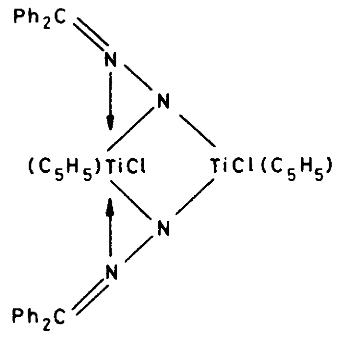
The Chemistry of Dinitrogen Residues. Part 3.[1,2] Hydrazido(2—)-derivatives of Titanium(IV). *X*-Ray Crystal Structure of $[\{Ti(C_5H_5)Cl(NNPh_2)\}_2]$ †

David L. Hughes, Ian A. Latham, and G. Jeffery Leigh *
AFRC Unit of Nitrogen Fixation at the University of Sussex, Brighton BN1 9RQ

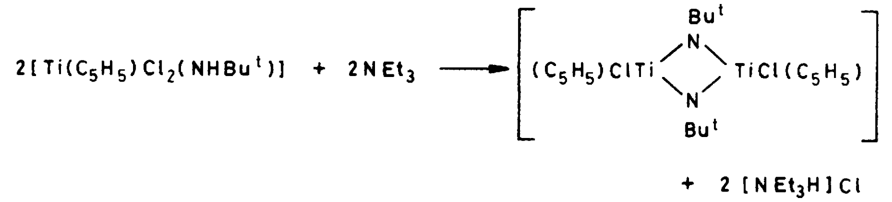
The preparations of 1,2-hydrazide(2−) and 1,1-hydrazide(2−) complexes of titanium(IV) are described. The ^1H n.m.r. spectra of dinuclear 1,1-disubstituted hydrazide(2−) complexes, such as $[\{Ti(C_5H_5)Cl(NNPh_2)\}_2]$, are anomalous, but can be explained on the basis of an *X*-ray structure analysis which shows that one hydrazide forms a symmetrical bridge whereas the other is both bridging and bound side-on to one of the titaniums.

In Parts 1 and 2 of this series we have discussed the chemistry of diazenido(1−)- and hydrazido(1−)-complexes of titanium(IV),[1,2] and shown how these ligands bind to the $Ti(C_5H_5)Cl_2$ moiety in the side-on, η^2, conformation. In this paper we consider hydrazide(2−) derivatives. These can be of two kinds, $NNH_2{}^{2-}$, which can bind to transition metals, either in a quasi-linear[3] form or as a bridge between metals, for example as $M\diagup\overset{NH_2}{N}\diagdown M'$,[4] and $NHNH^{2-}$ which is a bridging ligand.[5] Only the first is directly derivable from dinitrogen in complexes by protonation,[6] and hydrazide(2−) appears to be a particularly stable stage in the protonation of co-ordinated dinitrogen. The neutral counterparts of these ligands, from which they may be indistinguishable in complexes, of course, are isodiazene and diazene.

There are no hydrazide(2−) complexes of titanium(IV) in the literature, unless the complex below, which has had its structure substantiated by a partial *X*-ray analysis, is admitted as such.[7]



However, a synthesis from hydrazido(1−)-complexes is suggested by analogy with reaction (1).[8] *X*-Ray structure analysis confirmed the centrosymmetric nature of this imido-complex, and the structure reflects the reluctance of Ti^{IV} to form double bonds, Ti=N.



$$2[Ti(C_5H_5)Cl_2(NHBu^t)] + 2NEt_3 \longrightarrow [(C_5H_5)ClTi(\mu\text{-}NBu^t)_2TiCl(C_5H_5)] + 2[NEt_3H]Cl \qquad (1)$$

Results and Discussion

We were interested in hydrazido(2−)-derivatives, both 1,1 and 1,2. It was not found possible to protonate $[Ti(C_5H_5)Cl_2(NNPh)]$[1] to yield a hydrazido(2−)-product. However, hydrazide(2−) complexes can be obtained by deprotonation of hydrazide(1−) complexes which are described[1] in Part 1 of this series. Deprotonation can be effected by bases such as NEt_3 and $LiBu^n$, and even a hydrazine. Consequently, the reaction of $[Ti(C_5H_5)Cl_3]$ with more than 2 mol equivalents of the hydrazine always yields at least some hydrazido(2−)-product although this is not a preferred method of synthesis.

We synthesised three 1,1-hydrazido(2−)-complexes as detailed in Table 1. The i.r. spectra are all as expected, but the ^1H n.m.r. spectra of all three were difficult to comprehend on the basis of the symmetrical structures we expected. Since the analyses were not altogether satisfactory, an *X*-ray structural analysis was desirable and this is described below.

