The Chemistry of Dinitrogen Residues. Part 2.[1] Organohydrazido(1 −)-derivatives of Titanium(IV). *X*-Ray Crystal Structures of [Ti(C_5H_5)Cl_2(NPhNH$_2$)] and [Ti(C_5H_5)Cl_2(NHNMe$_2$)] †

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The structures of [Ti(C_5H_5)Cl_2(NPhNH$_2$)] and [Ti(C_5H_5)Cl_2(NHNMe$_2$)] are described. Both contain side-on hydrazide(1 −) fragments with N–N single bonds but an asymmetric TiNN unit. These compounds, and several other homologues, react with protic acids to generate the hydrazine.

The conversion of co-ordinated dinitrogen into ammonia is believed to involve intermediate hydrazido(2 −)-complexes which have been isolated from reaction mixtures and characterised, detected kinetically, and even been postulated in the natural system.[2] Although certain hydrazido(2 −)-complexes can be protonated to ammonia, no reaction pathway has been delineated. Hydrazide(1 −) is a plausible first protonation product of hydrazide(2 −) [equation (1)], and examples of

$$NH_2{}^{2-} + H^+ \rightleftharpoons NHNH_2{}^- \qquad (1)$$

protonation of organohydrazido(2 −)-complexes are known.[3] They are not common. Only two‡ unsubstituted hydrazido-(1 −)-complexes have been claimed, and they have not been structurally characterised.[4]

Substituted hydrazido(1 −)-complexes and the 'isoelectronic' hydroxylaminato-compounds often exhibit unusual side-on bonding.[5] We decided to investigate hydrazide(1 −) compounds of titanium(IV) to establish the basic chemistry and binding of hydrazide(1 −) when combined with a transition metal. Titanium(IV) was selected to avoid any reductive influence of the metal upon the hydrazide. Preliminary reports of some of these results have already appeared.[6]

Results and Discussion

Titanium hydrazido(1 −)-complexes of the general formula [Ti(C_5H_5)Cl_2(NR^{1}NR^{2}R^3)] were prepared by the reaction of the appropriate lithium or trimethylsilyl derivative Li(NR^{1}NR^{2}R^3) or Me$_3$SiNR^{1}NR^{2}R^3 with [Ti(C_5H_5)Cl_3]. It is also possible to use the direct reaction of [Ti(C_5H_5)Cl_3] with the hydrazine. In this case, an excess of hydrazine is necessary to bind the HCl eliminated, and there is the added complication that if any of R^1, R^2, or R^3 is H then further protons can be extracted, giving complex mixtures. The simple reaction with a trimethylsilylhydrazine, followed by removal of solvent and SiMe$_3$Cl *in vacuo*, yielded analytically pure products. The new complexes are detailed in Table 1. One zirconium compound was also isolated from [Zr(C_5H_5)Cl_3], and it seems likely that many more could be synthesised. Similarly, [Ti(C_5Me_5)Cl_3] probably will be the source of a series of homologues.

The complexes are all moisture-sensitive, and the majority are stable indefinitely under dinitrogen at 25 °C. The silyl derivative is very unstable, and the complexes containing phenyl groups all decompose in a matter of months at 25 °C. The zirconium complex is stable for weeks. The i.r. spectra present no difficulties in assignment, and all the compounds exhibit prominent bands associated with the C_5H_5 group. The u.v. spectra are uninformative. However, the n.m.r. spectra of the trimethylhydrazide complexes (see below) provided an additional stimulus to the structure determinations, the results of which we now describe.

The structures of [Ti(C_5H_5)Cl_2(NPhNH$_2$)] and [Ti(C_5H_5)Cl_2(NHNMe$_2$)] are shown in Figures 1—3, and selected bond lengths and angles are displayed in Table 2. Suitable crystals of [Ti(C_5H_5)Cl_2(NMeNMe$_2$)] could not be prepared. The complex [Ti(C_5H_5)Cl_2(NPhNH$_2$)] crystallises in the space group $P\bar{1}$, with two molecules per unit cell. The molecules occur as hydrogen-bonded (N–H ··· Cl) dimers with a centre of inversion, making the beautiful assemblage in Figure 1. The bridging hydrogens were all located. The hydrazide(1 −) ligand is actually of the form NPhNH$_2$, although a different arrangement, NHNHPh, might have been expected from the synthetic procedure. The structure of the starting hydrazine used in the synthesis, Me$_3$SiNHNHPh, was established by ^{15}N n.m.r. spectroscopy, so that a 1,2-hydrogen shift occurs upon complex formation. A similar situation pertains in [W(C_5H_5)$_2$(NPhNH$_2$)]BF$_4$, the formation of which also involves a 1,2-hydrogen shift.[7] The hydrazide(1 −) is bonded to the titanium side-on, as was reported earlier for the diazenido-complex [Ti(C_5H_5)Cl_2(NNPh)],[1] from which it differs formally by two hydrogen atoms (Figure 1). However, the orientations of, and electronic distributions in, the two dinitrogen fragments are very different. The hydrazide(1 −) fragment is rotated through 90° with respect to the diazenide(1 −), when referred to the Ti(C_5H_5)Cl_2 residue. It lies within the idealised mirror plane which bisects the cyclopentadienyl ring and the two chlorines and passes through the titanium.

The hydrogen bonds between the units are separated by the centre of inversion. Hence each pair of bonds is equivalent although the members of each pair are different. The shorter N–H bond [1.03(4) Å] is accompanied by the shorter H ··· Cl interaction [2.53(4) Å], whereas the longer N–H bond [1.25(4) Å] is accompanied by a longer H ··· Cl interaction [2.93(4) Å]. However, the N ··· Cl separations are identical. The hydrogen bonds have correspondingly different angles (see Table 2). However, the errors associated with the hydrogen positions are relatively large, and these differences may not be very significant.

