The Chemistry of Dinitrogen Residues. Part 7.† Hydrazido(1 −)- and *N,N*-Dimethylhydroxylaminato(1 −)-complexes of Titanium(IV)‡

David L. Hughes, Manuel Jimenez-Tenorio, G. Jeffery Leigh,* and David G. Walker
AFRC Institute of Plant Science Research Nitrogen Fixation Laboratory at the University of Sussex, Brighton BN1 9RQ

The crystal structures of [Ti(C_5H_5)Cl_2(NMeNMe$_2$)], [Ti(C_5H_5)Cl_2(ONMe$_2$)], [Ti(C_5H_5)Cl_2{NMeNMe(SiMe$_3$)}], and [TiCl$_2$(NMeNMe$_2$)$_2$] have been determined. They are all very similar, with the hydrazido- (or hydroxylaminato-) residue bound side-on and asymmetrically in the usual way, and an N–N (or N–O) separation indicating a single bond. Some related dithiocarbamato-derivatives have also been characterized.

We have shown in earlier papers in this series[1] how the hydrazide(1 −) anion binds side-on to titanium(IV) in the moiety Ti(η^5-C_5H_5)Cl_2. This is part of a programme to determine the bonding properties and reactivity of hydrazide ligands bound to transition elements, a study intended eventually to cover the chemistry of elements in Groups 4—6. In this paper we describe the synthesis and properties of several hydrazide(1 −) complexes, namely [Ti(C_5H_5)Cl_2(NMeNMe$_2$)] (**1**),[2] [Ti(C_5H_5)Cl_2(NEtNMe$_2$)] (**2**), [Ti(C_5H_5)Cl_2{NMeNMe(SiMe$_3$)}] (**3**), and [Ti(C_5H_5)Cl(S_2CNEt$_2$)(NPhNH$_2$)] (**4**), as well as of the first bis[hydrazide(1 −)] complex of titanium(IV), [TiCl$_2$(NMeNMe$_2$)$_2$] (**5**), and of a dimethylhydroxylaminato-complex, [Ti(C_5H_5)Cl_2(ONMe$_2$)] (**6**). The paper includes descriptions of the crystal structures of (**1**), (**3**), (**5**), and (**6**). Some of this material has been published in preliminary form.[2]

Results

The complexes (**1**)—(**3**) were obtained as air-sensitive crystals by reaction of [Ti(C_5H_5)Cl_3] with the appropriate trimethylsilylhydrazine, and complex (**6**) was synthesized by a similar route but employing Me$_2$NOSiMe$_3$. To synthesize complex (**4**), the reaction of [Ti(C_5H_5)Cl_3] and NHPhNH(SiMe$_3$) was carried out in the presence of Na(S_2CNEt$_2$), but the product was always apparently amorphous. This, and homologous complexes, could not be obtained directly from [Ti(C_5H_5)Cl_2(S_2CNEt$_2$)] and a hydrazine derivative. The formulation as a complex containing PhNNH$_2^-$ rather than PhNHNH$^-$ is by analogy with [Ti(C_5H_5)Cl_2(NH$_2$NPh)].[3] Finally, complex (**5**) was obtained by the reaction of either TiCl$_3$ or TiCl$_4$ with NMe$_2$NHMe. In the former case, this would appear to be an oxidation by the hydrazine. All the compounds are moisture-sensitive and are detailed in Table 1.

The complex [Ti(C_5H_5)Cl_2(NMeNMe$_2$)] (**1**) was obtained directly from the reaction mixture as yellow-brown crystals, and was not recrystallized. We have previously reported that the ^{1}H spectrum shows split resonances assignable to C_5H_5 and to NMe, which we rationalized in terms of two isomers,[3] containing side-on and end-on hydrazide (1 −), respectively. In addition, we had difficulty in obtaining satisfactory ^{1}H n.m.r. integrals for the number of protons involved, although our preparations were clean, as judged by microanalysis and by *X*-ray structure analysis. We have now clarified the situation by measuring the spin–lattice relaxation time (T_1) by the inversion-recovery method,[4] and we no longer believe that two isomers are involved. We showed that the T_1 values for the C_5H_5, NCH$_3$, and N(CH$_3$)$_2$ protons of [Ti(C_5H_5)Cl_2(NMeNMe$_2$)] are 19.4, 4.9, and 3.1 s, respectively. Consequently we ran proton spectra with a 100-s pulse delay, when perfectly satisfactory integrations were obtained.

We have not yet explained the splitting observed in occasional spectra. It is due neither to [Ti(C_5H_5)Cl_3] nor to NMe$_2$NHMe which could be produced from (**1**) by the action of DCl derived from the n.m.r. solvent CD$_2$Cl$_2$. The ^{1}H n.m.r. spectra of complexes (**2**) and (**3**) are entirely consistent with side-on co-ordination of hydrazide(1 −), but splittings become evident in the signals if the samples are stored where air may have access for a month or more. Side-on co-ordination was proved by an *X*-ray structure analysis of (**3**).

In view of the tendency of hydroxylaminato-ligands to bind side-on to molybdenum,[5] it seemed likely that Me$_2$NO$^-$, which is 'isoelectronic' with Me$_2$NNMe$^-$, should also bind side-on to titanium(IV) in Ti(C_5H_5)Cl_2. In fact the complex [Ti(ONEt$_2$)$_4$] has already been shown[6] to exhibit side-on co-ordination. The synthesis of (**6**) was achieved simply and cleanly by direct reaction of [Ti(C_5H_5)Cl_3] and NMe$_2$(OSiMe$_3$). However, attempts to ring the changes, using NHMe(OSiMe$_3$) and NMe(SiMe$_3$)OMe prepared *in situ* did not give satisfactory products. This does not appear to be a general pathway to hydroxylaminatotitanium(IV) compounds.