The ^1H n.m.r. spectrum of recrystallised $[\{Ti(C_5H_5)Cl(NNPh_2)\}_2]$ at 25 °C in CD_2Cl_2 contains a complex multiplet of peaks associated with the four phenyl rings (7.19—7.42 p.p.m.) and a sharp singlet at 5.96 p.p.m. associated with a cyclopentadienyl group. However, the peak areas are not in the ratio 10:5, as expected, but about 22:5. This suggests that one cyclopentadienyl group has been lost. However, for non-recrystallised samples, there is also a broad resonance centred at 6.50 p.p.m., situated between the phenyl and the cyclopentadienyl resonances, which also integrates for five protons.

The initial red solution of this complex changes to yellow in about 2 h at 25 °C. The spectrum of this solution contains no cyclopentadienyl resonance at 5.96 p.p.m., but a sharp singlet at 6.62 p.p.m. with an intensity relative to phenyl of 1:2.5. After 72 h, this has increased to the expected 1:2. The change is not reversed by cooling to −40 °C. The change from red to yellow is slower in toluene and about as rapid in $CDCl_3$. The yellow

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† μ-[2,2-Diphenylhydrazido(2−)-$N^1(Ti^{1,2}),N^2(Ti^1)$]-[μ-2,2-diphenylhydrazido(2−)-N^1]-bis[chloro(η-cyclopentadienyl)titanium(IV)].

Supplementary data available (No. SUP 56399, 6 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.

Table 1. Hydrazido(2 –)-complexes of titanium

Complex	Colour as isolated	Analysis[a] (%) C	H	N	Selected i.r. data (cm^{-1})	^1H N.m.r. spectra (see text)[b] (p.p.m.)
$[\{Ti(C_5H_5)Cl(NNMe_2)\}_2]$[c]	Orange	42.9 (40.9)	5.3 (5.3)	11.9 (13.6)	TiN 620, 570 TiCl, TiC_5H_5 420	6.50 (br, m), 6.17 (s) (C_5H_5), 2.95 (s), 2.55 (s) (Me) (CD_2Cl_2)
$[\{Ti(C_5H_5)Cl(NNHPh)\}_2]$[d]	Dark brown	53.4 (52.1)	5.2 (4.3)	10.3 (11.0)	TiN 600 TiC_5H_5 440 TiCl 410	6.97 (v. complex m) (Ph + C_5H_5) (CD_2Cl_2)
$[\{Ti(C_5H_5)Cl(NNPh_2)\}_2]$	Red-brown	61.4 (61.9)	4.9 (4.6)	8.3 (8.4)	TiN 650, 625, 590 TiC_5H_5 ? TiCl 410, 390	7.33 (m, 20 H, Ph), 5.96 (s, 5, C_5H_5) (CD_2Cl_2)
$[\{Ti(C_5H_5)Cl_2\}_2NMeNMe]$	Yellow	34.8 (34.0)	4.0 (3.8)	7.7 (6.6)		6.02—6.28 (3 × s, C_5H_5), 2.35—2.58 (3 × s, Me) (C_6D_6)
$[\{Ti(C_5H_5)Cl_2\}_2NPhNPh]$	Brown	44.9 (48.0)	3.6 (3.6)	4.5 (5.1)		7.6 (complex m, Ph), 6.9 (m, C_5H_5) ($CDCl_3$)

[a] Required values in parentheses. [b] br = Broad, s = singlet, and m = multiplet. [c] *M* 458 (calc. 415). [d] *M* 527 (calc. 506).

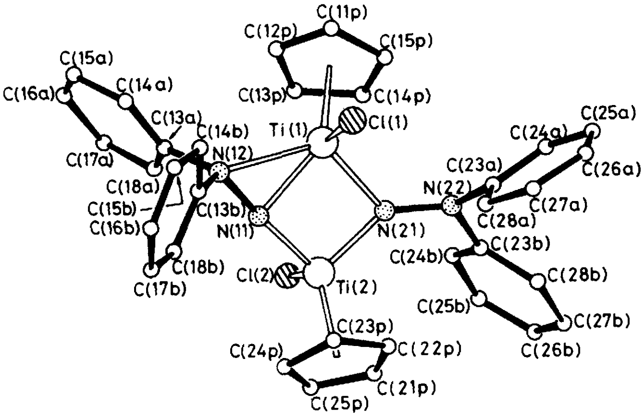
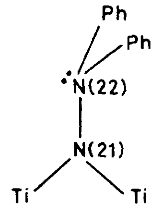


Figure 1. Molecular structure of $[\{Ti(C_5H_5)Cl(NNPh_2)\}_2]$, with the atomic numbering scheme

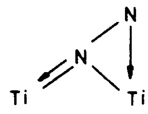
solution gives an n.m.r. spectrum fully consistent with a completely symmetrical structure such as we had expected. However, the red form must be rather different. The anomalous ^1H n.m.r. spectrum can be comfortably rationalised by the crystal structure.