The complex [Ti(C_5H_5)Cl_2(NHNMe$_2$)] crystallises in the space group *Pnma*, with four molecules in the unit cell. Each

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† Dichloro(η-cyclopentadienyl)-[N^1-phenylhydrazido(1 −)-N^1,N^2]-titanium(IV)and-[N^2,N^2-dimethylhydrazido(1 −)-N^1,N^2]titanium(IV).
Supplementary data available (No. SUP 56397, 5 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

‡ *Note added in proof.* A third has now been claimed: R. C. Murray and R. R. Schrock, *J. Am. Chem. Soc.*, 1985, **107**, 4557.

Table 1. Hydrazido(1 –)-complexes of titanium and zirconium

Complex	Colour	Analysis[a] (%) C	H	N	Selected i.r. bands[b] (cm^{-1})		U.v. spectra ($\lambda_{max.}$/nm, ε/l mol^{-1} cm^{-1})	^{1}H N.m.r. spectra (p.p.m.)[c]
$[Ti(C_5H_5)Cl_2(NMeNMe_2)]$	Yellow	35.7 (37.5)	6.9 (5.5)	10.3 (10.9)	ν(NC) ν(TiN) ν(TiCl)	1 130 not assignable 410, 400	368 (8 986) (thf)	6.62 + 6.50 (2 s, 5, C_5H_5), 3.53 + 2.80 (2 s, 3, NMe), 2.90 (s, 6, NMe_2) ($CDCl_3$) (see text)
$[Ti(C_5H_5)Cl_2(NHNMe_2)]$	Yellow	35.2 (34.7)	6.2 (5.4)	11.8 (11.6)	ν(NH) ν(TiN) ν(TiCl)	3 260, 3 120 620, 640 420	370 (4 059) (CH_2Cl_2)	8.20 (s, 1, NH), 6.45 (s, 5, C_5H_5), 2.90 (s, 6, Me) ($CDCl_3$)
$[Ti(C_5H_5)Cl_2(NHNHBu^t)]$	Yellow	39.6 (40.0)	6.2 (5.9)	10.3 (10.3)	ν(NH) ν(TiN) ν(TiCl)	3 260, 3 190 575 380	—	6.45 (s, 5, C_5H_5), 5.08 + 4.85 (2 s, 2, NH), 1.35 (s, 9, Me) ($CDCl_3$)
$[Ti(C_5H_5)Cl_2(NHNHSiMe_3)]$	Yellow	33.2 (33.5)	5.4 (5.6)	10.1 (9.8)	ν(NH) ν(TiN) ν(TiCl)	3 210 705 (?) 390	—	6.55 (s, 5, C_5H_5), 5.40 (s, br, NH), 0.30 (m, 9, Me) (CD_2Cl_2)
$[Ti(C_5H_5)Cl_2(NPhNH_2)]$	Orange	45.2 (45.5)	4.2 (4.1)	9.5 (9.6)	ν(NH) ν(TiN) ν(TiCl)	3 200, 3 100 630, 570 390	369 (2 491) (CH_2Cl_2)	7.25 (m, 5, Ph), 6.69 + 6.62 (2 s, 5, C_5H_5), 5.17 (s, br, 2, NH) (CD_2Cl_2)
$[Ti(C_5H_5)Cl_2(NHNPh_2)]$	Yellow	54.4 (55.7)	4.2 (4.3)	7.6 (7.6)	ν(NH)	3 210	387 (3 833) (CH_2Cl_2)	11.11 (s, 1, NH), 7.31 (m, 10, Ph), 6.63 (s, 5, C_5H_5) (CD_2Cl_2)
$[Ti(C_5Me_5)Cl_2(NPhNH_2)]$	Red	53.3 (53.3)	6.0 (6.1)	7.8 (7.7)	ν(NH) ν(TiN) ν(TiCl)	3 310, 3290 630, 570 380	—	6.85 (m, 5, Ph), 4.47 (s, 2, NH), 2.05 (s, 15, Me) (C_6D_6)
$[Zr(C_5H_5)Cl_2(NMeNMe_2)]$	White	31.3 (31.9)	4.6 (4.6)	8.5 (9.3)	ν(ZrN) ν(ZrCl)	550 370	—	6.72 + 6.47 + 6.46 (3 s, 5 H, C_5H_5), 3.21 + 2.68 (s, 3, NMe), 2.75 (s, 6, NMe_2) (CD_2Cl_2)
$[Ti(C_5H_5)Cl_2(NPhNH_2)(thf)]$	Black	48.1 (49.7)	5.1 (5.5)	7.5 (7.5)	ν(NH) ν(TiCl)	3 230 not assigned	—	7.21 (m, 5, Ph), 6.55 (s, 5, C_5H_5), 5.70 (s, br, NH), 3.65 (m, 4, thf), 1.80 (m, 4, thf) (CD_3CN)
$[Ti(C_5H_5)Cl_2(NPhNH_2)(MeCN)]$	Brown	47.5 (47.1)	4.7 (4.6)	11.6 (12.6)	ν(CN) ν(NH) ν(TiCl)	not assignable 3 230 not assigned	—	6.22 (s, 5, C_5H_5), 4.27 (s, 2, NH_2), 1.80 (s, 3, MeCN) (C_6D_6)

[a] Calculated values in parentheses. [b] Nujol mulls. [c] s = Singlet, m = multiplet, and br = broad; spectra run at *ca.* 20 °C.