We had also wished to synthesize a titanium(III) hydrazido-(1 −)-complex, to determine whether the extra electron might not force the hydrazide into end-on binding. In fact, [{Ti(C_5H_5)Cl_2}$_2$] is inert to all our reagents. We therefore investigated the reactions of TiCl$_3$. This reacts with phenylhydrazine to give deep red or even purple products which were never characterized. The reaction of TiCl$_4$ seemed to give the same materials. In parallel reactions, TiCl$_3$ or TiCl$_4$ with NMe$_2$NHMe also gives the same product, yellow crystalline, air-sensitive [TiCl$_2$(NMeNMe$_2$)$_2$], notable for being produced even under what are presumably reducing conditions, and for being the only bis[hydrazido(1 −)]titanium complex reported to date.

Crystal Structure of Dichloro(cyclopentadienyl)(trimethylhydrazido)titanium(IV) (**1**).—The complex (Figure 1) may be regarded as a pseudo-tetrahedral array of two chlorine atoms, one cyclopentadienyl, and an NMeNMe$_2$ bound side-on to the titanium atom. The molecule contains a precise mirror plane

---

† Part 6, D. L. Hughes, G. J. Leigh, and D. G. Walker, *J. Chem. Soc., Dalton Trans.*, 1989, 1413.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Analyses and n.m.r. spectra of hydrazide and related complexes of titanium(IV)

	Colour	Analysis			^{1}H N.m.r. (δ)
		C	H	N	
(**1**) $[Ti(C_5H_5)Cl_2(NMeNMe_2)]$ *	Yellow-brown				6.48 (s, 5, C_5H_5), 3.51 (s, 3, NMe), 2.84 (s, 6, NMe_2) (CD_2Cl_2)
(**2**) $[Ti(C_5H_5)Cl_2(NEtNMe_2)]$	Yellow	41.0 (39.8)	6.0 (5.9)	10.1 (10.3)	6.61 (s, 5, C_5H_5), 4.04—3.80 (q, 2, NCH_2), 2.92 (s, 6, NMe_2), 1.41—1.22 (t, 3, CH_2CH_3) (CD_2Cl_2)
(**3**) $[Ti(C_5H_5)Cl_2\{NMeNMe(SiMe_3)\}]$	Yellow	32.0 (32.0)	3.9 (4.0)	3.9 (4.0)	6.75 (s, 5, C_5H_5)
(**4**) $[Ti(C_5H_5)Cl(S_2CNEt_2)(NPhNH_2)]$	Red	47.2 (47.6)	5.1 (5.6)	9.8 (10.4)	7.4—7.0 (m, 5, Ph), 6.58 (s, 5, C_5H_5), 4.9 (s, br, 3, NH), 3.8—3.6 (m, CH_2), 1.3—1.1 (m, CH_3) (CD_2Cl_2)
(**5**) $[TiCl_2(NMeNMe_2)_2]$	Yellow	27.5 (27.2)	6.4 (6.8)	20.2 (21.1)	3.50 (s, 6, NMe), 2.89 (s, 12, NMe_2) (CH_2Cl_2)
(**6**) $[Ti(C_5H_5)Cl_2(ONMe_2)]$	Yellow	34.5 (34.4)	4.5 (4.5)	5.7 (5.7)	6.69 (s, 5, C_5H_5), 3.13 (s, 6, Me)
(**7**) $[Ti(C_5H_5)Cl_2(S_2CNEt_2)]$	Red	36.0 (36.1)	4.8 (4.5)	4.4 (4.2)	6.81 (s, 5, C_5H_5), 3.91—3.67 (q, CH_2), 1.37—1.20 (t, CH_3)
(**8**) $[Ti(C_5H_5)Cl_2(S_2CNMePh)]$	Red	43.1 (42.6)	3.9 (3.6)	4.0 (3.8)	7.5—7.3 (m, Ph), 6.8 (s, C_5H_5), 3.7 (s, Me) (CD_2Cl_2)

* $^{13}C-\{^1H\}$ N.m.r. (in CD_2Cl_2, reference $SiMe_4$): δ 117 (C_5H_5), 46 (NMe_2), and 44 p.p.m. (NMe).

Table 2. Final atomic co-ordinates (fractional $\times 10^4$) for complex (**1**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Ti	2 323.5(6)	2 500	2 297.5(8)
Cl(1)	2 245.0(8)	754.2(6)	4 418(1)
N(3)	559(3)	2 500	−173(4)
C(31)	−255(5)	2 500	−2 485(6)
N(4)	−378(3)	2 500	1 205(5)
C(41)	−1 357(4)	1 338(3)	1 074(6)
C(51)	5 192(5)	2 500	3 359(8)
C(52)	4 672(4)	1 437(4)	2 107(6)
C(53)	3 793(3)	1 840(3)	75(5)
Cp*	4 424	2 500	1 544

Cp* is the calculated centre of the cyclopentadienyl ring.

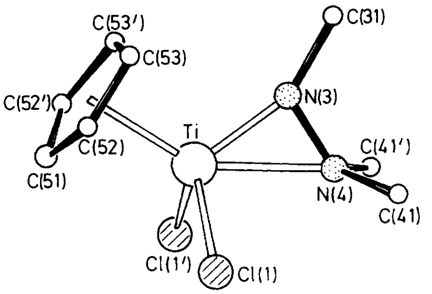


Figure 1. A view of a molecule of $[Ti(C_5H_5)Cl_2(NMeNMe_2)]$ (**1**). Note that the complexes in all the Figures have a common projection with respect to the $TiCl_2$ moiety

Table 3. Bond lengths (Å) and angles (°) with e.s.d.s in parentheses for complex (**1**)