Molecular Structure of $[\{Ti(C_5H_5)Cl(NNPh_2)\}_2]$.—The structure of the dinuclear unit is shown in Figure 1. Noteworthy is the fact that only one of the hydrazido(2 –)-groups is coordinated symmetrically. The other is bridging, but also bound side-on to one titanium. Selected bond lengths and angles are given in Table 2. The TiNTiN ring is almost planar with the atoms forming a shallow tetrahedron with each atom displaced by 0.05 Å from their mean plane. The Ti–N separations are unequal, and Ti(2)–N(11) corresponds to a double bond of the form $Ti \leftrightharpoons N$ as observed in $[Ti(C_5H_5)Cl_2(NCBu^nBu^t)]$.[1] The remaining bonds are of single-bond length, though shorter than observed for $Ti \leftarrow N$.[9] The average Ti–N separation (1.933 Å) compares with the average in the symmetrical complex $[\{Ti(C_5H_5)Cl(NPh)\}_2]$ (1.920 Å)[10] and there is no obvious alternation of bond lengths Ti=N, and $N \rightarrow Ti$. The Ti···Ti separation [2.831(1) Å] precludes metal–metal bonding, consistent with which TiNTi is *ca.* 94.0°, and not <85°, as would be expected were it present. Similarly, there is no N···N interaction across the ring.

Considering now the hydrazide groups themselves, the symmetrically bound $NNPh_2$ has N–N 1.390(4) Å, which corresponds to a single bond[11] and is the same order as in $[WBr(NNH_2)(dppe)_2]^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$)[3,12] and in $[\{Mn(C_5H_5)[NN(SiMe_3)_2]_2\}_2]$.[4] Both Ti–N distances are formal single bonds, but the phenyls are displaced towards Ti(2). The bonds about N(21) are planar, suggestive of sp^2 hybridisation, but N(22) is clearly approaching tetrahedral, so that it will retain a localised lone pair of electrons. Hence its bonding is best represented as shown below. The N–C(Ph) bond lengths in both hydrazides (mean 1.45 Å) are normal for single bonds.



The side-on hydrazide is different. The N–N separation is again, at 1.383(3) Å, a single bond. The binding of N(11) to the titaniums is best represented as below.



A similar bent structure has been observed in $[\{Mo(C_5H_5)(NO)I\}_2(NNMe_2)]$.[13] This also has an N–N single bond but the MoNN angle is 135°, whereas in our case Ti(2)–N(11)–N(12) is almost linear [171.4(2)°]. However, the Mo–N bond lengths are similarly unsymmetrical and can be analogously defined in valence-bond terms. The bond angles suggest that N(12) is best described as sp^3 hybridised, and that Ti(1)–N(12) is then formally written $N \rightarrow Ti$. However, the hybridisation about N(11), which exhibits an almost perfect T-shaped coordination, is not so easy to describe.

The side-on structure is not unique, but the occurrence of side-on and simple bridges in the same structure has not been observed before. The TiNN ring associated with this side-on hydrazide is strikingly similar to the TiNN ring already demonstrated in $[Ti(C_5H_5)Cl_2(NPhNH_2)]$ whose dimensions are shown in Figure 2. The principal difference concerns the

Table 2. Selected bond lengths (Å) and angles (°) in $[\{Ti(C_5H_5)Cl(NNPh_2)\}_2]$ with estimated standard deviations in parentheses

