Dialkylamido derivatives of [(η⁵-C₅Me₅)TiCl₃], [{(η⁵-C₅Me₅)TiCl₂}₂(μ-O)] and [{(η⁵-C₅Me₅)TiCl}₃(μ-O)₃]: X-ray crystal structure of [(η⁵-C₅Me₅)Ti(NMe₂)₃]

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Abstract

Reactions of [(η⁵-C₅Me₅)TiCl₃] with dialkyl and diarylamido-lithium complexes in 1:1, 1:2 or 1:3 molar ratios afford the mono(pentamethylcyclopentadienyl)titanium(IV) dialkylamido-complexes [(η⁵-C₅Me₅)TiCl₃₋ₙ(NR₂)ₙ] (*n* = 1; R = Me or SiMe₃) (*n* = 2, R = Me or Ph) (*n* = 3, R = Me or Et). Similar reactions of [{(η⁵-C₅Me₅)TiCl₂}₂(μ-O)] and [{(η⁵-C₅Me₅)TiCl}₃(μ-O)₃] gave the corresponding complexes [{(η⁵-C₅Me₅)TiCl₂₋ₙ(NR₂)ₙ}₂(μ-O)] (*n* = 1; R = Me or Ph) (*n* = 2, R = Me) and [(η⁵-C₅Me₅)₃Ti₃Cl₃₋ₙ(NMe₂)ₙ(μ-O)₃] (*n* = 1 or 3). The crystal structure of [(η⁵-C₅Me₅)Ti(NMe₂)₃] has been established by X-ray crystallography and is shown to be monomeric with the typical three-legged piano-stool structure.

Key words: Titanium; Amide; Oxide

1. Introduction

We are carrying out an investigation into the chemistry of mono(pentamethylcyclopentadienyl)titanium (IV) derivatives, and have previously reported a series of alkyls, oxides, carboxylates and alkoxides [1]. These compounds can be considered formally as 12-electron species, and the presence of strong Ti–O, Ti ⋯ C–C or Ti ⋯ H–C interactions in the coordination sphere of the metal helps to stabilize these systems. The utilization of amido ligands, isoelectronic with alkyl and alkoxide groups with the possibility of M–NR₂ π

bonding, may be an alternative method of stabilization and prompted us to investigate the reactivity of some of the halo compounds that have been reported previously [2] with amido-lithium complexes.

Many dialkyl- and diaryl-amido complexes have been reported [3], but there are only a few examples of mono(cyclopentadienyl)titanium(IV) complexes [4,5]. In this paper the synthesis and spectroscopic properties of several mono-, di- and trinuclear mono(pentamethylcyclopentadienyl)titanium(IV) amides are described. We also describe the X-ray structure determination of [(η⁵-C₅Me₅)Ti(NMe₂)₃].

2. Results and discussion

Amidohalo(pentamethylcyclopentadienyl)titanium complexes can be prepared easily by anion exchange
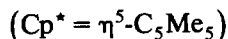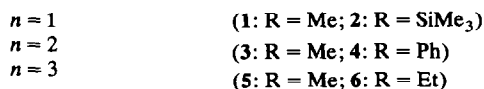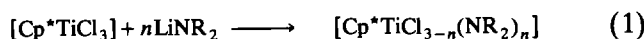

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[†] In memory of Professor Ricardo Serrano who died on January 30, 1992 and whom we remember with affection.

TABLE 1. ^{1}H and ^{13}C{^{1}H} NMR data of the new compounds [a,b]