(*a*) About the Ti atom			
Ti–Cl(1)	2.323(1)	Ti–C(51)	2.348(4)
Ti–N(3)	1.837(3)	Ti–C(52)	2.358(4)
Ti–N(4)	2.210(3)	Ti–C(53)	2.346(3)
Ti–Cp*	2.038		
Cl(1)–Ti–Cl(1')	104.0(1)	Cl(1)–Ti–Cp*	110.7
Cl(1)–Ti–N(3)	111.1(1)	N(3)–Ti–Cp*	109.2
Cl(1)–Ti–N(4)	87.7(1)	N(4)–Ti–Cp*	148.6
N(3)–Ti–N(4)	39.4(1)		
(*b*) In the ligands			
N(3)–C(31)	1.462(5)	C(51)–C(52)	1.375(5)
N(3)–N(4)	1.408(4)	C(52)–C(53)	1.379(5)
N(4)–C(41)	1.470(4)	C(53)–C(53')	1.384(7)
Ti–N(3)–C(31)	155.3(2)	N(3)–N(4)–C(41)	113.9(2)
Ti–N(3)–N(4)	84.7(2)	C(41)–N(4)–C(41')	111.9(2)
C(31)–N(3)–N(4)	119.9(1)	C(52)–C(51)–C(52')	108.4(4)
Ti–N(4)–N(3)	55.9(1)	C(51)–C(52)–C(53)	107.9(4)
Ti–N(4)–C(41)	123.2(2)	C(52)–C(53)–C(53')	107.9(3)

The primed atoms are symmetry related, at $x, \frac{1}{2} - y, z$.

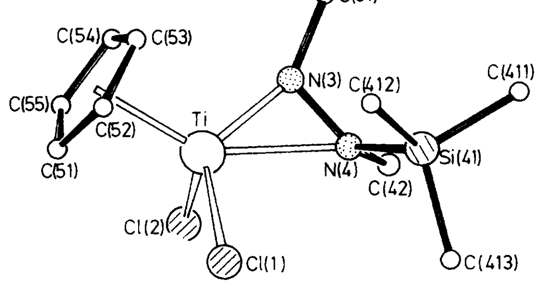


Figure 2. A view of a molecule of $[Ti(C_5H_5)Cl_2\{NMeNMe(SiMe_3)\}]$ (**3**)

passing through the Ti, N(3), N(4), and C(51) atoms, and also through the centroid of the cyclopentadienyl ring (Cp*). All intermolecular distances are equal to, or greater than, the sum of van der Waals radii. The co-ordination is very similar to that observed in other titanium(IV) hydrazido(1 −)-complexes.[1] Atomic co-ordinates are listed in Table 2, and selected bond lengths and angles in Table 3.

Crystal structure of dichloro(cyclopentadienyl)(1,2-*dimethyl*-2- *trimethylsilylhydrazido)titanium*(IV) (**3**).—The molecules in the crystal of this compound have pseudo-tetrahedral co-ordination (Figure 2), similar to that observed in (**1**). However, the presence of an $SiMe_3$ group rather than a Me on N(4) causes some distortion, as well as the loss of the mirror symmetry. The plane containing Ti, N(3), N(4), and C(51) is approximately perpendicular (*ca.* 86.4°) to the plane containing Ti, Cl(1), and Cl(2). The bulk of the $SiMe_3$ group forces Cl(1)

Table 4. Final atomic co-ordinates (fractional × 10^4), for complex (**3**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Ti	2 666(2)	983.2(4)	2 514(1)
Cl(1)	366(2)	1 681.8(6)	2 405(2)
Cl(2)	634(2)	262.6(6)	2 738(2)
N(3)	4 979(7)	949(2)	4 088(5)
C(31)	7 176(10)	858(3)	4 751(9)
N(4)	3 727(6)	1 107(2)	5 028(5)
Si(41)	4 252(3)	1 752.6(7)	5 854(2)
C(411)	6 281(13)	1 693(4)	7 633(9)
C(412)	5 206(11)	2 190(3)	4 586(9)
C(413)	1 889(13)	1 995(4)	6 240(11)
C(42)	3 412(13)	689(3)	6 053(8)
C(51)	1 833(13)	987(6)	−105(8)
C(52)	3 270(18)	1 392(4)	401(10)
C(53)	5 043(13)	1 154(4)	1 157(8)
C(54)	4 773(12)	624(4)	1 116(8)
C(55)	2 792(15)	521(4)	308(9)
Cp*	3 542	935	576

Table 5. Bond lengths (Å) and angles (°) with e.s.d.s in parentheses for complex (**3**)

(a) About the Ti atom			
Ti–Cl(1)	2.338(2)	Ti–C(51)	2.349(7)
Ti–Cl(2)	2.325(2)	Ti–C(52)	2.350(7)
Ti–N(3)	1.837(4)	Ti–C(53)	2.330(7)
Ti–N(4)	2.278(4)	Ti–C(54)	2.350(7)
Ti–Cp*	2.045	Ti–C(55)	2.383(8)
Cl(1)–Ti–Cl(2)	101.3(1)	N(3)–Ti–N(4)	38.7(2)
Cl(1)–Ti–N(3)	119.0(1)	Cl(1)–Ti–Cp*	110.6
Cl(1)–Ti–N(4)	88.0(1)	Cl(2)–Ti–Cp*	110.4
Cl(2)–Ti–N(3)	106.8(2)	N(3)–Ti–Cp*	108.4
Cl(2)–Ti–N(4)	92.8(1)	N(4)–Ti–Cp*	145.8
(b) In the ligands			
N(3)–C(31)	1.466(7)	Si(41)–C(413)	1.832(8)
N(3)–N(4)	1.425(5)	C(51)–C(52)	1.403(12)
N(4)–Si(41)	1.799(4)	C(51)–C(55)	1.352(12)
N(4)–C(42)	1.477(7)	C(52)–C(53)	1.358(10)
Si(41)–C(411)	1.853(8)	C(53)–C(54)	1.351(10)
Si(41)–C(412)	1.852(7)	C(54)–C(55)	1.374(10)
Ti–N(3)–C(31)	153.4(4)	N(4)–Si(41)–C(412)	109.4(3)
Ti–N(3)–N(4)	87.6(3)	N(4)–Si(41)–C(413)	107.7(3)
C(31)–N(3)–N(4)	119.0(5)	C(411)–Si(41)–C(412)	108.5(4)
Ti–N(4)–N(3)	53.7(2)	C(411)–Si(41)–C(413)	109.2(4)
Ti–N(4)–Si(41)	122.4(2)	C(412)–Si(41)–C(413)	113.1(4)
Ti–N(4)–C(42)	120.3(4)	C(52)–C(51)–C(55)	107.8(8)
N(3)–N(4)–Si(41)	115.8(3)	C(51)–C(52)–C(53)	106.6(8)
N(3)–N(4)–C(42)	113.9(5)	C(52)–C(53)–C(54)	109.4(8)
Si(41)–N(4)–C(42)	114.8(4)	C(53)–C(54)–C(55)	108.0(8)
N(4)–Si(41)–C(411)	108.8(3)	C(54)–C(55)–C(51)	108.2(9)