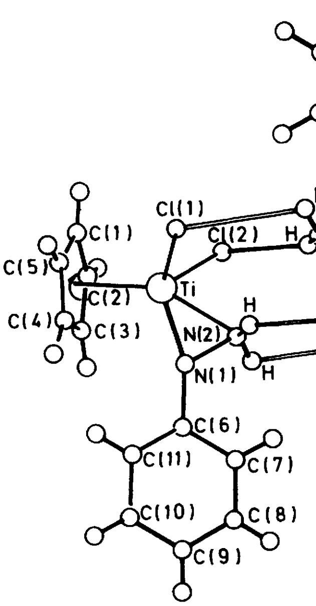


Figure 1. The structure of the dinuclear unit of [Ti(C_5H_5)Cl_2(NPhNH$_2$)]

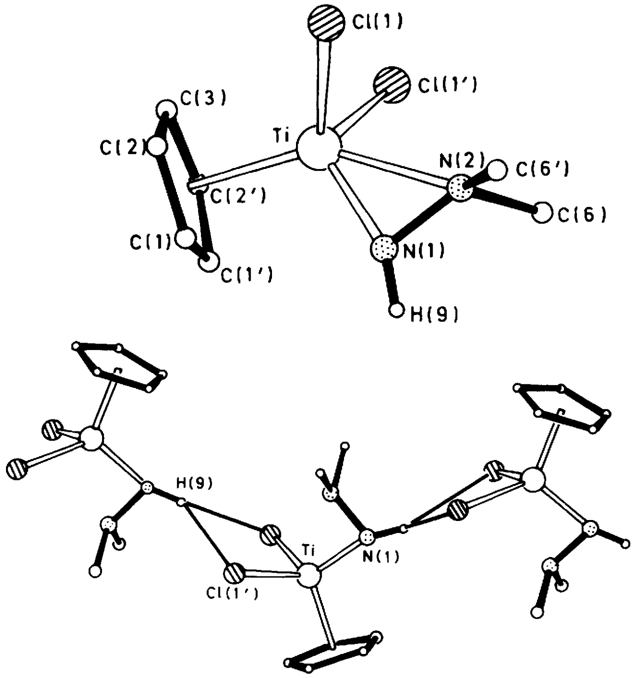


Figure 2. The structure of [Ti(C_5H_5)Cl_2(NHNMe$_2$)] showing intermolecular hydrogen bonding

molecule has a mirror plane which contains the TiNN system and bisects the cyclopentadienyl ring and the angle ClTiCl. The atom numbering, in which an atom such as C(2) is related to C(2′) by the mirror plane, shows this. There is no pairing of molecules through hydrogen bonding such as we observed in the phenylhydrazido(1 –)-derivative and all the hydrogens were located.

We had surmised that intermolecular hydrogen bonding could have been the driving force both for the hydrogen-atom shift observed in the formation of [Ti(C_5H_5)Cl_2(NPhNH$_2$)] and for the side-on hydrazide bonding. Figure 2 shows that the structure of [Ti(C_5H_5)Cl_2(NHNMe$_2$)] also contains hydrogen bonding, but in this case the single N-hydrogen is shared symmetrically between two chlorines leading to a chain structure. The separation between nitrogen in one molecule and chlorine in its neighbour is 3.536(5) Å, with the individual H • • • Cl and N–H bond separations being 2.79(2) and 0.93(1) Å, respectively. The NHCl angles are 137.8°, leaving the ClHCl angle as 84.4°. The Cl • • • N separation is *ca.* 0.2 Å less than might have been expected in the absence of hydrogen bonding. Clearly, we cannot say whether hydrogen bonding is the driving force for the side-on orientation of hydrazide(1 –), but it seems highly unlikely. The orientation of the hydrazide(1 –) relative to the Ti(C_5H_5)Cl_2 fragment is almost identical to that of the phenylhydrazide(1 –).

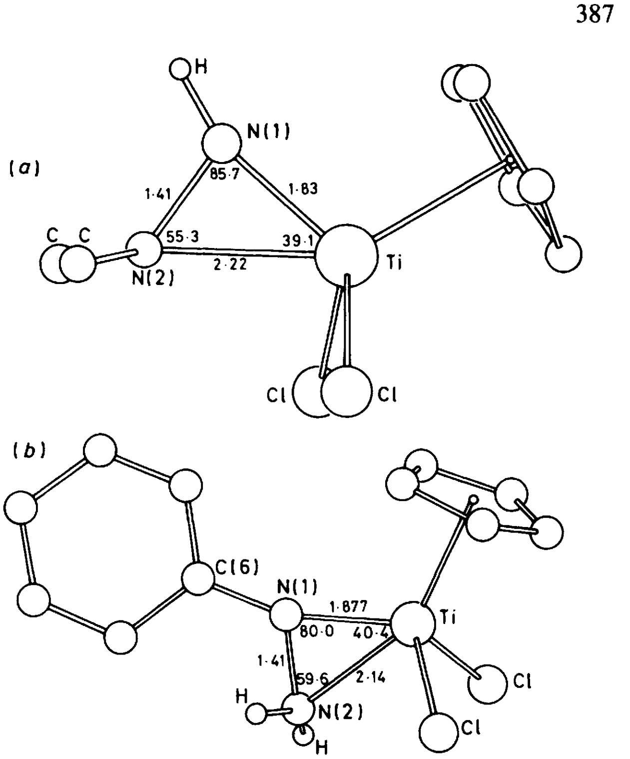


Figure 3. Comparison of the essential molecular structures (distances in Å, angles in °) of [Ti(C_5H_5)Cl_2(NHNMe$_2$)] (*a*) and of [Ti(C_5H_5)Cl_2(NPhNH$_2$)] (*b*)