Compound		δ (ppm)	
		^{1}H NMR	^{13}C NMR
[Cp*TiCl₂(NMe₂)]	1	1.87 (s, 15H, C₅Me₅)	12.7 (s, C₅Me₅)
		3.19 (s, 6H, NMe₂)	49.3 (s, NMe₂)
			128.4 (s, C₅Me₅)
[Cp*TiCl₂{N(SiMe₃)₂}]	2	1.95 (s, 15H, C₅Me₅)	6.4 (s, SiMe₃)
		0.38 (s, 18H, SiMe₃)	13.5 (s, C₅Me₅)
			131.1 (s, C₅Me₅)
[Cp*TiCl(NMe₂)₂]	3	1.90 (s, 15H, C₅Me₅)	11.7 (s, C₅Me₅)
		3.08 (s, 12H, NMe₂)	47.5 (s, NMe₂)
			122.0 (s, C₅Me₅)
[Cp*TiCl(NPh₂)₂]	4	1.74 (s, 15H, C₅Me₅)	12.8 (s, C₅Me₅)
		6.80–6.87 (m, 4H, Ph)	124.4 (s, p-Ph)
		6.97–7.10 (m, 16H, Ph)	125.5 (s, o-Ph)
			128.5 (s, m-Ph)
			129.5 (s, C₅Me₅)
			155.4 (s, ipso-Ph)
[Cp*Ti(NMe₂)₃]	5	1.95 (s, 15H, C₅Me₅)	11.9 (s, C₅Me₅)
		3.09 (s, 18H, NMe₂)	48.5 (s, NMe₂)
			118.4 (s, C₅Me₅)
[Cp*Ti(NEt₂)₃]	6	2.00 (s, 15H, C₅Me₅)	12.5 (s, C₅Me₅)
		3.67 (c, 12H, $^3J_{HH}$ = 7 Hz, Et)	15.3 (s, NEt₂)
		1.04 (t, 18H, Et)	48.9 (s, NEt₂)
			118.7 (s, C₅Me₅)
[{Cp*TiCl(NMe₂)}₂(μ-O)]	7	1.98 (s, 30H, C₅Me₅)	11.4 (s, C₅Me₅) [c]
		3.11 (s, 12H, NMe₂)	47.7 (s, NMe₂)
			123.9 (s, C₅Me₅)
[{Cp*TiCl(NPh₂)}₂(μ-O)]	8	1.79 (s, 30H, C₅Me₅)	12.8 (s, C₅Me₅)
		6.80–6.97 (m, 4H, Ph)	123.6 (s, p-Ph)
		7.05–7.23 (m, 16H, Ph)	126.2 (s, o-Ph)
			128.6 (s, m-Ph)
			129.7 (s, C₅Me₅)
			156.1 (s, ipso-Ph)
[{Cp*Ti(NMe₂)₂}₂(μ-O)]	9	1.98 (s, 30H, C₅Me₅)	11.6 (s, C₅Me₅)
		3.13 (s, 24H, NMe₂)	49.0 (s, NMe₂)
			119.0 (s, C₅Me₅)
[{Cp*₃Ti₃Cl₂(NMe₂)}(μ-O)₃]	10	2.13 (s, 15H, C₅Me₅)	11.5 (s, C₅Me₅)
		2.11 (s, 15H, C₅Me₅)	12.2 (s, C₅Me₅)
		1.97 (s, 15H, C₅Me₅)	12.4 (s, C₅Me₅)
		3.02 (s, 6H, NMe₂)	46.4 (s, NMe₂)
			122.2 (s, C₅Me₅)
			126.2 (s, C₅Me₅)
			126.4 (s, C₅Me₅)
[{Cp*Ti(NMe₂)}₃(μ-O)₃]	11	2.05 (s, 30H, C₅Me₅)	11.2 (s, C₅Me₅)
		2.02 (s, 15H, C₅Me₅)	11.3 (s, C₅Me₅)
		3.15 (s, 6H, NMe₂)	49.2 (s, NMe₂)
		3.03 (s, 12H, NMe₂)	50.5 (s, NMe₂)
			119.4 (s, C₅Me₅)
			120.5 (s, C₅Me₅)

[a] δ is relative to the solvent.

[b] Spectra recorded in benzene-d_6 at 20°C unless stated otherwise.

[c] Spectra recorded in chloroform-d_1.

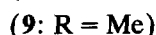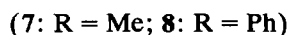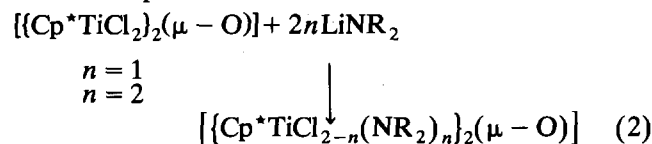reactions involving stoichiometric amounts of lithium amides

$$[Cp^*TiCl_3] + n\text{LiNR}_2 \longrightarrow [Cp^*TiCl_{3-n}(NR_2)_n] \quad (1)$$

$n = 1$ (1: R = Me; 2: R = SiMe₃)
$n = 2$ (3: R = Me; 4: R = Ph)
$n = 3$ (5: R = Me; 6: R = Et)

$$(Cp^* = \eta^5\text{-}C_5Me_5)$$

With bulky groups such as $N(SiMe_3)_2$ and NPh_2, only monosubstitution and disubstitution occur at room temperature, even when an excess of lithium amide was added.