slightly towards the cyclopentadienyl ring, and this in turn is displaced slightly towards Cl(2). There are no significant intermolecular contacts. Atomic co-ordinates are listed in Table 4 and selected bond lengths and angles in Table 5.

Table 6. Final atomic co-ordinates (fractional × 10^4) for complex (**5**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Ti	1 635.4(3)	723.8(7)	2 088.0(6)
Cl(1)	2 977.6(5)	1 025(1)	2 644.7(9)
Cl(2)	1 185.5(6)	−2 137(1)	2 026.4(9)
N(3)	1 251(2)	2 076(4)	566(3)
C(31)	858(3)	3 561(6)	−191(5)
N(4)	1 545(2)	687(4)	−116(3)
C(41)	2 178(3)	1 221(7)	−778(5)
C(42)	935(3)	−312(7)	−1 057(4)
N(5)	1 139(2)	2 118(4)	3 138(3)
C(51)	606(6)	3 477(9)	3 401(8)
N(6)	1 541(2)	1 027(4)	4 211(3)
C(61)	2 129(4)	1 924(13)	5 252(7)
C(62)	1 024(3)	−19(8)	4 846(5)

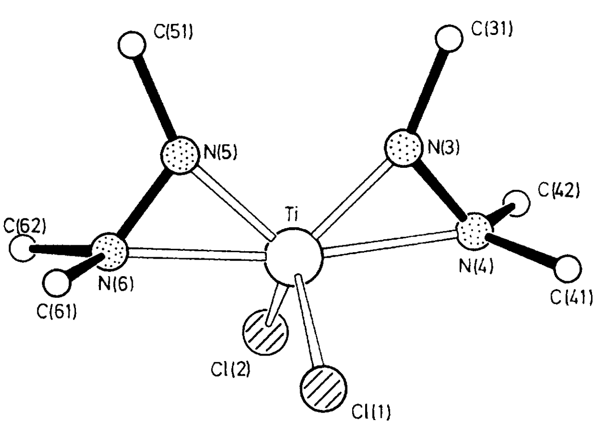


Figure 3. A view of a molecule of [$TiCl_2(NMeNMe_2)_2$] (**5**)

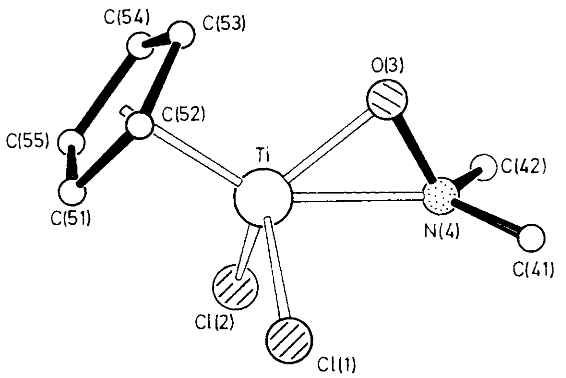


Figure 4. A view of a molecule of [$Ti(C_5H_5)Cl_2(ONMe_2)$] (**6**)

Crystal Structure of Dichlorobis(trimethylhydrazido)titanium(IV) (**5**).—The structure of these molecules is represented in Figure 3. Once again, this may be regarded as having pseudotetrahedral symmetry, with each hydrazido-residue being bound side-on. There are two approximate mirror planes perpendicular to each other, one passing through Ti, Cl(1), and Cl(2), and the other through Ti, all the nitrogen atoms, and the NMe carbon atoms. The bond lengths and angles (Table 7) fall within the ranges now expected for these species and the atomic co-ordinates are in Table 6.

*Crystal Structure of Dichloro(cyclopentadienyl)(*N,N*-dimethylhydroxylaminato)titanium*(IV) (**6**).—The molecules in the crystal of this compound possess a structure which is very similar to that of (**1**). The hydroxylaminato-ligand is also side-on, with its oxygen atom taking the place of the NMe group (Figure 4). There is an approximate mirror plane through Ti, O, N, and Cp*, and there are no intermolecular contacts significantly shorter than van der Waals contacts. Atomic co-ordinates are listed in Table 8, and selected bond lengths and angles in Table 9.

Table 7. Bond lengths (Å) and angles (°) for complex (**5**) with e.s.d.s in parentheses

(*a*) About the Ti atom

Ti–Cl(1)	2.315(1)	Ti–N(4)	2.191(3)
Ti–Cl(2)	2.305(1)	Ti–N(5)	1.846(3)
Ti–N(3)	1.845(3)	Ti–N(6)	2.193(3)
Cl(1)–Ti–Cl(2)	115.2(1)	Cl(2)–Ti–N(3)	116.1(1)
Cl(1)–Ti–N(3)	108.3(1)	Cl(2)–Ti–N(4)	90.7(1)
Cl(1)–Ti–N(4)	95.1(1)	Cl(2)–Ti–N(5)	110.6(1)
Cl(1)–Ti–N(5)	113.0(1)	Cl(2)–Ti–N(6)	91.5(1)
Cl(1)–Ti–N(6)	92.6(1)	N(4)–Ti–N(5)	130.6(1)
N(3)–Ti–N(4)	39.9(1)	N(4)–Ti–N(6)	170.2(1)
N(3)–Ti–N(5)	91.4(1)	N(5)–Ti–N(6)	40.0(1)
N(3)–Ti–N(6)	131.3(1)		