Ti(1)–Ti(2)	2.831(1)	Ti(1)–cp1*	2.043(4)
		Ti(2)–cp2*	2.044(6)
Ti(1)–Cl(1)	2.294(1)		
Ti(2)–Cl(2)	2.347(1)	N(11)–N(12)	1.383(3)
		N(21)–N(22)	1.390(4)
Ti(1)–N(11)	2.025(2)		
Ti(1)–N(12)	2.272(2)	N(12)–C(13a)	1.471(4)
Ti(1)–N(21)	1.983(2)	N(12)–C(13b)	1.466(4)
Ti(2)–N(11)	1.819(2)	N(22)–C(23a)	1.430(5)
Ti(2)–N(21)	1.903(3)	N(22)–C(23b)	1.434(4)
Cl(1)–Ti(1)–N(11)	111.6(1)	Ti(1)–N(11)–N(12)	81.3(1)
Cl(1)–Ti(1)–N(12)	94.1(1)	Ti(1)–N(11)–Ti(2)	94.7(1)
N(11)–Ti(1)–N(12)	37.0(1)	N(12)–N(11)–Ti(2)	171.4(2)
Cl(1)–Ti(1)–N(21)	103.2(1)	Ti(1)–N(12)–N(11)	61.7(1)
N(11)–Ti(1)–N(21)	81.8(1)	Ti(1)–N(12)–C(13a)	119.2(2)
N(12)–Ti(1)–N(21)	117.9(1)	N(11)–N(12)–C(13a)	114.4(2)
Cl(1)–Ti(1)–cp1*	112.6(1)	Ti(1)–N(12)–C(13b)	124.6(2)
N(11)–Ti(1)–cp1*	128.7(1)	N(11)–N(12)–C(13b)	114.2(2)
N(12)–Ti(1)–cp1*	115.3(1)	C(13a)–N(12)–C(13b)	112.0(2)
N(21)–Ti(1)–cp1*	111.6(1)		
		Ti(1)–N(21)–Ti(2)	93.5(1)
N(11)–Ti(2)–Cl(2)	99.3(1)	Ti(1)–N(21)–N(22)	128.1(2)
N(11)–Ti(2)–N(21)	89.6(1)	Ti(2)–N(21)–N(22)	138.1(2)
Cl(2)–Ti(2)–N(21)	107.9(1)	N(21)–N(22)–C(23a)	118.9(3)
N(11)–Ti(2)–cp2*	127.1(2)	N(21)–N(22)–C(23b)	117.6(3)
Cl(2)–Ti(2)–cp2*	112.7(2)	C(23a)–N(22)–C(23b)	116.4(3)
N(21)–Ti(2)–cp2*	116.6(2)		

* Centroid of the cyclopentadienyl ring.

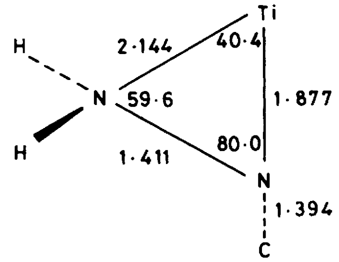


Figure 2. Side-on binding in $[Ti(C_5H_5)Cl_2(NPhNH_2)]$

TiNC axis in one case, and the Ti(1)–N(11)–Ti(2) ensemble in the other (Figures 1 and 2). The Ti–N separation in the hydrazide(1−) is a simple electron-pair bond shortened by some degree of π overlap. In the hydrazide(2−), Ti(1)–N(11) is also an electron-pair bond, but the withdrawal of electron density towards Ti(2), which is a strong interaction, presumably militates against multiple bonding in, and shortening of, Ti(1)–N(11).

The side-on structure of the hydrazide(1−) may actually account for the unusual conformation observed in the hydrazide(2−) complex. If the side-on TiNN interaction is strong it may persist in solution after the hydrazide(1−) has been deprotonated. Consequently, a metastable form or forms of hydrazide(2−) may exist as hydrazide(2−) straightens its conformation. The solid-state structure and the solution n.m.r. data are consistent with this. Of course, form (**a**) below might equally have both NR_2 groups bonded to a single titanium, as in the hydrazido(2−)-complex cited above,[7] but this does not affect the rationalisation.

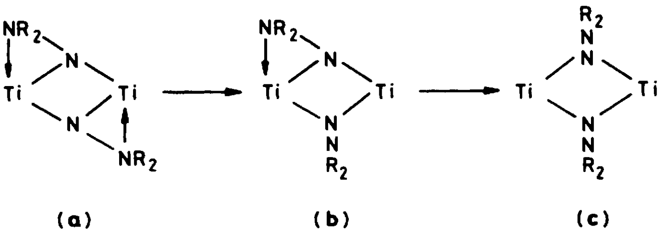


Figure 3 shows some intramolecular contacts within the dinuclear molecule, specifically those involving the phenyl carbons of the side-on hydrazide(2−) and the hydrogen atoms of a cyclopentadienyl ring. An analysis of the thermal parameters of that cyclopentadienyl ring shows that it is much more restricted in its movement than the other; the mean U_{eq} for atoms C(11p)—C(15p) is 0.067 Å^2, whereas for C(21p)—C(25p) it is 0.093 Å^2. The distance between the cyclopentadienyl hydrogens (in idealised positions) and three of the phenyl carbons is *ca.* 2.76 Å, compared with the sum of van der Waals radii of 2.90 Å. In addition, those affected hydrogens [H(12p) and H(13p)] are situated on the face of the phenyl group, and are exposed to the magnetic field arising from the phenyl-ring current. This has two consequences. First, the cyclopentadienyl hydrogens are no longer equivalent. Secondly, the individual hydrogens will show chemical shifts influenced strongly by a paramagnetic contribution from the phenyl ring. To our knowledge, this differentiation of cyclopentadienyl protons has not been observed before.

