# Hydrazido-complexes of Titanium(IV) with Tris(pyrazolyl)borates. Crystal Structures of $[TiLCl_2(NMeNMe_2)]$ and $[TiLCl_2(NPhNH_2)]$, L = Tris(pyrazolyl)borate†

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The reactions of $[TiLCl_3]$ [L = tris(pyrazolyl)borate] with $Me_2NNMeH$ and $PhNHNH_2$ yield complexes $[TiLCl_2(NMeNMe_2)]$ and $[TiLCl_2(NPhNH_2)]$, whose crystal structures have been determined. They are very similar to the homologous $C_5H_5$ derivatives, with side-on binding of the hydrazido(1 −)-moiety.

We have shown how hydrazide(1 −) and hydroxylamide(1 −) bond to the moiety $Ti(C_5H_5)Cl_2$ in a side-on fashion.[1,2] However, we initially experienced difficulty when trying to extend this chemistry to the corresponding tris(pyrazolyl)borato-derivatives. In this paper we now report some completely characterized hydrazido(1 −)-complexes of titanium(IV) containing pyrazolylborates.

## Results

The reaction of $[TiLCl_3]$ [L = tris(pyrazolyl)borate] with $Me_2NNMeH$ in tetrahydrofuran (thf) gives a mixture of products including both $[TiLCl_2(NMeNMe_2)]$ (**1**) (red) and $[NHMe_2NHMe][TiLCl_3]$ (blue), and some white uncharacterized material. The best and purest sample of (**1**), characterized structurally, was obtained from a reaction carried out at room temperature, and the blue product was generated only at −60 °C. Reaction of the tris(3,5-dimethylpyrazolyl)borato-analogue $[TiL'Cl_3][L'$ = tris(3,5-dimethylpyrazolyl)borate] gave only $[NHMe_2NHMe][TiL'Cl_3]$, as described earlier.[1]

Analogous reactions with phenylhydrazine rather than trimethylhydrazine yielded samples of phenylhydrazido(1 −)-complexes $[TiLCl_2(NPhNH_2)]$ (**2**) and $[TiL'Cl_2(NPhNH_2)]$. This formulation, rather than that containing the alternative, expected hydrazide(1 −) anion, $PhNHNH^-$, is based on the *X*-ray crystal structure determination of the former (see below) and on that of $[Ti(C_5H_5)Cl_2(NPhNH_2)]$.[3] In order to obtain further insights into the relative ligating abilities of L, L′, and $C_5H_5$, we also obtained electrochemical data for $[Ti(C_5H_5)Cl_3]$, $[TiLCl_3]$, and $[TiL'Cl_3]$.

*Crystal Structure of Dichloro[trimethylhydrazido(1 −)][tris(pyrazolyl)borato]titanium(IV)* (**1**).—Figure 1 shows the structure of this molecule. Atomic co-ordinates are in Table 1 and selected bond dimensions in Table 2. The structure is very similar to that of $[Ti(C_5H_5)Cl_2(NMeNMe_2)]$,[4] with the $C_5H_5$ ring replaced by the tris(pyrazolyl)borate ligand which occupies three *facial* sites in the pseudo-octahedral complex. The dimensions of the two complexes are compared in Table 3. The hydrazido(1 −)-ligand lies in the plane of the pyrazolyl group *trans* to it, giving the molecule approximate mirror symmetry. All intermolecular distances are consistent with van der Waals contacts.