The molecular dimensions of the two hydrazide(1 –) complexes are very similar. The Ti–N bond length for the nitrogen carrying one substituent (the formally anionic centre) is shorter than that for the nitrogen carrying two substituents (the donor for the formal N⟶Ti bond). The basic units are depicted in Figure 3. The former distance (1.8—1.9 Å) is also considerably shorter than the Ti–N separations in [Ti(C_5H_5)Cl_2(NNPh)] (> 2.0 Å), but for that complex a π-acetylenic-type metal–dinitrogen residue interaction was postulated.[1] The separation is of the same order as in the end-on structures [Ti(C_5H_5)Cl_2(NCBu^{n}Bu^t)] [1.872(4) Å] and [Ti(C_5H_5)Cl_2(NPPh$_3$)] [1.775(13) Å], which we believe[1] are best represented by N$\rightleftarrows$Ti and effectively titanium–nitrogen double bonds. The latter distance (2.1—2.2 Å) is of the order of that found in [Ti(C_5H_5)Cl(C_9H_6ON)$_2$] (C_9H_6ON = 8-hydroxyquinolinate) (2.25 Å).[8] Consequently, the bond is best represented by N⟶Ti, and the titanium–dinitrogen residue interaction by $\mathrm{Ti}\begin{array}{l}\swarrow\mathrm{NR^1}\\ \quad|\\ \nwarrow\mathrm{NR^2R^3}\end{array}$. This suggests that the hydrazide is formally a six-electron donor.

Table 2. Selected bond lengths (Å) and angles (°)

$[Ti(C_5H_5)Cl_2(NHNMe_2)]$		$[Ti(C_5H_5)Cl_2(NPhNH_2)]$	
Ti–N(1)	1.83(1)	Ti–N(1)	1.877(9)
Ti–N(2)	2.22(1)	Ti–N(2)	2.14(1)
Ti–Cl(1)	2.319(5)	Ti–Cl(1)	2.316(4)
Ti–Cl(1′)	2.319(5)	Ti–Cl(2)	2.315(4)
Ti–C_5H_5*	2.05(1)	Ti–C_5H_5*	2.03(2)
N(1)–N(2)	1.41(2)	N(1)–N(2)	1.41(2)
N(2)–C(av.)	1.48(2)	N(1)–C(6)	1.39(1)
N(1)–H	0.93(1)	N(2)–H_x	1.03(4)
C–C(cp)(av.)	1.40(2)	N(2)–H_y	1.25(4)
Cl ··· N	3.536(5)	C–C(Ph)(av.)	1.38(1)
Cl ··· H	2.79(2)	C–C(cp)(av.)	1.39(1)
		Cl(2) ··· H_x	2.53(4)
		Cl(1) ··· H_y	2.93(4)
Ti–N(1)–N(2)	85.7(8)	Ti–N(1)–N(2)	80.0(6)
N(1)–N(2)–Ti	55.3(7)	N(1)–N(2)–Ti	59.6(5)
N(2)–Ti–N(1)	39.1(5)	N(2)–Ti–N(1)	40.4(4)
C_5H_5*–Ti–N(1)	108.6(6)	C_5H_5*–Ti–N(1)	112.3(5)
C_5H_5*–Ti–N(2)	147.6(6)	C_5H_5*–Ti–N(2)	152.6(5)
C_5H_5*–Ti–Cl(1)	111.8(3)	C_5H_5*–Ti–Cl(1)	109.9(2)
C_5H_5*–Ti–Cl(1′)	111.8(3)	C_5H_5*–Ti–Cl(2)	110.3(2)
Cl(1)–Ti–Cl(1′)	101.7(2)	N(1)–N(2)–H_x	123(8)
N(1)–N(2)–C(6′)	114.8(8)	N(1)–N(2)–H_y	79(7)
N(1)–N(2)–C(6)	114.8(8)	H_y–N(2)–H_x	147(8)
C(6)–N(2)–C(6′)	110(1)	Ti–N(2)–H(av.)	106(8)
Ti–N(2)–C(av.)	124.1(7)	N(2)–N(1)–C(6)	118.8(9)
N(2)–N(1)–H	114(1)	Ti–N(1)–C(6)	161.0(9)
Ti–N(1)–H	160(1)	N–H_y ··· Cl(1)	97(1)
N–H ··· Cl	138(1)	N–H_x ··· Cl(2)	146(1)
H ··· Cl–Ti	88(1)	H_y–Cl ··· Ti	108(1)
		H_x–Cl(2) ··· Ti	91(1)

* Centroid of the cyclopentadienyl (cp) ring.

Such a situation is not very likely, but the differences in length between the two Ti–N bonds (0.267 in the dimethylhydrazide and 0.391 Å in the phenylhydrazide) do suggest localised bonding rather than the delocalised pseudo-acetylene structure postulated for $[Ti(C_5H_5)Cl_2(NNPh)]$.[1]

The N–N separation is *ca.* 1.4 Å, which compares well with that (*ca.* 1.47 Å) in hydrazine itself.[9] Consequently, the nitrogen–nitrogen bond is single. The N–H and N–C bond lengths are normal single bonds; the N–H distances in the NH_2NPh group appear to be slightly longer than in hydrazine (1.04 Å)[9] and the N(α)–C(6) bond is slightly shorter than the usual N–Ph bond. This could be due to conjugation of the aromatic π electrons with the electrons of the $\overline{\text{TiNN}}$ system. In the dimethylhydrazide the N–H separation is very close to that in hydrazine.