(*b*) In the ligands

N(3)–C(31)	1.447(5)	N(5)–C(51)	1.456(6)
N(3)–N(4)	1.416(4)	N(5)–N(6)	1.419(5)
N(4)–C(41)	1.475(5)	N(6)–C(61)	1.468(6)
N(4)–C(42)	1.474(5)	N(6)–C(62)	1.456(5)
Ti–N(3)–C(31)	156.2(3)	Ti–N(5)–C(51)	156.1(4)
Ti–N(3)–N(4)	83.3(2)	Ti–N(5)–N(6)	83.3(2)
N(4)–N(3)–C(31)	120.4(3)	N(6)–N(5)–C(51)	120.5(4)
Ti–N(4)–N(3)	56.8(1)	Ti–N(6)–N(5)	56.7(2)
Ti–N(4)–C(41)	124.2(3)	Ti–N(6)–C(61)	123.6(3)
Ti–N(4)–C(42)	122.5(2)	Ti–N(6)–C(62)	124.1(3)
N(3)–N(4)–C(41)	114.1(3)	N(5)–N(6)–C(61)	115.4(5)
N(3)–N(4)–C(42)	113.7(3)	N(5)–N(6)–C(62)	113.4(3)
C(41)–N(4)–C(42)	111.4(3)	C(61)–N(6)–C(62)	110.3(4)

Table 8. Final atomic co-ordinates (fractional × 10^4) for complex (**6**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Ti	1 139.9(4)	2 515.1(3)	1 315.0(4)
Cl(1)	3 122.0(8)	3 730.6(6)	2 497.7(9)
Cl(2)	2 062(1)	468.6(5)	1 983.5(9)
O(3)	1 229(2)	2 979(1)	−1 396(2)
N(4)	3 036(2)	2 401(2)	−1 548(2)
C(41)	4 481(4)	3 296(3)	−2 368(4)
C(42)	3 210(5)	1 288(3)	−2 788(4)
C(51)	−1 015(3)	2 963(3)	4 413(3)
C(52)	−1 173(3)	3 954(2)	3 026(4)
C(53)	−1 833(3)	3 475(2)	1 436(4)
C(54)	−2 060(3)	2 192(2)	1 824(4)
C(55)	−1 577(3)	1 887(2)	3 695(4)
Cp*	−1 532	2 894	2 879

Discussion

The syntheses of all the materials are straightforward, and present no problems. There are certain inexplicable difficulties associated with general syntheses of hydroxylaminato-complexes, and the reactions of dithiocarbamato-complexes. We do not intend to pursue these further. The reactions of hydrazines with simple halides are very complex, and it is curently not possible to explain the products obtained. Titanium(III) or titanium(IV) chloride and phenylhydrazine give the same uncharacterized, reproducible product. With trimethylhydrazine, as here, the titanium(IV) complex (**5**) can be isolated. On the other hand, reaction of $[VCl_3(MeCN)_3]$ with $NMePhNH_2$ produces $[VCl_2(NNMePh)(NH_2NMePh)_2]^+$, a vanadium(V) complex.[7] Clearly oxidation also takes place here, but the mechanism is equally obscure. The reaction of $[VCl_3(thf)_3]$ (thf = tetrahydrofuran) with NMe_2NHMe seems to produce $[VCl_3(NMe_2NHMe)_2]$,[8] which suggests yet another variant of reaction pathway.

Table 9. Bond lengths (Å) and angles (°) in complex (**6**) with e.s.d.s in parentheses

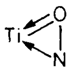
(*a*) About the Ti atom

Ti–Cl(1)	2.291(1)	Ti–C(51)	2.383(2)
Ti–Cl(2)	2.314(1)	Ti–C(52)	2.369(2)
Ti–O(3)	1.866(1)	Ti–C(53)	2.348(2)
Ti–N(4)	2.128(2)	Ti–C(54)	2.342(2)
Ti–Cp*	2.044	Ti–C(55)	2.383(2)
Cl(1)–Ti–Cl(2)	105.6	O(3)–Ti–N(4)	40.9(1)
Cl(1)–Ti–O(3)	108.1	Cl(1)–Ti–Cp*	109.0
Cl(1)–Ti–N(4)	90.8	Cl(2)–Ti–Cp*	110.0
Cl(2)–Ti–O(3)	116.8	O(3)–Ti–Cp*	107.2
Cl(2)–Ti–N(4)	87.7	N(4)–Ti–Cp*	147.7

(*b*) In the ligands

O(3)–N(4)	1.418(2)	C(51)–C(55)	1.386(4)
N(4)–C(41)	1.470(3)	C(52)–C(53)	1.398(4)
N(4)–C(42)	1.470(3)	C(53)–C(54)	1.400(4)
C(51)–C(52)	1.403(4)	C(54)–C(55)	1.406(4)
Ti–O(3)–N(4)	79.5(1)	C(42)–N(4)–C(41)	112.2(2)
Ti–N(4)–O(3)	59.6(1)	C(55)–C(51)–C(52)	108.5(2)
Ti–N(4)–C(41)	125.3(2)	C(51)–C(52)–C(53)	107.6(2)
Ti–N(4)–C(42)	121.8(2)	C(52)–C(53)–C(54)	108.3(2)
O(3)–N(4)–C(41)	110.6(2)	C(55)–C(54)–C(53)	107.6(2)
O(3)–N(4)–C(42)	109.2(2)	C(51)–C(55)–C(54)	108.0(2)

Most of the angles around Ti have e.s.d.s less than 0.05°.