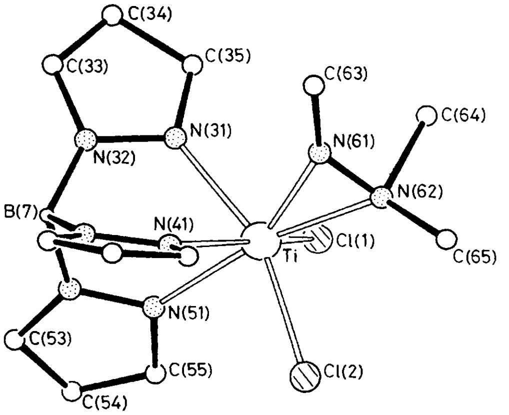

**Figure 1.** View of a molecule of $[TiLCl_2(NMeNMe_2)]$ (**1**) showing the atomic numbering scheme

*Crystal Structure of Dichloro[*N*-phenylhydrazido(1 −)-*N*][tris(pyrazolyl)borato]titanium(IV)* (**2**).—This molecule crystallizes as a hydrogen-bonded dimer (Figure 2) in which the two halves are related by a centre of symmetry. The atomic coordinates are in Table 4, and molecular dimensions are in Table 5. The corresponding cyclopentadienyl complex, $[Ti(C_5H_5)Cl_2(NPhNH_2)]$[3] has a very similar dimeric structure; dimensions are compared in Table 3. The alignment and orientation of the hydrazido(1 −)-ligand are typical of those we have found in this series of titanium complexes, and in agreement with the electronic interactions proposed by Latham *et al.*[3]

## Discussion

We have shown that the $TiLCl_2$ and $TiL'Cl_2$ moieties are capable of supporting the same kind of chemistry as $Ti(C_5H_5)Cl_2$.[1] However, reactions are often complicated by breakdown of the L and L′ ligands, leading to a variety of other complexes incorporating, for example, pyrazolyl residues, as well as the general decomposition products. We are not able to predict what will happen in any given case.

The data of Table 6 show that all the trihalides undergo one-

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† Dichloro[trimethylhydrazido(1 −)]- and dichloro[*N*-phenylhydrazido(1 −)-*N*]-[tris(pyrazolyl)borato]titanium (IV).

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

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

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Ti | 1 533(2) | 1 747(2) | 1 551(1) |
| Cl(1) | −233(3) | 1 337(3) | 1 576(2) |
| Cl(2) | 1 504(4) | 2 794(4) | 2 456(2) |
| N(31) | 1 608(10) | 1 184(8) | 485(6) |
| N(32) | 2 004(10) | 1 662(8) | −86(6) |
| C(33) | 1 977(13) | 1 120(11) | −661(7) |
| C(34) | 1 591(13) | 352(11) | −510(8) |
| C(35) | 1 355(13) | 403(11) | 247(8) |
| N(41) | 3 001(10) | 2 327(8) | 1 213(6) |
| N(42) | 3 188(9) | 2 655(8) | 572(5) |
| C(43) | 4 181(12) | 2 957(10) | 548(7) |
| C(44) | 4 639(14) | 2 789(11) | 1 180(8) |
| C(45) | 3 893(13) | 2 400(11) | 1 592(7) |
| N(51) | 924(10) | 2 866(9) | 907(6) |
| N(52) | 1 347(10) | 3 132(9) | 298(7) |
| C(53) | 827(14) | 3 833(12) | −12(9) |
| C(54) | −25(15) | 3 977(12) | 448(8) |
| C(55) | 74(13) | 3 409(11) | 1 015(8) |
| B(7) | 2 341(16) | 2 600(14) | 25(9) |
| N(61) | 2 309(15) | 662(12) | 1 778(9) |
| N(62) | 1 762(15) | 744(13) | 2 307(10) |
| C(63) | 3 207(19) | 118(17) | 1 647(11) |
| C(64) | 1 257(19) | −270(16) | 2 189(12) |
| C(65) | 2 123(16) | 849(14) | 3 050(10) |