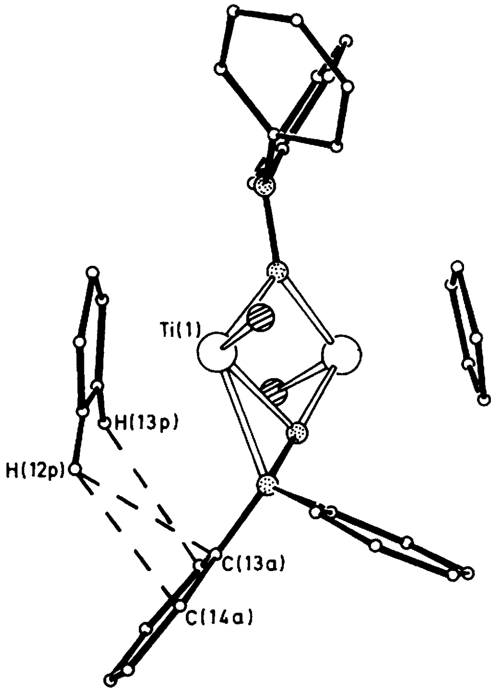


Figure 3. Significant intramolecular interactions between one cyclopentadienyl ring and a phenyl ring in a molecule of $[\{Ti(C_5H_5)Cl(NNPh_2)\}_2]$

The n.m.r. spectra can thus be explained as follows. The initial spectrum of the unrecrystallised material shows cyclopentadienyl resonances attributable to structures (**a**) and (**b**) above, with some of the cyclopentadienyl resonances for (**b**) perturbed into a very broad resonance, which is lost in the background, and a sharp singlet. Recrystallisation yields pure (**b**), and this is the form found in the structure determined. Finally, form (**b**) passes over into (**c**), which has a spectrum of

Table 3. Final atomic co-ordinates (fractional × 10^4) of the non-hydrogen atoms in $[\{\mathrm{Ti(C_5H_5)Cl(NNPh_2)}\}_2]$ plus calculated co-ordinates for two further hydrogen atoms (see text), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Ti(1)	2 837.4(3)	5 089.3(4)	8 237.7(4)
Cl(1)	2 200.0(5)	6 033.9(7)	9 150.9(6)
N(11)	2 888(1)	5 997(2)	7 137(2)
N(12)	3 360(1)	6 658(2)	7 788(2)
C(13a)	4 187(2)	6 660(3)	7 764(2)
C(14a)	4 702(2)	7 252(3)	8 418(2)
C(15a)	5 491(2)	7 247(3)	8 439(3)
C(16a)	5 755(2)	6 636(4)	7 823(3)
C(17a)	5 238(2)	6 043(4)	7 176(3)
C(18a)	4 445(2)	6 067(3)	7 141(2)
C(13b)	3 061(2)	7 790(3)	7 846(2)
C(14b)	3 084(2)	8 258(3)	8 672(3)
C(15b)	2 852(2)	9 379(4)	8 697(3)
C(16b)	2 583(3)	9 961(4)	7 897(4)
C(17b)	2 559(3)	9 477(4)	7 097(4)
C(18b)	2 805(2)	8 392(3)	7 061(3)
C(11p)	3 623(2)	4 380(4)	9 626(3)
C(12p)	4 106(2)	4 650(3)	9 076(3)
C(13p)	3 923(2)	3 976(3)	8 310(3)
C(14p)	3 330(2)	3 272(3)	8 423(3)
C(15p)	3 139(2)	3 526(4)	9 212(3)
Ti(2)	2 152.3(3)	5 178.3(5)	6 364.4(4)
Cl(2)	2 966.1(5)	4 121.8(7)	5 676.7(6)
N(21)	1 979(1)	4 343(2)	7 356(2)
N(22)	1 522(2)	3 452(2)	7 502(2)
C(23a)	1 053(2)	3 580(3)	8 138(2)
C(24a)	968(2)	2 654(3)	8 650(2)
C(25a)	451(3)	2 684(4)	9 195(3)
C(26a)	31(3)	3 632(5)	9 241(3)
C(27a)	133(3)	4 558(4)	8 760(3)
C(28a)	655(2)	4 543(3)	8 211(3)
C(23b)	1 230(2)	2 708(3)	6 763(2)
C(24b)	1 718(2)	2 283(3)	6 281(3)
C(25b)	1 439(2)	1 583(3)	5 557(3)
C(26b)	666(3)	1 287(4)	5 333(3)
C(27b)	174(2)	1 690(3)	5 815(3)
C(28b)	445(2)	2 406(3)	6 532(2)
C(21p)	1 026(3)	4 899(5)	5 190(4)
C(22p)	805(2)	5 357(5)	5 870(4)
C(23p)	1 113(3)	6 401(5)	6 024(3)
C(24p)	1 524(3)	6 571(5)	5 369(5)
C(25p)	1 459(3)	5 591(8)	4 864(3)
H(12p)	4 513	5 223	9 202
H(13p)	4 164	3 995	7 796