In Table 10 are collected selected bond lengths of the compounds described here and also of appropriate compounds in the literature. It would appear that there is little variation in Ti–Cp* distances whatever the hydrazido-ligand. The Ti–Cl distances do not show real variations for the three hydrazido-(1−)-complexes quoted. This is surprising since the crystal structure of $[Ti(C_5H_5)Cl_2(NHNMe_2)]$ shows extensive intermolecular hydrogen bonding.[3] The expected Ti^{IV}–Cl separation is *ca.* 2.32 Å. There is a slight shortening of Ti–Cl in the hydroxylaminato-derivative (**6**) and a slight lengthening in the trimethylsilyl derivative (**3**), which is apparently steric in origin. The bond lengths in the titanium–nitrogen–nitrogen(oxygen) ring are also relatively invariant. The Ti–NMe separation (*ca.* 1.84 Å) is consistent with considerable Ti–N double bonding, the N–N separations are of the order of that in hydrazine itself, but the Ti–NMe_2 separations show much greater variation, and the large value of 2.278(4) observed in the trimethylsilyl compound may be a consequence of Si–N π overlap as well as steric factors. The hydroxylaminato-complex shows some changes as compared to the mono(trimethylhydrazido)-complex with a longer Ti–O separation, a shorter Ti–N separation, and a very similar N–N/O separation. The bond lengths are consistent with a structure 

There are few literature data which are immediately comparable, but the two structures cited in Table 10[5,6] would appear to fit the same general pattern. No more detailed analysis is justified at this stage.

Experimental

All operations were carried out using standard Schlenk-tube or glove-box techniques under pure, dry dinitrogen. Solvents were distilled under dinitrogen from appropriate drying agents before use. The compounds $[Ti(C_5H_5)Cl_3]$,[9] $[Ti(C_5H_5)Cl_2(NMeNMe_2)]$ (**1**),[2] NMe_2NHMe,[10] $NMe_2(OSiMe_3)$,[11] and $NMe_2NMe(SiMe_3)$[12] were prepared by literature methods,

Table 10. Selected bond lengths (Å) of some hydrazido(1 –)- and hydroxylaminato(1 –)-complexes

Complex	Ti–Cp*	Ti–Cl	M–N_α/O	M–N_β	N–N/O	Ref.
[Ti(cp)Cl_2(NMeNMe_2)] (**1**)	2.038	2.323(1)	1.837(3)	2.210(3)	1.408(4)	This work
[Ti(cp)Cl_2{NMeNMe(SiMe_3)}] (**3**)	2.045	2.332(7)[a]	1.837(4)	2.278(4)	1.425(5)	This work
[Ti(cp)Cl_2(NHNMe_2)]	2.041	2.319(5)	1.832(15)	2.223(15)	1.405(18)	3
[Ti(cp)Cl_2(NPhNH_2)]	2.026	2.315(1)[a]	1.877(9)	2.144(11)	1.411(16)	3
[TiCl_2(NMeNMe_2)$_2$] (**5**)		2.310(5)[a]	1.845(1)[a]	2.192(1)[a]	1.417(1)[a]	This work
[Ti(cp)Cl_2(ONMe_2)] (**6**)	2.044	2.303(11)[a]	1.866(1)	2.128(2)	1.418(2)	This work
[Ti(ONEt_2)$_4$]			1.980(3)	2.108(5)	1.402(7)	6
[(Mo(ONMe_2)(PhCONO)(PhCONHO)]			1.969(3)	2.172(4)	1.399(4)	5

Cp* is the centroid of the cp (C_5H_5) ring.

[a] Mean (with s.d. of the mean) of two independent values.

and $NMe_2OH{\cdot}HCl$, $Na(S_2CNEt_2)$, and $Na(S_2CNMePh)$ were obtained commercially. The following instruments were used: i.r., Pye Unicam SP 2000 and SP3-200; n.m.r., JEOL FX90Q. Microanalyses were by Mr. C. J. Macdonald, AFRC IPSR Nitrogen Fixation Laboratory.

Dichloro(cyclopentadienyl)(1-ethyl-2,2-dimethylhydrazido)-titanium(IV) (**2**).—A solution of $[Ti(C_5H_5)Cl_3]$ (1.74 g, 7.9 mmol) in CH_2Cl_2 (20 cm^3) was treated with Et_3N (1.1 cm^3, 7.9 mmol) and NMe_2NHEt (0.9 cm^3, 7.9 mmol) and the mixture stirred at 20 °C for 1.5 h. The mixture was then filtered, and the filtrate layered with Et_2O (20 cm^3). Storage at –20 °C for 3 d produced yellow *crystals*, yield 73%.

Dichloro(cyclopentadienyl)(1,2-dimethyl-2-trimethylsilyl-hydrazido)titanium(IV) (**3**).—A solution of $[Ti(C_5H_5)Cl_3]$ (4.47 g, 20 mmol) in CH_2Cl_2 (20 cm^3) was treated with $(Me_3SiMeN)_2$ (2.5 cm^3, 10 mmol) and the solution stirred at 20 °C for 1 h. The orange filtrate was layered with hexane (40 cm^3). Storage at –20 °C for several days produced a crystalline *mixture* of $[Ti(C_5H_5)Cl_3]$ and yellow (**3**), separated manually. Less than 15% of the titanium was recovered as product in this fashion.

*Chloro(cyclopentadienyl)(diethyldithiocarbamato)(1-phenyl-hydrazido-*N*)titanium*(IV) (**4**).—A solution of $[Ti(C_5H_5)Cl_3]$ (0.65 g, 3.0 mmol) in CH_2Cl_2 (40 cm^3) was treated with $Na(S_2CNEt_2)$ (0.51 g, 3.0 mmol). The solution was stirred for 1 h at 20 °C and then $NHPhNH(SiMe_3)$ was added. After stirring for a further 6 h, the solution was filtered, layered with hexane (60 cm^3), and stored at –20 °C for 7 d. The red *crystals* were washed with hexane (2 × 10 cm^3) and dried *in vacuo*, yield 27%.