**Table 2.** Selected molecular dimensions (lengths in Å, angles in °) in complex (**1**) with e.s.d.s in parentheses

| | | | |
|---|---|---|---|
| (*a*) About the Ti atom | | | |
| Ti–Cl(1) | 2.350(5) | Ti–Cl(2) | 2.342(5) |
| Ti–N(31) | 2.204(12) | Ti–N(41) | 2.175(13) |
| Ti–N(51) | 2.229(13) | | |
| Ti–N(61) | 1.965(19) | Ti–N(62) | 2.112(19) |
| Cl(1)–Ti–Cl(2) | 98.5(2) | Cl(2)–Ti–N(61) | 114.0(5) |
| Cl(1)–Ti–N(31) | 87.7(3) | N(31)–Ti–N(61) | 82.0(6) |
| Cl(2)–Ti–N(31) | 160.2(4) | N(41)–Ti–N(61) | 87.8(7) |
| Cl(1)–Ti–N(41) | 161.4(4) | N(51)–Ti–N(61) | 158.5(6) |
| Cl(2)–Ti–N(41) | 87.7(3) | Cl(1)–Ti–N(62) | 86.1(5) |
| N(31)–Ti–N(41) | 81.1(4) | Cl(2)–Ti–N(62) | 88.9(6) |
| Cl(1)–Ti–N(51) | 82.6(4) | N(31)–Ti–N(62) | 110.4(6) |
| Cl(2)–Ti–N(51) | 83.7(4) | N(41)–Ti–N(62) | 111.7(6) |
| N(31)–Ti–N(51) | 78.4(4) | N(51)–Ti–N(62) | 165.5(6) |
| N(41)–Ti–N(51) | 80.6(5) | N(61)–Ti–N(62) | 35.1(6) |
| Cl(1)–Ti–N(61) | 105.4(6) | | |
| (*b*) In the hydrazido(1 −) ligand | | | |
| N(61)–N(62) | 1.236(19) | N(62)–N(61)–C(63) | 130.9(20) |
| N(61)–C(63) | 1.437(24) | N(61)–N(62)–C(64) | 91.0(16) |
| N(62)–C(64) | 1.676(31) | N(61)–N(62)–C(65) | 127.4(19) |
| N(62)–C(65) | 1.499(21) | N(64)–N(62)–C(65) | 110.1(16) |

electron reversible reduction processes on the electrochemical time-scale in MeCN, if not in thf. The cyclopentadienyl complex is less easily reducible than the pyrazolylborate complexes by *ca.* 400 mV, which suggests that the cyclopentadienyl is a better donor. This may be why the pyrazolylborate complexes are reducible to titanium(III) species by trimethylhydrazine. Such a conclusion is at variance with i.r. data on complexes [MoL$(CO)_3]^-$ and $[Mo(C_5H_5)(CO)_3]^-$, which suggest the opposite order of donor power.[5] On the other hand $[MoL(CO)_3H]$ is a stronger acid than $[Mo(C_5H_5)(CO)_3H]$,[6] consistent with our findings. The data are not unambiguous, and there may be an as yet undefined metal dependence.

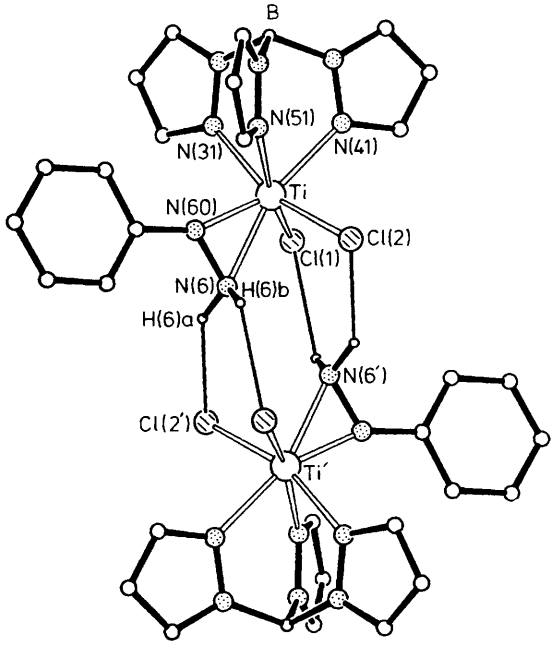

**Figure 2.** View of a hydrogen-bonded dimer pair of $[TiLCl_2(NPhNH_2)]$ (**2**)

When titanium hydrazide complexes do form, they are very similar to their cyclopentadienyl homologues. In the $NPhNH_2$ systems the positions of all the NH hydrogen atoms are indicated by the N···Cl alignments (Figure 2) which are clearly a consequence of hydrogen bonding. This hydrogen bonding is presumably the driving force for the 1,2-hydrogen shifts.[3] However, there do seem to be occasional differences between comparable bond lengths in the complexes containing $C_5H_5$ and those containing L (Table 3). Thus the pyrazolylborato-complexes have slightly longer Ti–Cl separations. In all cases the distance from titanium to $N(R_2)$ is longer than that from titanium to N(R). This is consistent with the formulation we have adopted, in which the latter bond is presented as $Ti \leftrightharpoons NR$.[1] There are no real differences in comparable Ti–N separations. These data would appear to support the contention that L and $C_5H_5$ are electronically very similar, even if they do allow different reaction routes to become available.