the kind originally expected, with two identical, superimposed cyclopentadienyl resonances. Work is continuing to isolate and characterise the two further isomers represented by the structures (**a**) and (**c**).

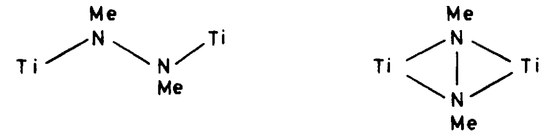
Reactions of 1,1-*Disubstituted Hydrazide*(2 −) *Complexes*.—Preliminary work on the reactions of these complexes with acids suggests that the deprotonation reactions of hydrazide(1 −) complexes are reversible. Thus, $[\{\mathrm{Ti(C_5H_5)Cl(NNR_2)}\}_2]$ (R = Me or Ph) react with 1 mol equivalent of HCl or HI to yield $[\mathrm{Ti(C_5H_5)Cl(X)(NHNR_2)}]$ (X = Cl or I). The products were not obtained analytically pure (see Experimental section) but yields are of the order of 80%. This means that unlike the complexes $[\mathrm{MBr(NNH_2)(dppe)_2}]^+$ (M = Mo or W),[14] $\mathrm{NNR_2}^{2-}$ in these systems can be protonated to give hydrazide(1 −) and then hydrazine, with no indication of N–N bond breaking. A closer parallel may be with the reactions of $[\mathrm{MBr_2(NNH_2)(PMe_2Ph)_3}]$[15] (although the $\mathrm{NNR_2}$ homologues of such species are not known) and $[\mathrm{Mo(NNMePh)_2(S_2CNMe_2)_2}]$.[16]

Preparation of 1,2-*Disubstituted Hydrazide*(2 −) *Complexes*.—We have also prepared examples (Table 1) of 1,2-disubstituted hydrazido-complexes by the route (2). A pure material was

$$2[\mathrm{Ti(C_5H_5)Cl_3}] + \begin{array}{c}\mathrm{Me_3SiNMeNHMe}\\ \text{or}\\ \mathrm{Li(NPhNPh)Li}\end{array} \longrightarrow$$
$$[\{\mathrm{Ti(C_5H_5)Cl_2}\}\mathrm{NRNR}\{\mathrm{Ti(C_5H_5)Cl_2}\}] \quad (2)$$

isolated only in the case of R = Me, though the compound with R = Ph is clearly formed. These complexes are related to the compounds such as $[\{\mathrm{Mn(C_5H_5)(CO)_2}\}\mathrm{NHNH}\{\mathrm{Mn(C_5H_5)(CO)_2}\}]$ described by Sellmann and co-workers.[17] These latter complexes are generally obtained by oxidation of bridging hydrazine; they react with acids to regenerate hydrazine, and they also suggest a tendency to disproportionate to give $\mathrm{N_2}$ and $\mathrm{N_2H_4}$, possibly co-ordinated.[17] Such disproportionations would not be expected in our alkylated systems.

The ^{1}H n.m.r. spectrum of $[\{\mathrm{Ti(C_5H_5)Cl_2}\}_2\mathrm{NMeNMe}]$ is complex and not yet understood. The cyclopentadienyl resonances appear as three singlets, all sharp, and the NMe resonances are similarly split into three. The overall integrations are in the expected ratio 10:6. The NMeNMe residue can conceivably bridge in two ways, as represented below. Either could give rise to isomers, which could explain the n.m.r. spectra. Unfortunately, we have not yet been able to grow crystals of a quality adequate for *X*-ray structural analysis.



Experimental

All operations were carried out using standard Schlenk-tube or glove-box techniques. Solvents were distilled from drying agents prior to use. The compounds $[\mathrm{Ti(C_5H_5)Cl_3}]$[18] and the various trimethylsilylhydrazines[19] were prepared by literature methods. All other compounds were obtained commercially.

