m, 298 m. − ^1H NMR ($CDCl_3$, 20°C): δ = 7.00 (m, 3 H, C$_6$*H$_3$*Me$_2$), 3.82 (m, 2 H, NC*H$_2$*), 3.05 (m, 2 H, C$_5$Me$_4$C*H$_2$*), 2.85 (m, 3 H, N*Me*), 2.18 (s, 6 H, C$_5$*Me$_4$*), 2.04 (s, 6 H, C$_6$H$_3$*Me$_2$*), 1.78 (s, 6 H, C$_5$*Me$_4$*). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20°C): δ = 197.2 (*C*N), 142.9, 132.2, 128.0 and 125.5 (C_6H$_3$Me$_2$), 128.9, 125.4 and 123.4 (C_5Me$_4$), 56.3 (N*C*H$_2$), 35.9 (N*Me*), 25.4 (C$_5$Me$_4$*C*H$_2$), 19.5 (C$_6$H$_3$*Me$_2$*), 13.0 and 12.4 (C$_5$*Me$_4$*). − EI MS (70 eV); *m/z* (%): 426 (4) [M^+], 295 (17) [$\{(C_5Me_4CH_2CH_2NMe)TiCl_2\}^+$], 252 (100) [$\{(C_5Me_4CH_2)TiCl_2\}^+$], 216 (35) [$\{(C_5Me_3(CH_2)_2)TiCl\}^+$].− $C_{21}H_{28}Cl_2N_2Ti$ (427.27): calcd. C 59.04, H 6.61, N 6.56; found C 59.20, H 6.37, N 6.93.

X-ray Structure Determination of **6**: An orange block of **6** crystallised from hexane at room temp. and was mounted in a glass capillary in a random orientation on an automatic Enraf-Nonius Cad-4 four-circle diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Crystallographic and experimental details of **6** are summarised in Table 2. Intensities were corrected for Lorentz and polarisation effects in the usual manner. No absorption or extinction corrections were made. Intensity measurements were performed by ω-2θ scans in the range 6° < 2θ < 50°.

Table 2. Crystal and X-ray structural analysis data for the compound $[\{\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2N(Me)CN(C_6H_3Me_2)\}TiCl_2]$ (**6**)

Empirical formula	$C_{21}H_{28}Cl_2N_2Ti$
Formula weight	427.25
Temperature	293(2) K
Crystal system	orthorhombic
Space group	*Pbca*
a, *b*, *c* [Å]	14.780(3), 16.059(3), 18.356(4)
V [Å^3], *Z*	4357(2), 8
Density (calculated)	1.303 g/cm^3
μ (Mo-K_α)	0.645 mm^{-1}
F(000)	1792
Crystal size	0.38 × 0.35 × 0.19 mm
Index ranges	$0 < h < 17, -19 < k < 0, 0 < l < 21$
Reflections collected	3904
Independent reflections	3834 (R_{int} = 0.0228)
Observed reflections [$I > 2\sigma(I)$]	1924
Data/restraints/parameters	3827/0/235
Goodness-of-fit on F^2	1.029
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.069$, $wR2 = 0.166$
R indices (all data)	$R1 = 0.200$, $wR2 = 0.260$
Largest diff. peak and hole	0.382 and −0.377 eÅ^{-3}

The structure was solved by direct methods (SHELXS-90)[27] and refined by least squares against F^2 (SHELXL-93).[28] Of the 3904 measured reflections, 3834 were independent; $R1 = 0.069$ and $wR2 = 0.166$ [for 1924 reflections with $F > 4\sigma(F)$]. The values of $R1$ and $wR2$ are defined as $R1 = \Sigma||F_o| - |F_c||/[\Sigma|F_o|]$; $wR2 = \{[\Sigma w(F_o{}^2$

− $F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.114P)^2 + 15.092P]$, $P = (F_o^2 + 2F_c^2)/3$ and σ was obtained from counting statistics. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced in the last cycle of refinement from geometrical calculations and refined using a riding model with thermal parameters fixed at $U = 0.08$ Å^2.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101283. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44(0)1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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