In all the products the IR spectra show the characteristic frequencies of the Cp* groups [6]: 1477, 1421, 1374, 1015–1030, 1005, 772–800 cm⁻¹. The Ti–N stretching vibrations are in the range 500–600 cm⁻¹, consistent with reported values [7], except for 2 where it appears at 424 cm⁻¹, a value similar to that found for [TiCl{N(SiMe₃)₂}₃] [8].

The ¹H NMR spectra of 1–6 in C_6D_6 show only one Cp* resonance, and the corresponding signals for R. All the complexes are monomeric in the solid state, as shown by X-ray crystallography for 5, and in the gas phase, as indicated by mass spectrometry. The ¹³C NMR spectra show features consistent with the ¹H NMR spectra (Table 1). For 1, 3 and 5, the signal corresponding to the ring carbon atoms of Cp* is shifted progressively upfield with the higher degree of halide replacement. A similar effect is observed for the dinuclear compounds 7 and 9, and for the trinuclear derivatives 10 and 11.

[{Cp*TiCl₂}₂(μ-O)], like [Cp*TiCl₃], can also yield amido complexes

$$[\{Cp^*TiCl_2\}_2(\mu - O)] + 2n\text{LiNR}_2$$

$n = 1$
$n = 2$

$$[\{Cp^*TiCl_{2-n}(NR_2)_n\}_2(\mu - O)] \quad (2)$$

(7: R = Me; 8: R = Ph)

(9: R = Me)

For R = Me, both mono and disubstituted derivatives were isolated but with an excess of $LiNPh_2$, only monosubstitution at each metal was observed, probably owing to the bulk of the phenyl groups.

Similarly, we have carried out the reaction of [{Cp*TiCl}₃(μ-O)₃] with an excess of $LiNMe_2$ under different conditions:

$$[\{Cp^*TiCl\}_3(\mu\text{-}O)_3]$$
$$+ \quad \xrightarrow{\text{Room temperature}}$$
LiNMe₂ (excess) $\longrightarrow$ [{Cp*₃Ti₃Cl₂(NMe₂)}(μ-O)₃]   (3)

10

$$\xleftarrow{\quad 60°C \quad}$$

$\longrightarrow$ [{Cp*Ti(NMe₂)}₃(μ-O)₃]   (4)

11
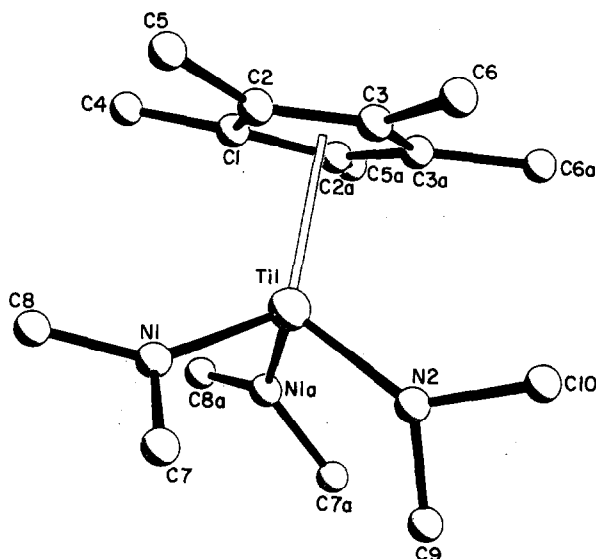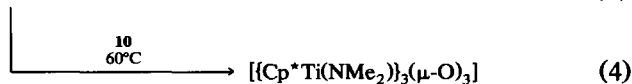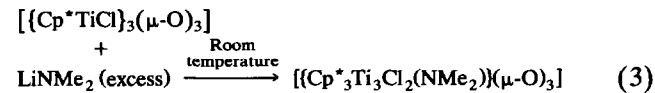

Fig. 1. Structure of 5. Disordered atoms omitted for clarity.