The dimensions of the $Ti(C_5H_5)Cl_2$ units are very similar to those found by us in the diazenido-complex and related species,[1] and are typical of titanium chloro-cyclopentadienyl compounds in general.

The formalism we have used earlier to explain the orientation of the phenyldiazenido-fragment with respect to the $Ti(C_5H_5)Cl_2$ can be used to explain the different orientation observed here. This involves regarding the complexes as formed from ionic fragments $Ti(C_5H_5)Cl_2^-$ and $NR^1NR^2R^{3+}$.[10] The latter has been termed an 'aminonitrene.' The d_{yz} orbital (see Figure 4) then donates electrons into the empty orbital on the nitrene, whereas the d_{z^2} is set up to receive a lone pair from the NR_2 moiety. Unlike the diazenido-system, there is no delocalised orbital to overlap with d_{xz} to determine the stereochemistry and consequently the two σ overlaps control the orientation of the hydrazine.

The structures described in the first two papers of this series thus demonstrate that it is possible for titanium(IV) to bind groups side-on in two different ways. In one way the group is a

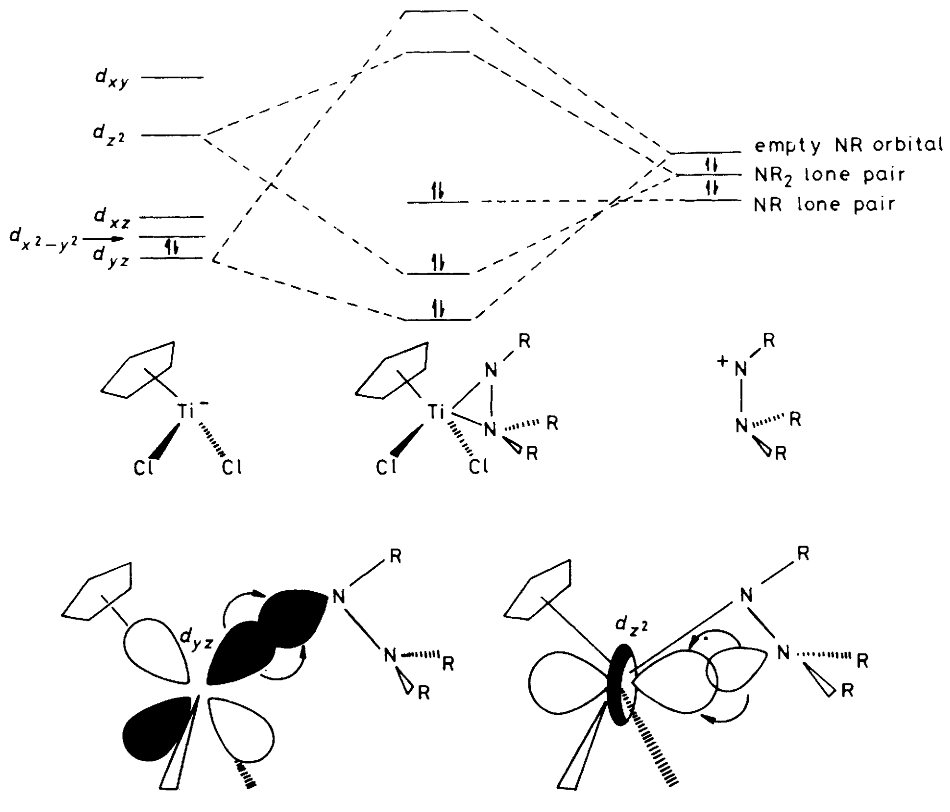


Figure 4. Correlation diagram for $[Ti(C_5H_5)Cl_2(NRNR_2)]$, and interaction of the d_{yz} and d_{z^2} orbitals with hydrazide(1−)

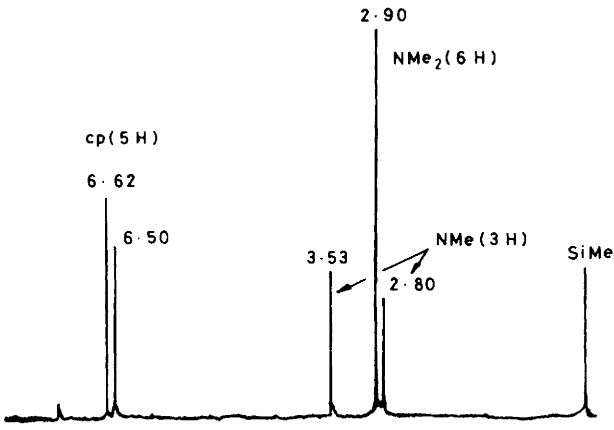


Figure 5. Proton n.m.r. spectrum of $[Ti(C_5H_5)Cl_2(NMeNMe_2)]$ in $CDCl_3$ solution at 20 °C

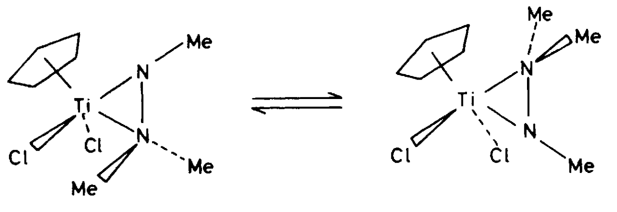
pseudo-acetylene and binds by virtue of its π electrons. In the other the requirement is for a simple covalent bond, and a lone pair on what would otherwise be an *exo*-atom. In the absence of such a lone pair the group binds end-on, even forming a multiple bond to titanium if no other option is available.