## Experimental

All compounds were prepared and manipulated under pure dry dinitrogen using pre-dried, air-free solvents. Pyrazole and 3,5-dimethylpyrazole were purchased and used to make potassium salts of the corresponding tris(pyrazolyl)borates by literature methods.[7,8] The complexes $[TiLCl_3]$[8] and $[TiL'Cl_3]$[9] were prepared as described in the literature. Trimethylhydrazine was prepared as described earlier,[10] and phenylhydrazine hydrochloride was purchased. Instruments used: i.r., Pye Unicam SP2000 and SP3-200 with Nujol mulls; n.m.r., JEOL FX90Q. Microanalyses were by Mr. C. J. Macdonald, AFRC IPSR Nitrogen Fixation Laboratory. Electrochemical measurements were undertaken in a conventional three-electrode cell with platinum and mercury-pool electrodes; the supporting electrolyte was 0.2 mol $dm^{-3}$ $[NBu^n{}_4][BF_4]$, and the concentration of the titanium complexes was *ca.* 5 × $10^{-4}$ mol $dm^{-3}$. The data are consistent with diffusion-controlled one-electron reversible reductions in MeCN.

*Dichloro*[*trimethylhydrazido*(1 −)][*tris*(*pyrazolyl*)*borato*]-*titanium*(IV) (**1**).—To a solution of $[TiLCl_3]$ (1.7 g, 4.6 mmol)

**Table 3.** Dimensions (Å) in analogous pairs of hydrazido(1 −)-complexes of titanium(IV)

| Complex | Ti–N(R)* | Ti–N($R_2$) | N–N | Ti–$Cl_A$ | Ti–$Cl_B$ | Ref. |
|---|---|---|---|---|---|---|
| $[Ti(C_5H_5)Cl_2(NMeNMe_2)]$ | 1.837(3) | 2.210(3) | 1.408(4) | 2.323(1) | 2.323(1) | 2, 5 |
| $[TiLCl_2(NMeNMe_2)]$ (**1**) | 1.965(19) | 2.112(19) | 1.236(19) | 2.350(5) | 2.342(5) | This work |
| $[Ti(C_5H_5)Cl_2(NPhNH_2)]$ | 1.877(9) | 2.144(11) | 1.411(16) | 2.316(4) | 2.315(4) | 3 |
| $[TiLCl_2(NPhNH_2)]$ (**2**) | 1.873(9) | 2.163(10) | 1.391(12) | 2.354(4) | 2.347(4) | This work |

* This is the nitrogen atom carrying the formal negative charge.

**Table 4.** Final atomic co-ordinates (fractional × $10^4$) for complex (**2**) with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Ti | 381(2) | 3 480(1) | 3 571(2) |
| Cl(1) | 1 878(3) | 4 509(2) | 4 031(3) |
| Cl(2) | −1 089(3) | 4 447(2) | 2 720(3) |
| N(31) | 1 588(7) | 2 387(6) | 3 779(8) |
| N(32) | 1 600(7) | 1 725(6) | 2 941(8) |
| C(33) | 2 398(10) | 1 111(9) | 3 384(11) |
| C(34) | 2 889(11) | 1 361(9) | 4 509(11) |
| C(35) | 2 368(9) | 2 162(8) | 4 735(10) |
| N(41) | 741(7) | 3 436(6) | 1 768(8) |
| N(42) | 893(7) | 2 661(7) | 1 163(8) |
| C(43) | 1 134(10) | 2 871(9) | 93(11) |
| C(44) | 1 148(10) | 3 791(9) | 1(12) |
| C(45) | 918(9) | 4 104(9) | 1 045(10) |
| N(51) | −709(8) | 2 368(7) | 2 795(8) |
| N(52) | −393(8) | 1 713(7) | 2 080(9) |
| C(53) | −1 240(11) | 1 083(10) | 1 855(12) |
| C(54) | −2 048(12) | 1 343(9) | 2 402(12) |
| C(55) | −1 712(10) | 2 158(9) | 2 972(11) |
| B | 753(11) | 1 749(10) | 1 777(13) |
| N(6) | −28(8) | 3 995(7) | 5 206(9) |
| N(60) | 76(7) | 3 069(6) | 5 026(8) |
| C(61) | −216(9) | 2 420(9) | 5 817(11) |
| C(62) | −608(9) | 2 671(9) | 6 806(10) |
| C(63) | −902(12) | 2 015(11) | 7 543(13) |
| C(64) | −752(12) | 1 094(11) | 7 336(13) |
| C(65) | −336(11) | 848(12) | 6 343(14) |
| C(66) | −48(11) | 1 499(9) | 5 588(12) |