As shown in eqn. (3), only one chlorine is substituted when the reaction is carried out at room temperature but, at 60°C, three dimethylamido groups can be introduced (eqn. (4)). Attempts to isolate the disubstituted derivative were unsuccessful, and we obtained only mixtures of different substitution products.

All the new compounds (7–11) were characterized by IR, ¹H and ¹³C NMR spectroscopy, and relevant data are presented in Table 1.

2.1. X-ray structure of [Cp*Ti(NMe₂)₃] (5)

The molecular structure of 5 is shown in Fig. 1, the final atomic coordinates for the non-hydrogen atoms are presented in Table 2, and selected bond distances

TABLE 2. Atomic coordinates (×10⁴) for 5

	x	y	z	Site occupancies (%)
Ti(1)	0	2364(2)	3831(1)	50
N(1)	1015(6)	2468(10)	4296(3)	100
N(2)	0	465(14)	3713(5)	50
C(1)	0	4545(14)	3466(7)	50
C(2)	821(8)	3871(14)	3261(5)	100
C(3)	475(8)	2900(13)	2960(4)	100
C(4)	0	5835(21)	3762(8)	50
C(5)	1804(10)	4302(18)	3295(7)	100
C(6)	1074(12)	1974(19)	2633(6)	100
C(7')	1991(25)	2301(36)	4231(14)	40
C(7)	1610(24)	1319(37)	4410(15)	60
C(8)	1416(23)	3539(32)	4544(13)	60
C(8')	942(26)	2874(37)	4836(14)	40
C(9)	−490(22)	−417(33)	4082(14)	50
C(10)	0	−432(42)	3249(17)	30
C(10')	−587(42)	−447(56)	3361(23)	20

TABLE 3. Selected bond distances (Å) and angles (°) for 5

Ti(1)–N(1)	1.912(9)	Ti(1)–C(1)	2.385(15)
Ti(1)–N(2)	1.923(14)	Ti(1)–C(2)	2.439(13)
Ti(1)–Cp ᵃ	2.132	Ti(1)–C(3)	2.471(11)
N(1)–Ti(1)–N(2)	99.2(4)	Cp–Ti(1)–N(1)	119.4
N(1)–Ti(1)–N(1A)	99.1(5)	Cp–Ti(1)–N(2)	116.5

ᵃ Cp is the centroid of the C₅Me₅ ring.

and angles are given in Table 3. The compound is monomeric and has a classical three-legged piano-stool structure with a symmetry plane defined by Ti(1)–N(2)–Cp*(centroid). The Cp(centroid)–Ti–substituent angles vary from 119.4° for N(1) to 116.5° for N(2); the angles formed by the legs are 99.1(5)° and 99.2(4)°. The N(1), N(2), N(1A) plane is essentially parallel to the Cp* plane (dihedral angle, 1.6°). The distances from titanium to cyclopentadienyl ring carbon atoms are in the normal range [1].

Distances from titanium to N(1), 1.912(9) Å, and to N(2), 1.923(14) Å, are similar to those found in the literature [9] and shorter than the theoretically calculated Ti–N distance, 1.981 Å [3,10]. This leads us to propose a pπ → dπ interaction between the nitrogen atoms and the metal centre.

3. Experimental details

All reactions were carried out under argon by Schlenk techniques. Hexane was refluxed over Na/K amalgam, toluene over sodium, and both distilled under argon. The lithium amides were prepared from the corresponding amines (freshly distilled) and n-butyllithium in hexane except LiNMe₂, purchased from Aldrich and used without further purification. [Cp*TiCl₃], [{Cp*TiCl₂}₂(μ-O)] and [{Cp*TiCl}₃(μ-O)₃] were prepared by published procedures [2,11]. IR spectra were measured on a Perkin–Elmer 883 spectrophotometer using Nujol mulls between CsI disks. ¹H and ¹³C NMR spectra were recorded on a Varian Unity 300 MHz spectrometer. Electron impact mass spectroscopy was carried out at 70 eV with a Hewlett–Packard 5988 spectrometer. C, H and N analysis was carried out with a Perkin–Elmer 240B microanalyser.