Side-on co-ordination for hydrazide(1 −) is usual, though there are attested examples of end-on binding. Further examples of side-on bonding include $[Mo(NHNMePh)(NNMePh)(S_2CNMe_2)]^+$,[11] $[W(C_5H_5)_2(NPhNH_2)]BF_4$,[7] and $[Mo(NHNHCO_2Me)(NNCO_2Me)(S_2CNMe_2)_2]$.[12] Although the metal–nitrogen bond lengths are not comparable, the N–N separations are all closely similar (*ca.* 1.4 Å) and the NMN angle is very acute (*ca.* 40°). The hydrazide in $[W(C_5H_5)_2(NPhNH_2)]^+$ is in common with one of our substances, and the bond lengths and angles are very similar [N–N 1.43(1), N–H 1.08(11) and 0.97(13), $N–C_{(Ph)}$ 1.39(1), $C–C_{(Ph)}$ 1.38(2) (average), $W–NH_2$ 2.156(9), and W–N(Ph) 2.034(9) Å; NWN 39.7(3), WHN(Ph) 74.8(6), and WN(Ph)N 65.6(5)°]. The difference between the two metal–nitrogen distances is less than in our titanium complexes, and this is consistent with the fact that in $[W(C_5H_5)_2(NPhNH_2)]^+$ one cannot envisage the hydrazide as contributing more than four electrons to the metal–ligand bonding.

End-on hydrazide(1 −), as demonstrated for $[Re(C_5H_5)(CO)_2(NHNMeR)]^+$ (R = C_6H_4Me-4),[13] has a shorter N–N separation [1.32(1) Å], and could be a four-electron donor on the basis of the effective atomic number rule. The factors which determine whether hydrazide is end-on or side-on have yet to be explained.

N.M.R. Spectra.—As shown in Table 1, the n.m.r. spectra of complexes are simple and easily explained, with the exception of those of the complexes $[M(C_5H_5)Cl_2(NMeNMe_2)]$ (M = Ti or Zr). For these complexes, both ^{13}C and ^1H n.m.r. spectra exhibit two bands assignable to cyclopentadienyl resonances, and three assignable to methyl. Integration suggests that it is the NMe signal which is split, rather than the NMe_2. A typical spectrum is shown in Figure 5.

In the current titanium complexes, in the solid state, the N–N axis lies in a symmetry plane, which also bisects the cyclopentadienyl ring. Consequently, the N*Me*$_2$ groups are equivalent, the N*Me* lies in the symmetry plane, and it seems highly unlikely that any rotational process or facile isomerism such as shown below could account for the observed spectra. The spectra can, nevertheless, be interpreted on the basis that $[Ti(C_5H_5)Cl_2(NMeNMe_2)]$ is first obtained as a mixture of isomers, designated (S) and (E), respectively, standing for side-on and end-on. The transformations observed in the spectra are summarised below, and we assume that each cyclopentadienyl and NMe resonance arises from a different isomer.



The mixture of isomers can be converted into one isomer by recrystallising from CH_2Cl_2. The ^1H n.m.r. spectrum for this material is virtually unchanged between −60 and +55 °C. The second isomer can be obtained by allowing a solution in $CDCl_3$ to stand for several days. Addition of Lewis base accelerates this change. On cooling a solution of (E) in $CDCl_3$ to −60 °C, the signal attributed to the NMe_2 group of this isomer also begins to broaden, though it is not fully resolved even at −90 °C.

A reasonable interpretation is that the isomers are side-on and end-on with respect to the $NMeNMe_2$. This accounts for the different NMe and C_5H_5 resonances. The NMe_2 resonance in the side-on form, (S), cannot, for symmetry reasons, be resolved. However, if there is facile rotation of the NMe_2 group about the N–N bond in the (E) form, it should be possible to resolve these resonances at low enough temperatures since the $NMeNMe_2$ ligand cannot have TiNN *ca.* 180°. Preliminary experiments show analogous behaviour for $[Zr(C_5H_5)Cl_2(NMeNMe_2)]$, and the cyclopentadienyl resonance of $[Ti(C_5H_5)Cl_2(NPhNH_2)]$ is also unexpectedly split.

Splitting of a side-on hydrazide(1 −) resonance has been observed in the ^1H n.m.r. spectrum of $[Mo(C_5H_5)(NO)I(NMeNMe_2)]$ and of $[MoL(NO)I(NHNMe_2)]$ (L = a pyrazolylborate), but this time of the NMe_2.[14] In that case the splitting was attributed to two different environments for the NMe_2 group, which follows from the demonstrated crystal structure. At higher temperatures the splitting disappears, presumably as a consequence of rotation about the N–N bond.

Reactions of Hydrazide(1 −) *Complexes.*—Crystallisation of the hydrazide(1 −) complex $[Ti(C_5H_5)Cl_2(NPhNH_2)]$ from solvents such as tetrahydrofuran (thf) and MeCN yields intensely coloured air-sensitive solids which are 1:1 adducts. The solvent molecules are lost upon heating *in vacuo* (see Table 1). Trituration of the adducts in toluene–diethyl ether also led to loss of solvent. It was not possible to form the adducts from $[Ti(C_5H_5)Cl_2(NPhNH_2)]$ once it had been isolated, and the adducts were isolated from the preparative reaction mixtures. It would appear that the side-on conformation, once established, is difficult to break up.