**Table 5.** Selected molecular dimensions (lengths in Å, angles in °) in complex (**2**) with e.s.d.s in parentheses

| | | | |
|---|---|---|---|
| (*a*) About the Ti atom | | | |
| Ti–Cl(1) | 2.354(4) | Ti–N(51) | 2.186(10) |
| Ti–Cl(2) | 2.347(4) | Ti–N(6) | 2.163(10) |
| Ti–N(31) | 2.166(9) | Ti–N(60) | 1.873(9) |
| Ti–N(41) | 2.188(9) | | |
| Cl(1)–Ti–Cl(2) | 101.4(1) | | |
| Cl(1)–Ti–N(31) | 88.5(3) | Cl(2)–Ti–N(31) | 161.1(3) |
| Cl(1)–Ti–N(41) | 86.4(3) | Cl(2)–Ti–N(41) | 84.8(3) |
| Cl(1)–Ti–N(51) | 163.3(3) | Cl(2)–Ti–N(51) | 86.2(3) |
| Cl(1)–Ti–N(6) | 83.3(3) | Cl(2)–Ti–N(6) | 81.7(3) |
| Cl(1)–Ti–N(60) | 107.0(3) | Cl(2)–Ti–N(60) | 107.1(3) |
| N(31)–Ti–N(41) | 79.8(3) | | |
| N(31)–Ti–N(51) | 80.4(3) | N(41)–Ti–N(51) | 79.4(3) |
| N(31)–Ti–N(6) | 115.8(4) | N(41)–Ti–N(6) | 161.0(4) |
| N(31)–Ti–N(60) | 85.0(4) | N(41)–Ti–N(60) | 159.4(4) |
| N(51)–Ti–N(6) | 112.7(4) | | |
| N(51)–Ti–N(60) | 84.5(4) | N(6)–Ti–N(60) | 39.5(3) |
| (*b*) In the hydrazido(1 −) ligand | | | |
| N(6)–N(60) | 1.391(12) | N(6)–H(6)a | 0.986(19) |
| N(60)–C(61) | 1.410(14) | N(6)–H(6)b | 0.978(19) |
| H(6)a–N(6)–N(60) | 113.3(55) | N(6)–N(60)–C(61) | 122.0(10) |
| H(6)b–N(6)–N(60) | 108.8(55) | N(60)–C(61)–C(62) | 121.4(12) |
| H(6)a–N(6)–H(6)b | 110.3(34) | N(60)–C(61)–C(66) | 118.1(11) |
| (*c*) Hydrogen-bond dimensions | | | |
| N(6) ··· Cl(2′) | 3.386(10) | H(6)a ··· Cl(2′) | 2.53(8) |
| N(6) ··· Cl(1′) | 3.393(10) | H(6)b ··· Cl(1′) | 2.67(8) |
| N(60)–N(6) ··· Cl(2′) | 137.2(7) | N(6)–H(6)a ··· Cl(2′) | 146(7) |
| N(60)–N(6) ··· Cl(1′) | 139.6(7) | N(6)–H(6)b ··· Cl(1′) | 131(6) |