3.1. [Cp*TiCl₂(NMe₂)] (1)

A suspension of 0.80 g (2.70 mmol) of [Cp*TiCl₃] and 0.16 g (3.14 mmol) of LiNMe₂ was stirred in 100 ml of hexane for 15 h and then filtered; the reddish solution was concentrated to half its volume and allowed to cool at about −40°C for 24 h. Red crystals of 1 were isolated with a 92% yield. Anal. Found: C, 47.96; H, 6.85; N, 4.50. C₁₂H₂₁Cl₂NTi calc.: C, 48.35;

H, 7.10; N, 4.70%. MS: m/e (assignment, rel. int. (%)) 298 (M⁺, 7), 253 ((M − NHMe₂)⁺, 39), 216 ((M − NHMe₂ − Cl − H)⁺, 23). IR: 1246w, 1132w, 1040w, 1023m, 904m, 788vs, 585w, 449s, 359s cm⁻¹.

3.2. [Cp*TiCl₂(N(SiMe₃)₂)] (2)

Hexane (40 ml) was added to a mixture of [Cp*TiCl₃] (0.40 g, 1.38 mmol) and LiN(SiMe₃)₂ (0.23 g, 1.37 mmol). After stirring at room temperature for 2 days, the mixture was filtered and the volatile products were removed in vacuo. The oily red solid was washed with several portions of cold pentane to yield 0.40 g (70%) of 2. Anal. Found: C, 46.15; H, 7.95; N, 3.25. C₁₆H₃₃Cl₂NSi₂Ti calc.: C, 46.37; H, 8.03; N, 3.38%. MS: m/e (assignment, rel. int. (%)) 414 (M⁺, 5), 398 ((M − CH₄)⁺, 41), 262 ((M − CH₄ − Cp*H)⁺, 46), 73 ((SiMe₃)⁺, 33). IR: 1249s, 1150w, 1070w, 1015w, 842vs, 797s, 424s, 379s, 349m cm⁻¹.

3.3. [Cp*TiCl(NMe₂)₂] (3)

The method used to prepare 1 was followed using 0.40 g (1.38 mmol) of [Cp*TiCl₃] and 0.15 g (2.94 mmol) of LiNMe₂ in hexane (50 ml). Red crystals of 3 were obtained with a 92% yield. Anal. Found: C, 54.53; H, 8.70; N, 8.92. C₁₄H₂₇ClN₂Ti calc.: C, 54.82; H, 8.87; N, 9.13%. MS: m/e (assignment, rel. int. (%)) 307 (M⁺, 22), 261 ((M − NHMe₂)⁺, 43), 218 ((M − 2NMe₂)⁺, 100). IR: 1241m, 1135m, 1049m, 1024w, 950s, 925s, 790vs, 572s, 434m, 399m, 365m cm⁻¹.

3.4. [Cp*TiCl(NPh₂)₂] (4)

Hexane (60 ml) was added to a mixture of [Cp*TiCl₃] (0.35 g, 1.21 mmol) and LiNPh₂ (0.42 g, 2.40 mmol). After stirring overnight, the dark-red solution was filtered. Concentration to about 15 ml followed by cooling to −40°C for 20 h afforded red crystals of 4 with a 91% yield (0.61 g). Anal. Found: C, 72.71; H, 6.24; N, 5.34. C₃₄H₃₅ClN₂Ti calc.: C, 73.58; H, 6.35; N, 5.05% MS: m/e (assignment, rel. int. (%)) 555 (M⁺, 4), 386 ((M − NHPh₂)⁺, 100), 217 ((M − 2NHPh₂)⁺, 16). IR: 1586vs, 1222vs, 1180s, 1162vs, 1071s, 1025m, 932s, 873s, 772s, 748vs, 696vs, 505s, 419m, 365 cm⁻¹.

3.5. [Cp*Ti(NMe₂)₃] (5)

This was prepared similarly to 1 from 2.00 g (6.91 mmol) of [Cp*TiCl₃] and 1.16 g (22.73 mmol) of LiNMe₂ in hexane (100 ml). Red crystals of 5 were obtained with a 95% yield. Anal. Found: C, 60.66; H, 10.11; N, 12.95. C₁₆H₃₃N₃Ti calc.: C, 60.94; H, 10.55; N, 13.32%. MS: m/e (assignment, rel. int. (%)) 315 (M⁺, 21), 270 ((M − NHMe₂)⁺, 51), 225 ((M − 2NHMe₂)⁺, 50), 180 ((M − 3NHMe₂)⁺, 93). IR: 1233s, 1137s, 1046m, 1020w, 944vs, 779vs, 562vs, 416vs cm⁻¹.