No adducts were isolated from other hydrazide(1 −) complexes. Attempts to form adducts from hydrazido(1 −)-complexes with hydrogen on the anionic nitrogen and proton bases such as pyridine resulted in the formation of hydrazido(2 −)-complexes, a reaction to be discussed later.[15] Presumably these adducts contain end-on hydrazide(1 −), but this remains to be proven.

The reactions of $[Ti(C_5H_5)Cl_2(NR^1NR^2R^3)]$ ($R^1 = R^2$ = H, R^3 = Bu^t; R^1 = Ph, $R^2 = R^3$ = H; or R^1 = H, $R^2 = R^3$ = Ph) with anhydrous HCl gave essentially quantitative yields of the appropriate hydrazine hydrochloride, as determined by analysis and spectroscopy. This is presumably a reaction common to all side-on hydrazides(1 −), and shows that such species may be an intermediate in the protonation of co-ordinated dinitrogen to hydrazine.

Table 3. Final co-ordinates (fractional × 10^4) for the refined atoms with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) $[Ti(C_5H_5)Cl_2(NPhNH_2)]$							
Ti	5 916(3)	2 804(2)	8 588(2)	C(5)	4 701(19)	226(13)	7 117(15)
Cl(1)	2 637(4)	1 779(3)	8 578(3)	C(6)	7 156(15)	5 586(12)	6 841(11)
Cl(2)	7 813(4)	3 686(3)	11 024(3)	C(7)	7 614(17)	5 061(12)	5 702(11)
N(1)	5 796(16)	5 071(10)	8 779(9)	C(8)	8 329(18)	6 073(14)	4 858(12)
N(2)	6 479(12)	4 561(9)	7 717(9)	C(9)	8 658(18)	7 674(13)	5 178(12)
C(1)	5 972(25)	273(15)	8 427(15)	C(10)	8 212(18)	8 190(12)	6 301(12)
C(2)	7 928(20)	1 394(15)	8 649(13)	C(11)	7 465(17)	7 186(12)	7 145(12)
C(3)	7 862(17)	2 109(12)	7 476(13)	H(11)	4 357(197)	4 965(148)	8 557(135)
C(4)	5 873(19)	1 373(13)	6 533(12)	H(12)	7 624(197)	5 981(149)	9 276(132)
(*b*) $[Ti(C_5H_5)Cl_2(NHNMe_2)]$ *							
Ti	11 112(3)	2 500	804(3)	C(6)	10 657(12)	1 376(12)	4 221(14)
Cl(1)	12 382(3)	4 171(2)	1 275(3)	C(1)	9 686(12)	3 111(12)	−1 016(14)
N(1)	9 806(12)	2 500	2 084(14)	C(2)	10 792(15)	3 560(14)	−1 517(15)
N(2)	10 665(12)	2 500	3 259(15)	C(3)	11 517(18)	2 500	−1 809(22)

* Atoms with *y* co-ordinates of 0.2500 lie on a crystallographic mirror plane.

Experimental

All operations were carried out under dinitrogen using standard Schlenk-tube or glove-box techniques. Solvents were distilled from drying agents prior to use. The compounds $[Ti(C_5H_5)Cl_3]$,[16] $[Zr(C_5H_5)Cl_3]$,[17] $NHMeNMe_2$,[18] and trimethylsilylhydrazines[19] were prepared by literature methods. All other compounds were obtained commercially.

The following instruments were used: u.v.–visible, Pye-Unicam SP 1800; i.r., Pye-Unicam SP2000 or SP3-200; n.m.r., JEOL FX 90Q. Analyses were by Mr. C. J. Macdonald, AFRC Unit of Nitrogen Fixation.

*Dichloro(cyclopentadienyl)[substituted hydrazido(1 −)-*N,N′]*titanium*.—The following general route was used. The complex $[Ti(C_5H_5)Cl_3]$ (0.5 g, 2.3 mmol) was dissolved in diethyl ether (25 cm^3) and the appropriate trimethylsilylhydrazine (1 mol equivalent) was added dropwise from a syringe. The resulting solution was stirred at room temperature for 2—3 h. In general, removal of volatiles at 10^{-3} mmHg (*ca.* 0.133 Pa) left the analytically pure product in *ca.* 90% yield. This method was used to produce dichloro(cyclopentadienyl)-[trimethylhydrazido(1 −)]titanium, -[N,N-*dimethylhydrazido*-(1 −)]*titanium*, -[N-*t-butylhydrazido*(1 −)]*titanium*, -[N,N-*diphenylhydrazido*(1 −)]*titanium*, and -[N-*phenylhydrazido*-(1 −)]*titanium*. *Dichloro(cyclopentadienyl)*[N-*trimethylsilylhydrazido*(1 −)]*titanium* was prepared in solution as above, but the crystalline product was filtered off about 0.5 h after mixing the reactants $[Ti(C_5H_5)Cl_3]$ and $Me_3SiNHNHSiMe_3$.

Analogous procedures were used for *dichloro(pentamethylcyclopentadienyl)*[N-*phenylhydrazido*(1 −)]*titanium* and *dichloro(cyclopentadienyl)[trimethylhydrazido*(1 −)]*zirconium.*

Dichloro(cyclopentadienyl)[N-*phenylhydrazido*(1 −)](*tetrahydrofuran*)*titanium*.—The complex $[Ti(C_5H_5)Cl_3]$ (0.5 g, 2.3 mmol) in thf (50 cm^3) was mixed with $Me_3SiNHNHPh$ (1 mol equivalent) to form an orange-red solution. Addition of hexane (25 cm^3) and allowing to stand at room temperature overnight produced a black-brown microcrystalline *solid* which was filtered off and dried at 10^{-3} mmHg for 2 h at 20 °C.