The following instruments were used: i.r., Pye-Unicam SP2000 and SP3-200; n.m.r., JEOL FX90Q. Molecular weights were determined cryoscopically in benzene. Analyses were by Mr. C. J. Macdonald, AFRC Unit of Nitrogen Fixation.

Di-μ-phenylhydrazido(2 −)-*bis*[*chloro*(*cyclopentadienyl*)*titanium*].—The complex $[\mathrm{Ti(C_5H_5)Cl_2(NPhNH_2)}]$ (2.0 g, 6.9 mmol) was dissolved in dichloromethane (60 cm^3) and $\mathrm{NH_2Bu^t}$ (0.7 cm^3, 6.9 mmol) was added. The red solution was stirred for 48 h at 20 °C. A white solid was removed by filtration and subsequently shown to be $[\mathrm{NH_3Bu^t}]\mathrm{Cl}$ on the basis of analysis and i.r. spectroscopy. The filtrate was taken to dryness at 10^{-3} mmHg (*ca.* 0.133 Pa), yielding a dark brown *solid* which was washed with hexane (30 cm^3) and dried *in vacuo*. Yield 1.50 g, 85%.

Di-μ-1,1-*diphenylhydrazido*(2 −)-*bis*[*chloro*(*cyclopentadienyl*)*titanium*].—Diphenylhydrazinium chloride (4.0 g, 18 mmol) was suspended in toluene (100 cm^3) and a 1.6 mol dm^{-3} solution in hexane of LiBu^n (23 cm^3, 36 mmol) was added. The solution was heated for 1 h until vigorous reaction had ceased, and then [Ti(C$_5$H$_5$)Cl$_3$] (4.0 g, 18 mmol) and a further 18 mmol of LiBu^n solution (11.5 cm^3) added. The mixture immediately turned red-brown. It was heated at 80 °C for 0.5 h, and then filtered, and the pale brown solid extracted with toluene, to leave a white residue of LiCl. The extract was evaporated at 10^{-3} mmHg to give an oily solid. This was dissolved in dichloromethane (25 cm^3) and hexane (60 cm^3) added. The resultant *solid* was filtered off and dried *in vacuo*. Yield 3.6 g, 60%. Recrystallisation from toluene–hexane at 20 °C afforded red crystals, m.p. 192—194 °C.

Di-μ-1,1-*dimethylhydrazido*(2 −)-*bis*[*chloro*(*cyclopentadienyl*)*titanium*].—Yellow [Ti(C$_5$H$_5$)Cl$_2$(NHNMe$_2$)] (0.2 g, 0.83 mmol) was dissolved in toluene (25 cm^3) and a 0.55 mol dm^{-3} solution of LiBu^n in hexane (1.5 cm^3, 0.83 mmol) added. The solution turned brown in *ca.* 3 min and was stirred at 18 °C for 18 h. The mixture was filtered to remove LiCl and the filtrate taken to dryness at 10^{-3} mmHg. The brown solid was recrystallised as orange *crystals* from dichloromethane–diethyl ether. Yield 0.1 g, 58%; m.p. 163 °C (decomp.).

μ-1,2-*Dimethylhydrazido*(2 −)-*bis*[*chloro*(*cyclopentadienyl*)-*titanium*].—The reaction of Me$_3$SiNMeNHMe (0.3 cm^3, 0.2 mmol) with [Ti(C$_5$H$_5$)Cl$_3$] dissolved in dichloromethane (25 cm^3) produced an immediate bright yellow precipitate. The mixture was stirred at 20 °C for 1 h, and hexane (50 cm^3) then added to produce a fine yellow *powder*. This was recrystallised from toluene as yellow microcrystals. Yield 0.58 g (60%).

μ-1,2-*Diphenylhydrazido*(2 −)-*bis*[*chloro*(*cyclopentadienyl*)-*titanium*].—A mixture of LiNPhNPhLi (0.72 g, 3.0 mmol) and [Ti(C$_5$H$_5$)Cl$_3$] (0.83 g, 3.8 mmol) in diethyl ether (30 cm^3) produced rapidly a dark brown suspension in a yellow-brown solution. This was stirred at 20 °C for 18 h. The *solid* was filtered off and reprecipitated from dichloromethane–diethyl ether as an amorphous brown powder.