in tetrahydrofuran (thf) (20 $cm^3$) at 210 K was added trimethylhydrazine (0.9 $cm^3$, 9.6 mmol) and the solution stirred magnetically for 1 h at −60 °C when it had become very dark green. After standing at −60 °C for 4 h, this solution was allowed to warm to 20 °C, giving a green liquid and a brown solid, which was filtered off. The solid was recrystallized from dichloromethane–hexane, giving a mixture of red *crystals* ($[TiLCl_2(NMeNMe_2)]$) (**1**) and blue crystals ($[NHMe_2NH\text{-}Me][TiLCl_3]$). No suitable crystallization system could be found, and the crystals were separated by hand [Found (red crystals): C, 35.0; H, 4.6; N, 26.6. $C_{12}H_{19}BCl_2N_8Ti$ requires C, 35.6; H, 4.7; N, 27.7%]. $^1H$ N.m.r. ($CD_2Cl_2$): δ 7.65(d), 6.30(t) (all L); 3.94(s) (NMe), and 2.80(s) ($NMe_2$).

Note that this reaction at 20 °C gives some of the required product, but no $[NHMe_2NHMe][TiLCl_3]$. The analogous reaction employing $[TiL'Cl_3]$ produces $[NHMe_2NHMe]$-$[TiL'Cl_3]$ at room temperature and $[TiL'Cl_2(dmpz)]$ (dmpz = 3,5-dimethylpyrazole) in thf at reflux.

*Dichloro*[N-*phenylhydrazido*(1 −)-N][*tris*(*pyrazolyl*)*borato*]-*titanium*(IV) (**2**).—To a solution of $[TiLCl_3]$ (2.02 g, 5.5 mmol) in thf (30 $cm^3$) was added $PhNHNH_2$ (1.1 $cm^3$, 11 mmol) and the solution stirred. The brown solution was taken to dryness *in vacuo* and dichloromethane (10 $cm^3$) added. Filtration gave a red-brown filtrate which was layered with hexane (40 $cm^3$). The crop of brown *crystals* was filtered off and recrystallized from diethyl ether–hexane (Found: C, 41.7; H, 4.1; N, 23.1. $C_{15}H_{17}BCl_2N_8Ti$ requires C, 41.0; H, 3.9; N, 25.5%). $^1H$ N.m.r. ($CD_2Cl_2$): δ *ca.* 7.7, 6.3(m) (L), and 7.0(m) (Ph).

*Dichloro*[N-*phenylhydrazido*(1 −)-N][*tris*(3,5-*dimethylpyrazolyl*)*borato*]*titanium*(IV).—This was prepared in a similar manner to the tris(pyrazolyl)borato-analogue (Found: C, 48.8; H, 5.5; N, 20.6. $C_{21}H_{30}BCl_2N_8Ti$ requires C, 48.2; H, 5.6; N, 21.0%). $^1H$ N.m.r. ($CD_2Cl_2$): δ 6.91, 6.48(m,5) (Ph), 5.89(s,1) and 5.66(s,2) (L′), 2.75(s,3), 2.46(s,2), and 1.63(s,6) (Me).

X-*Ray Structure Analyses*.—*Compound* (**1**). *Crystal data*: $C_{12}H_{19}BCl_2N_8Ti$, *M* = 404.9, orthorhombic, space group *Pbca* (no. 61), *a* = 12.841(3), *b* = 15.083(4), *c* = 19.074(5) Å, *U* = 3 694.3 Å$^3$, *Z* = 8, $D_c$ = 1.46 g $cm^{-3}$, *F*(000) = 1 664, $\mu(Mo\text{-}K_\alpha)$ = 7.6 $cm^{-1}$, $\lambda(Mo\text{-}K_{\bar{\alpha}})$ = 0.710 69 Å.