3.6. [Cp*Ti(NEt₂)₃] (6)

Hexane (50 ml) was added to a mixture of [Cp*TiCl₃] (0.40 g, 1.38 mmol) and LiNEt₂ (0.36 g, 4.55 mmol). After stirring at room temperature for 10 h, the mixture was filtered and the volatile products were removed *in vacuo*. The oily dark-red solid was washed with several portions of cold pentane to yield 0.53 g (96%) of 6. Anal. Found: C, 66.28; H, 11.40; N, 10.35. C₂₂H₄₅N₃Ti calc.: C, 66.14; H, 11.35; N, 10.52%. MS: *m/e* (assignment, rel. int. (%)) 399 (M⁺, 11), 326 ((M − NHEt₂)⁺, 24), 253 ((M − 2NHEt₂)⁺, 12). IR: 1176w, 1144m, 1089w, 1030w, 1002s, 872s, 795s, 590s, 405s cm⁻¹.

3.7. [{Cp*TiCl(NMe₂)}₂(μ-O)] (7)

A suspension of 0.40 g (0.76 mmol) of [Cp*TiCl₂]₂ (μ-O) and 0.08 g (1.57 mmol) of LiNMe₂ was stirred overnight in 60 ml of toluene and then filtered; the reddish solution was concentrated to about 10 ml and allowed to cool at −40°C for 24 h. Red crystals of 7 were isolated with a 75% yield. Anal. Found: C, 52.95; H, 7.67; N, 5.02. C₂₄H₄₂Cl₂N₂OTi₂ calcd.: C, 53.26; H, 7.82; N, 5.17%. MS: *m/e* (assignment, rel. int. (%)) 497 [(M − NHMe₂)⁺, 17), 452 [(M − 2NHMe₂)⁺, 100), 317 [(M − 2NHMe₂ − Cp*)⁺, 79). IR: 1243m, 1148m, 1058w, 1024w, 945s, 779s, 745vs, 570s, 430s, 405m, 364s, 319m cm⁻¹.

3.8. [{Cp*TiCl(NPh₂)}₂(μ-O)] (8)

Toluene (100 ml) was added to a mixture of [{Cp*TiCl₂}₂(μ-O)] (1.00 g, 1.91 mmol) and LiNPh₂ (0.70 g, 4.00 mmol). After stirring at room temperature for 3 days, the mixture was filtered, concentrated to about 30 ml and allowed to cool at −30°C for 24 h. The yield of the red microcrystalline 8 was 73%. Anal. Found: C, 66.67; H, 6.20; N, 3.34. C₄₄H₅₀Cl₂N₂OTi₂ calc.: C, 66.93; H, 6.38; N, 3.55%. MS: *m/e* (assignment, rel. int. (%)) 620 ((M − NHPh₂)⁺, 100), 452 ((M − NHPh₂ − NPh₂)⁺, 56). IR: 1586s, 1239s, 1187m, 1168m, 1075m, 1024m, 916m, 862s, 791m, 715vs, 500s, 426s, 375s cm⁻¹.

3.9. [{Cp*Ti(NMe₂)₂}₂ (μ − O)] (9)

This was prepared similarly to 7 from 0.17 g (3.33 mmol) of LiNMe₂ and 0.40 g (0.76 mmol) of [{Cp*TiCl₂}₂ (μ-O)]. The orange crystals of 9 were obtained with a 87% yield. Anal. Found: C, 59.95; H, 9.65; N, 9.85. C₂₈H₅₄N₄OTi₂ calc.: C, 60.21; H, 9.74; N, 10.03%. MS: *m/e* (assignment, rel. int. (%)) 558 (M⁺, 12), 513 ((M − NHMe₂)⁺, 4), 423 ((M − Cp*)⁺, 100), 288 ((M − 2Cp*)⁺, 94). IR: 1235s, 1148s, 1049m, 1020w, 950vs, 789s, 735vs, 415s cm⁻¹.