Dichlorobis(trimethylhydrazido)titanium(IV) (**5**).—A suspension of $TiCl_3$ (1.84 g, 1.2 mmol) in thf (25 cm^3) was treated with NMe_2NHMe (7 cm^3, 72 mmol) and stirred at 20 °C for 24 h. The mixture was filtered, and the filtrate at –20 °C yielded yellow *crystals*, *ca.* 20% of recovered material.

*Dichloro(cyclopentadienyl)(*N,N*-dimethylhydroxylaminato-*O*)titanium*(IV) (**6**).—A solution of $[Ti(C_5H_5)Cl_3]$ (5.0 g, 23 mmol) in thf (20 cm^3) was mixed with a solution of $Me_2NOSiMe_3$ (23 mmol) in thf (20 cm^3). The $Me_2NOSiMe_3$ was itself prepared *in situ* by reaction of $Me_2NOH{\cdot}HCl$ (2.4 g, 23 mmol) with 9 mmol of a 1.55 mol dm^{-3} solution of $LiBu^n$ in hexane, then $SiMe_3Cl$ (2.9 cm^3, 23 mmol) The mixture was stirred at 20 °C for 0.5 h, and the volume was then reduced *in vacuo* to *ca.* 5 cm^3. Addition of hexane (60 cm^3) produced a yellow *precipitate*, which was filtered off, washed with diethyl ether (1 cm^3), and recrystallized from diethyl ether (5 cm^3)–hexane (60 cm^3) at –20 °C, yield 26%.

Dichloro(cyclopentadienyl)(diethyldithiocarbamato)titanium-(IV) (**7**).—A mixture of $[Ti(C_5H_5)Cl_3]$ (1.17 g, 5.3 mmol) and $Na(S_2CNEt_2)$ (0.91 g, 5.3 mmol) was stirred in CH_2Cl_2 (20 cm^3) for 8 h. The mixture was then filtered and hexane (30 cm^3) was added to the filtrate. Upon storing at –20 °C, red *crystals* were produced, which were filtered off, washed with hexane (3 × 50 cm^3), and dried *in vacuo*, yield 40%.

Dichloro(cyclopentadienyl)(methylphenyldithiocarbamato)-titanium(IV) (**8**).—This was prepared similarly as red *crystals*, in 50% yield.

1-*Ethyl*-2,2-*dimethylhydrazine*.—Acetaldehyde (90 cm^3, 0.8 mol) was added dropwise to a stirred solution of NMe_2NH_2 (57 cm^3, 0.75 mol) in water (*ca.* 350 cm^3). An excess of NaOH (*ca.* 500 g) was added, to produce a red-brown oil. Distillation [*ca.* 105 °C, 1 atm (101 325 Pa)] under N_2 yielded a pale yellow oil, assumed to be $Me_2NN{=}CHMe$. This was redistilled from NaOH (*ca.* 200 g), yielding *ca.* 120 cm^3 of a fraction boiling at 105 °C, 1 atm. This was added dropwise to a stirred solution of $Li[AlH_4]$ (14 g) in diethyl ether (300 cm^3). When the addition was complete, the mixture was heated under reflux for 1 h. After cooling, the excess of $Li[AlH_4]$ was destroyed by careful, slow addition of degassed, distilled water. Dropwise addition of hydrochloric acid (350 cm^3, 1.2 mol dm^{-3}) and reduction of the volume to *ca.* 500 cm^3 using a rotary evaporator produced a solution which was added dropwise into a vigorously stirred solution of NaOH (400 g) in water (150 cm^3). The separated oil was mixed with xylene (40 cm^3) and distilled from NaOH (*ca.* 50 g). The distillation was repeated twice, adding xylene each time as a chaser. The *product* was collected at 88 °C, 1 atm in essentially quantitative yield. ^1H N.m.r. (CH_2Cl_2); δ 2.78—2.59 (q, 2, CH_2), 2.29 (s, 6, NMe_2), 2.00 (s, 1 NH), and 1.02—0.86 (t, 3, CH_2CH_3).

X-*Ray Crystallographic Analyses of Complexes* (**1**), (**3**), (**5**), *and* (**6**).—The crystal structure analyses of the four complexes followed very similar courses. The analysis of complex (**1**) is described below and details for all are in Table 11. Crystal data are in Table 12.

Crystals of (**1**) (and of the other complexes) were air-sensitive, and single crystals were mounted under dinitrogen in a glove-box. After preliminary photographic examination, the selected crystal was transferred to our Enraf-Nonius CAD4 diffractometer [with monochromated radiation, $\lambda(\text{Mo-}K_{\bar{\alpha}}) = 0.710\,69$ Å] for determination of accurate cell dimensions (from the goniometer settings of 25 centred reflections with $10 < \theta < 11°$) and measurement of diffraction intensities to $\theta_{max.} = 25°$.

During processing, data were corrected for Lorentz polarization effects, absorption (by semi-empirical ψ-scan methods), and to eliminate negative intensities (by Bayesian

Table 11. Details of experimental crystallography, structure determination, and refinement

Complex	(1)	(3)	(5)	(6)
Appearance	Pale yellow-brown needles	Pale yellow needles	Pale yellow square prisms	Pale yellow diamond-shaped plates
Crystal size (mm)	0.10 × 0.17 × 0.60	0.14 × 0.14 × 0.95	0.19 × 0.29 × 0.71	0.20 × 0.30 × 0.40
Mounted	In capillary	In capillary	In capillary	On fibre, coated with epoxy resin
On CAD4 diffractomter:				
For cell dimensions, θ/°	10—11	10—11	14—15	11—12
$\theta_{max.}$/°	25	25	25	30
No. of unique reflections	1 061	2 673	2 290	3 027
Corrections to diffraction data made for:				
Lorentz-polarization effects	Yes	Yes	Yes	Yes
Absorption	Yes	No	Yes	Yes
Negative intensities	Yes	Yes	Yes	Yes
Deterioration	No	Yes	Yes	Yes
final intensities of standards (%)	100	90	67	86
Method of structure determination	Direct methods (EEES) for Ti and Cl atoms; then e.d. maps[13]	Automated Patterson methods (SHELXS)[14]	As for (3)	Heavy-atom method (Patterson + e.d. maps)[13]
Refinement results: *				
R	0.039	0.106	0.058	0.042
R′	0.039	0.083	0.064	0.048
g	0.000 63	0.000 28	0.002 32	0.001 32