Complex (**1**) was obtained as chunky, red, air-sensitive crystals. A single crystal, *ca.* 0.8 × 0.2 × 0.4 mm, was mounted on a glass fibre and coated with epoxy resin. Preliminary photographic examination showed the sample to diffract poorly. On our Enraf-Nonius CAD4 diffractometer (with monochromated Mo radiation) accurate cell dimensions were

**Table 6.** Reduction potentials of titanium complexes *vs.* ferrocenium–ferrocene*

| | thf | | MeCN | |
|---|---|---|---|---|
| Complex | $E_{\frac{1}{2}}$/V | $E_{p(red)} - E_{p(ox)}$/mV | $E_{\frac{1}{2}}$/V | $E_{p(red)} - E_{p(ox)}$/mV |
| $[Ti(C_5H_5)Cl_3]$ | — | — | −0.70 | 80(60) |
| $[TiLCl_3]$ | −0.48 | 90(100) | −0.32 | 60(60) |
| $[TiL'Cl_3]$ | −0.52 | 120(100) | −0.28 | 60(60) |

* Values of $E_{\frac{1}{2}} \pm 0.1$ V; those in parentheses are for ferrocenium–ferrocene under the same conditions.

calculated from the settings of 25 centred reflections having $\theta$ = 14—15°, and diffraction intensities to $\theta_{max.} = 20°$ were measured. The 1 725 unique intensities were corrected for deterioration (steady decrease of monitored reflections to *ca.* 80% of their starting intensities), Lorentz and polarization effects, absorption and negative intensities. These data were entered into the SHELX system[11] for structure determination (by automated Patterson routes in SHELXS[12] and subsequent electron-density maps) and full-matrix least-squares refinement which converged at $R = 0.170$, $R' = 0.191$[11] for all 1 725 reflections with a refined weighting scheme $w = (\sigma_F^2 + 0.00904 F^2)^{-1}$. Using only the 783 reflections with $I > 2\sigma_I$, $R = 0.103$, $R' = 0.111$.

The Ti and Cl atoms were refined anisotropically, and all others isotropically, with some bond lengths in the pyrazolyl and hydrazine ligands restrained towards ideal values. No hydrogen atoms were included. A final difference synthesis showed all features in the range −0.70 to 1.03 e Å$^{-3}$, the only peak of significance lying between the Ti atom and the hydrazine ligand.

*Compound* (**2**). *Crystal data.* $C_{15}H_{17}BCl_2N_8Ti$, $M$ = 439.0, monoclinic, space group $P2_1/n$ (equivalent to no. 14), $a$ = 12.215(3), $b$ = 14.746(3), $c$ = 11.414(3) Å, $\beta$ = 101.40(2)°, $U$ = 2 015.2 Å$^3$, $Z$ = 4, $D_c$ = 1.447 g cm$^{-3}$, $F(000)$ = 896, $\mu$(Mo-$K_\alpha$) = 7.0 cm$^{-1}$.

Crystals of this complex are deep red-brown diamond-shaped prisms and are air-sensitive; most appear to be multiplet crystals. A single crystal, *ca.* 0.17 × 0.21 × 0.36 mm, was sealed under dinitrogen in a capillary for the diffraction measurements which followed a procedure very similar to that described above. The crystal showed signs of slight movement in the capillary and required frequent reorientation during the data collection; one small batch of reflections was considered suspect and ten reflections of this group were later omitted from the data set.

Intensity data for 2 632 unique reflections ($\theta_{max.} = 22.5°$) were entered into the SHELX program[11] for structure determination from a Patterson synthesis (for the Ti atom co-ordinates) and electron-density maps (for the remaining non-hydrogen atoms). Co-ordinates of H atoms on the pyrazolyl and phenyl rings were calculated for idealized positions and were set to ride on those of the bonded C atoms. One hydrazido-H atom was located in a difference map, the position of the second being estimated; both were refined, with geometrical restraints applied. Only the Ti and Cl atoms were allowed anisotropic thermal parameters. Refinement by full-matrix least-squares methods was terminated with $R = R' = 0.090$[11] for 1 558 reflections (those with $I > 2\sigma_I$), weighted $w = (\sigma_F^2 + 0.0011 F_o^2)^{-1}$. A final difference map showed features between −0.57 and 0.73 e Å$^{-3}$, the major peaks lying close to one of the pyrazolyl rings.

For both *X*-ray analyses, scattering factor curves for neutral atoms were taken from ref. 13. Computer programs used, in addition to those noted above, have been listed in Table 4 of ref. 14, and were run on the AFRC VAX 11/750 machine at IHR Littlehampton Laboratory.

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