Acetonitriledichloro(cyclopentadienyl)[N-*phenylhydrazido*-(1 −)]*titanium* was prepared analogously in MeCN. Removal of MeCN at 10^{-3} mmHg and 20 °C produced a brown oil which slowly solidified.

The complex *dichloro(cyclopentadienyl)*[N-*methyl*-N′-*trimethylsilylhydrazido*(1 −)]*titanium* was obtained in less than analytical purity. The complex $[Ti(C_5H_5)Cl_3]$ (0.5 g, 2.3 mmol) was dissolved in diethyl ether (30 cm^3) and $Me_3SiNHNHMe$ (0.31 cm^3, 2.3 mmol) added from a syringe. A flocculent white solid appeared immediately but gradually redissolved to a yellow solution and then a yellow solid after stirring for 18 h at room temperature. The yellow solid was filtered off and dried at 10^{-3} mmHg. It changes colour upon standing under N_2 at 20 °C during several weeks, with little change in analysis {Found: C, 33.0; H, 4.9; N, 9.4. $[Ti(C_5H_5)Cl_2(NHNHMe)]$ requires C, 31.6; H, 4.4; N, 12.3. $[Ti(C_5H_5)Cl_2(Me_3SiNHNMe)]$ requires C, 35.8; H, 6.0; N, 9.3%}. The i.r. and ^1H n.m.r. spectra show that the Me_3Si group is retained. This complex requires further characterisation.

Protonation of Hydrazido(1 −)*-complexes*.—The hydrazido-complex (2.0 mmol) was dissolved in diethyl ether (20 cm^3) and anhydrous HCl [4—6 mmol, generated from $SiMe_3Cl$ and EtOH in diethyl ether (5 cm^3)] was added. This produced an immediate white precipitate, which was filtered off, washed with diethyl ether, and dried *in vacuo*. The identity of this material was checked by analysis and i.r. spectroscopy of genuine samples. Results: $Bu^tNHNH_2{\cdot}HCl$ (Found: C, 38.7; H, 9.7; N, 22.9. Requires C, 39.1; H, 10.6; N, 22.8%), yield 86%; $PhNHNH_2{\cdot}HCl$ (Found: C, 50.3; H, 6.4; N, 19.6. Requires C, 49.8; H, 6.2; N, 19.4%), yield 88%; $Ph_2NNH_2{\cdot}HCl$ (Found: C, 67.2; H, 6.1; N, 11.0. Requires C, 65.3; H, 5.9; N, 12.7%), yield 90%.

Deprotonation of Hydrazido(1 −)*-complexes*.—These reactions produce hydrazido(2 −)-complexes in cases where the anionic hydrazido-nitrogen carries a hydrogen. The reactions and products will be described in the following paper.

Structure Determinations.—$[Ti(C_5H_5)Cl_2(NPhNH_2)]$. The compound was prepared as described above. Recrystallisation from diethyl ether yielded dark red crystals which were sealed in Lindemann capillaries.

Crystal data. $C_{11}H_{12}Cl_2N_2Ti$, M = 279.9, triclinic, a = 7.655(8), b = 9.322(8), c = 9.85(1) Å, α = 95.27(8), β = 105.80(8), γ = 112.59(7)°, U = 610 Å^3, space group $P\bar{1}$, Z = 2, D_c = 1.59 g cm^{-3}, $\mu(Mo\text{-}K_\alpha)$ = 11.3 cm^{-1}, $\bar{\lambda}(Mo\text{-}K_\alpha)$ = 0.710 69 Å.

Data collection. Syntex *P*3 diffractometer, ω—2θ mode with ω scan width 1.0°, ω scan speed 2.0—29.3° min^{-1}, Mo-K_{α} radiation, graphite monochromator. 1 313 Reflections ($2 < 2\theta < 42°$ at −42 °C), no absorption correction, 1 200 with $I > 2\sigma(I_o)$, $F(000) = 296$.

Structure analysis and refinement. Direct methods using SHELXTL program incorporating the automatic direct methods routine EEES; hydrogens attached to nitrogens both found, other hydrogens inserted at ideal positions during final cycles of refinement. Final R and R' values are 0.0700 and 0.0836; $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R' = [\{\Sigma w(|F_o| - |F_c|)^2\}/(\Sigma w|F_o|^2)]^{\frac{1}{2}}$ where $w = 1/(\sigma^2|F_o| + 0.0078|F_o|^2)$. The atomic co-ordinates are given in Table 3.

$[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_2(\text{NHNMe}_2)]$. The compound was prepared as described above, and recrystallised from thf at −15 °C, yielding yellow needles which were sealed in Lindemann capillaries.

Crystal data. $C_7H_{12}Cl_2N_2Ti$, $M = 242.9$, orthorhombic, $a = 11.04(2)$, $b = 10.76(1)$, $c = 8.83(1)$ Å, $U = 1\,049$ Å^3, space group *Pnma*, $Z = 4$, $D_c = 1.54$ g cm^{-3}, $\mu(\text{Mo-}K_{\alpha}) = 13.0$ cm^{-1}.

Data collection. As above. 599 Reflections ($2 < 2\theta < 42°$ at −55 °C), 535 with $I > 2\sigma(I_o)$, $F(000) = 496$.

Structure analysis. Direct methods using SHELXTL program as above; all hydrogens located. Final R and R' values are 0.0636 and 0.0840. The atomic co-ordinates are given in Table 3.

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