Reactions of Monosubstituted and 1,1-*Disubstituted Hydrazido*(2 −)-*complexes with Acid*.—The brown solution of [{Ti(C$_5$H$_5$)Cl(NNMe$_2$)}$_2$] (0.71 g, 1.6 mmol) in toluene (36 cm^3) was allowed to react with a solution of HI generated from SiMe$_3$I (0.48 cm^3, 3.2 mmol) and ethanol (0.20 cm^3, 3.2 mmol) in toluene (10 cm^3). The orange mixture was stirred at 20 °C for 3 h, the volume reduced to 5 cm^3 at 10^{-3} mmHg, and pentane added. The bright orange precipitate was not analytically pure. However, the i.r. spectrum did not differ in any considerable degree from that of [Ti(C$_5$H$_5$)Cl$_2$(NHNMe$_2$)], and the product is probably impure.

The reaction of [{Ti(C$_5$H$_5$)(NNHPh)}$_2$] under similar conditions gave an 80% yield of a red-brown solid, formulated as *chloro*(*cyclopentadienyl*)*iodo*[*phenylhydrazido*(1 −)]*titanium* (Found: C, 33.1; H, 3.7; N, 7.2. C$_{11}$H$_{12}$ClIN$_2$Ti requires C, 34.6; H, 3.1; N, 7.3%). The i.r. spectrum is virtually superimposable upon that of [Ti(C$_5$H$_5$)Cl$_2$(NPhNH$_2$)]. Analogous reactions with HCl regenerated the compounds [Ti(C$_5$H$_5$)Cl$_2$(NR^1-NR^{2}R^3)] (R^1 = Ph, R^2 = R^3 = H; and R^1 = H, R^2 = R^3 = Me).

Reaction of toluene solutions of the phenylhydrazido(2 −)-species (*ca.* 1 mmol in 10 cm^3) with anhydrous HCl in excess (*ca.* 10 mmol, generated from SiMe$_3$Cl and EtOH) gave yellow solutions with white precipitates. The precipitates were filtered off, washed with diethyl ether, and dried *in vacuo*. Analysis and i.r. spectroscopy confirmed that the solids were [PhNHNH$_3$]Cl (77% yield) and [Ph$_2$NNH$_3$]Cl (87% yield). The filtrates, taken to dryness *in vacuo* and triturated with diethyl ether–pentane, yielded [Ti(C$_5$H$_5$)Cl$_3$], as determined by ^{1}H n.m.r. and i.r. spectroscopy.

Structure Determination of [{Ti(C$_5$H$_5$)Cl(NNPh$_2$)}$_2$].—The compound was prepared as described above and recrystallised from toluene. The crystals are dark red, almost square prisms, and were mounted in Lindemann capillaries under dinitrogen.

Crystal data. C$_{34}$H$_{30}$Cl$_2$N$_4$Ti$_2$, M = 661.3, monoclinic, space group $P2_1/a$ (equivalent to no. 14), a = 17.683(8), b = 11.979(3), c = 15.295(4) Å, β = 103.97(3)°, U = 3 144 Å^3, Z = 4, D_c = 1.40 g cm^{-3}, F(000) = 1 360, μ(Mo-K_α) = 7.0 cm^{-1}, λ(Mo-K_α) = 0.710 69 Å.

Data collection. After photographic examination, intensity data were recorded on an Enraf–Nonius CAD4 diffractometer in θ—ω scanning mode, with Mo-K_α radiation and graphite monochromator. 3 855 Unique reflections ($1 < \theta < 22°$ at 21 °C) were corrected for Lorenz-polarisation effects, slight crystal deterioration (overall 6%), and absorption.

Structure analysis and refinement. Combination of Patterson and direct methods, followed by electron-density maps, using SHELX routines.[20] The best E map from EEES in the SHELX suite showed a possible arrangement for two Ti atoms (on the $y = \frac{1}{2}$ plane) and two Cl atoms plus their mirror-related images; a Patterson map confirmed the arrangement. Electron-density maps, starting from two Ti atoms plus one Cl atom, produced the remainder of the structure. Refinement in two large-block matrices, by least-squares methods. All non-hydrogen atoms refined anisotropically; H atoms included in calculated positions but with isotropic thermal parameters refined. At convergence, R = 0.044 and R' = 0.055[20] for 3 665 reflections with $I > 0$, weighting scheme: $w = (\sigma_F^2 + 0.005\,36\,F^2)^{-1}$. Scattering factors were from ref. 21. Final difference map showed peaks of maximum intensity *ca.* 0.32 e Å^{-3} in the region of one cyclopentadienyl group.

Refined atomic co-ordinates are in Table 3. All computing was run on the VAX 11/750 machine at the AFRC Glasshouse Crops Research Institute, Littlehampton, using programs, listed in ref. 22, transferred from a Prime 550 computer at Rothamsted Experimental Station, Harpenden.

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