3.10. [{Cp*₃Ti₃Cl₂(NMe₂)}(μ-O)₃] (10)

Hexane (100 ml) was added to a mixture of [{Cp*TiCl}₃(μ-O)₃] (0.88 g, 1.25 mmol) and LiNMe₂ (0.10 g, 1.96 mmol). After stirring at room temperature for 3 days, the dark-red solution was filtered. Concentration to about 20 ml followed by cooling to −30°C for 20 h afforded red crystals of 10 with a 82% yield (0.73 g). Anal. Found: C, 53.43; H, 7.42; N, 1.80. C₃₂H₅₁Cl₂NO₃Ti₃ calc.: C, 53.96; H, 7.22; N, 1.96%. MS: *m/e* (assignment, rel. int. (%)) 667 ((M − NHMe₂)⁺, 4), 576 ((M − Cp*H)⁺, 13), 531 ((M − NHMe₂ − Cp*H)⁺, 25), 395 ((M − NHMe₂ − 2Cp*H)⁺, 22), 262 ((M − NHMe₂ − 3Cp*)⁺, 22). IR: 1244w, 1144m, 1054w, 1022w, 947s, 750vs, 571m, 440vs, 356s cm⁻¹.

3.11. [{Cp*Ti(NMe₂)}₃(μ-O)₃] (11)

Toluene (100 ml) was added to a mixture of [{Cp*TiCl}₃(μ-O)₃] (0.50 g, 0.71 mmol) and LiNMe₂ (0.13 g, 2.55 mmol). After stirring at 60°C for 3 days, the dark-red solution was filtered. Concentration to about 10 ml followed by cooling to −30°C for 2 days afforded red crystals of 11 with a 74% yield (0.38 g). Anal. Found: C, 59.03; H, 8.61; N, 5.63. C₃₆H₆₃N₃O₃Ti₃ calc.: 59.27; H, 8.70; N, 5.76%. MS: *m/e* (assignment, rel. int. (%)) 611 ((M − 2NMe₃)⁺, 14), 476 ((M − 2NMe₃ − Cp*)⁺, 16), 341 ((M − 2NMe₃ − 2Cp*)⁺, 27), 206 ((M − 2NMe₃ − 3Cp*)⁺, 38). IR: 1240s, 1148s, 1057m, 1023w, 956vs, 730vs, 564s, 412vs, 331vs cm⁻¹.

3.12. Crystallographic structural determination

Crystallographic and experimental details for the X-ray crystal structure determination are given in Table 4. Intensity data were collected on a Nicolet R3mV four-circle diffractometer with graphite-monochromated Mo-Kα radiation (0.71073 Å). Three check reflections were monitored periodically throughout data collection and showed no significant variations. All intensity data were corrected for Lorentz polarization effects; no absorption or extinction corrections were made. Calculations were carried out on a Viglen PC computer using the SHELXTL PLUS (PC version) [12].

The structure was solved by a combination of direct methods and Fourier difference techniques and refined by the full-matrix least-squares method with Ti, N and Cp* carbon atoms assigned anisotropic displacement parameters. The −NMe₂ groups were found to be severely positionally disordered, and each methyl carbon atom was refined in two sites with partial occupancies in the ratio 60:40. Methyl hydrogen atoms from the Cp* group were placed in idealized positions (C−H, 0.96 Å; H−C−H, 109.5°) and the methyl was allowed to refine as a rigid group. A weighting scheme, which

TABLE 4. Crystal and X-ray structural analysis data for 5

Empirical formula	$C_{16}H_{33}N_3Ti$
Molecular weight	315.4
Crystal colour	Red
Crystal habit	Prismatic
Crystal system	Orthorhombic
Space group	*Cmca*
a (Å)	14.327(3)
b (Å)	9.990(2)
c (Å)	26.585(5)
U (Å^3)	3805(2)
D_c (g cm^{-3})	1.101
μ (Mo Kα) (cm^{-1})	4.46
$F(000)$	1376
Z	8
Reflections measured	1365
Unique reflections	1317
Observed reflections [$F_o > 4\sigma(F_o)$]	692
Number of parameters refined	97
Goodness of fit	1.36
R	0.0855
R_w	0.1124
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0040F^2$

gave satisfactory agreement analyses, was introduced in the final cycles of refinement. The final converged agreement factors were $R = 0.085$, $R_w = 0.112$ and a goodness of fit of 1.36.

Acknowledgments

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