* *R* And *R′* values are at convergence, for all data, weighted $w = (\sigma_F^2 + gF^2)^{-1}$.[13]

Table 12. Crystal data for complexes (**1**), (**3**), (**5**), and (**6**)

Compound	$[Ti(C_5H_5)Cl_2(NMeNMe_2)]$	$[Ti(C_5H_5)Cl_2\{NMeNMe(SiMe_3)\}]$	$[TiCl_2(NMeNMe_2)_2]$	$[Ti(C_5H_5)Cl_2(ONMe_2)]$
No.	(**1**)	(**3**)	(**5**)	(**6**)
Elemental formula	$C_8H_{14}Cl_2N_2Ti$	$C_{10}H_{20}Cl_2N_2SiTi$	$C_6H_{18}Cl_2N_4Ti$	$C_7H_{11}Cl_2NOTi$
M	257.0	315.2	265.0	244.0
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/m$	$P2_1/n$	$P2_1/a$	$P\bar{1}$
and no.	11	equiv. to 14	equiv. to 14	2
a/Å	8.663(5)	6.754(5)	17.593(3)	7.341(2)
b/Å	10.489(5)	25.305(6)	7.580(2)	10.709(8)
c/Å	6.633(7)	9.300(2)	10.073(1)	6.758(2)
α/°	90	90	90	87.57(5)
β/°	109.08(7)	105.41(4)	102.74(1)	77.47(2)
γ/°	90	90	90	86.87(5)
U/Å^3	569.6	1 532.3	1 310.3	517.6
Z	2	4	4	2
F(000)	264	656	552	248
D_c/g cm^{-3}	1.500	1.366	1.343	1.565
μ(Mo-K_α)/cm^{-1}	11.8	9.6	10.3	12.9

methods). Two reflections, monitored throughout the data collection, showed no significant change in intensity, and no deterioration correction was necessary. 1 061 Unique reflections were entered into the SHELX program[13] for structure determination by the automated direct methods routine EEES, which showed the Ti and Cl atoms clearly; the remaining non-hydrogen atoms were located in electron-density maps.

Refinement was by full-matrix least-squares methods.[13] The non-hydrogen atoms were allowed anisotropic thermal parameters. Hydrogen atoms, located in difference maps, were refined isotropically, independently and satisfactorily. In complexes (**3**) and (**5**), geometrical restraints were placed on some hydrogen atoms, and the thermal parameters of some hydrogen atoms in (**3**) were set to ride on the values of their bonded C atoms. The H atoms in (**6**) were treated as in (**1**).

Final difference maps for each complex showed no significant residual density. The major peaks, the highest being 0.68 e Å^{-3} for (**5**), were generally close to the Ti–Cl bonds.

Scattering factors for neutral atoms were from ref. 15. Computer programs used in the analyses include those noted above and those listed in Table 4 of ref. 16; they were run on the VAX 11/750 machine at the AFRC IHR's Littlehampton Laboratory.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

We acknowledge support under E.E.C. Grant ST2* 410 (to M. J.-T.)

References

1 D. L. Hughes, G. J. Leigh, and D. G. Walker, *J. Chem. Soc., Dalton Trans.*, 1988, 1153.

2 R. Hemmer, U. Thewalt, D. L. Hughes, G. J. Leigh, and D. G. Walker, *J. Organomet. Chem.*, 1987, **323**, C29; E. M. R. Kiremire, G. J. Leigh, J. R. Dilworth, and R. A. Henderson, *Inorg. Chim. Acta*, 1984, **83**, L83.

3 I. A. Latham, G. J. Leigh, G. Huttner, and I. Jibril, *J. Chem. Soc., Dalton Trans.*, 1986, 385.

4 E. D. Becker, 'High Resolution N.M.R.,' Academic Press, New York, 1980.

5 See, for example, S. F. Gheller, T. W. Hambley, P. R. Traill, R. T. C. Brownlee, M. J. O'Connor, M. R. Snow, and A. G. Wedd, *Aust. J. Chem.*, 1982, **35**, 2183.

6 K. Wieghardt, I. Tohlsdorf, J. Weiss, and W. Swiridoff, *Z. Anorg. Allg. Chem.*, 1982, **490**, 182.

7 J. Bultitude, L. F. Larkworthy, D. C. Povey, G. W. Smith, J. R. Dilworth, and G. J. Leigh, *J. Chem. Soc., Chem. Commun.*, 1986, 1748.

8 G. J. Leigh, unpublished work.

9 R. D. Gorsich, *J. Am. Chem. Soc.*, 1958, **50**, 4774.

10 J. B. Glass, J. G. Aston, and T. S. Oakwood, *J. Am. Chem. Soc.*, 1953, **75**, 2937.

11 U. Wannagat and O. Smrekar, *Monatsh. Chem.*, 1969, **100**, 750; O. Smrekar and U. Wannagat, *ibid.*, p. 760.

12 U. Wannagat and F. Hofler, *Monatsh. Chem.*, 1966, **97**, 982; U. Wannagat and W. Luhr, *Z. Anorg. Allg. Chem.*, 1959, **299**, 341.

13 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.

14 G. M. Sheldrick, SHELXS 86, see 'Crystallographic Computing 3,' eds. G. M. Sheldrick, C. Krüger, and R. Goddard, Oxford University Press, 1986, pp. 175—189.

15 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.

16 S. N. Anderson, R. L. Richards, and D. L. Hughes, *J. Chem. Soc., Dalton Trans.*, 1986, 245.

Received 27*th September* 1988; *Paper* 8/03813I