The Chemistry of Dinitrogen Residues. Part 5.† [Tris(pyrazolyl)borato]-complexes of Titanium(III); the Crystal Structures of Trimethylhydrazinium Trichloro[tris(3,5-dimethylpyrazolyl)borato]titanate(III) and Dichloro(3,5-dimethylpyrazole)[tris(3,5-dimethylpyrazolyl)borato]titanium(III)‡

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The reaction of trichloro[tris(pyrazolyl)borato]titanium(IV) with hydrazines yields titanium(IV) hydrazido(1 –)-species, whereas the corresponding derivative of 3,5-dimethylpyrazole yields titanium(III) compounds which do not contain hydrazine residues. The *X*-ray crystal structures of two of the latter products, trimethylhydrazinium trichloro[tris(3,5-dimethylpyrazolyl)borato]-titanate(III) and dichloro(3,5-dimethylpyrazole)[tris(3,5-dimethylpyrazolyl)borato]titanium(III), are described.

We have recently synthesized several hydrazido-derivatives of titanium(IV) containing the η^5-cyclopentadienyl group.[1] In the furtherance of these studies, aimed at elucidating possible pathways in the protonation of co-ordinated dinitrogen, we turned our attention to tris(pyrazolyl)borato-complexes of titanium(IV), because tris(pyrazolyl)borate can be regarded as a formal analogue of cyclopentadienide when acting as a ligand, occupying three co-ordination sites and donating six electrons to the metal. Consequently, it might be expected to induce a rather similar chemistry in titanium(IV), just as one sees parallel chemistries in cyclopentadienyl- and [tris(pyrazolyl)borato]-molybdenum derivatives.[2]

Results

The cyclopentadienyl complex $[Ti(\eta^5\text{-}C_5H_5)Cl_3]$ reacts with organohydrazines, and with trimethylsilyl or lithium organohydrazides, to give hydrazido(1 –)-complexes $[Ti(\eta^5\text{-}C_5H_5)Cl_2(NR^1NR^2R^3)]$ in which the hydrazide is bound side-on to the titanium. The reaction of the tris(pyrazolyl)borato-complex $[Ti\{BH(C_3H_3N_2)_3\}Cl_3]$[3] with NMe_2NMeH does indeed give rise to $[Ti\{BH(C_3H_3N_2)_3\}Cl_2(NMeNMe_2)]$, which contains a side-bound hydrazide(1 –) moiety,[4] but the reaction of NMe_2NMeH with the 3,5-dimethylpyrazole homologue $[Ti\{BH(C_3HMe_2N_2)_3\}Cl_3]$ does not produce a hydrazido-derivative but a blue, crystalline titanium(III) salt, namely $[NHMe_2NHMe][Ti\{BH(C_3HMe_2N_2)_3\}Cl_3]$. Similarly, reaction of $MePhNNH_2$ did not give the expected hydrazide, but another titanium(III) complex, purple, moderately air-stable $[Ti\{BH(C_3HMe_2N_2)_3\}Cl_2(C_3H_2Me_2N_2)]$, containing neutral pyrazole as a ligand. The structures of these two titanium(III) compounds were determined by *X*-ray crystal structure analysis.

A view of the molecule of $[Ti\{BH(C_3HMe_2N_2)_3\}Cl_2(C_3H_2Me_2N_2)]$ is given in Figure 1, selected bond lengths and angles in Table 1, and fractional atomic co-ordinates in Table 2.

The complex exhibits pseudo-octahedral co-ordination about the titanium, with three nitrogen atoms of the tris(dimethylpyrazolyl)borato-ligand assuming their normal facial tridentate positions. The pyrazolyl rings of the tris(dimethylpyrazolyl)borate are each planar, the normals to these planes intersecting at angles of *ca.* 120°. The co-ordinated dimethylpyrazole is also planar, and this plane is approximately coincident with the plane of the pyrazolyl ring containing N(31) on the opposite side of the titanium atom. The two Ti–N bonds *trans* to the two chlorine atoms are each *ca.* 2.19 Å, as is the Ti–N bond to the dimethylpyrazole. The third Ti–N pyrazolyl bond [to N(31)] is slightly less, 2.146(3) Å, suggesting that N(31) may be the most negative of the three pyrazolyl nitrogens or that the chlorines have a lesser *trans* influence than the pyrazole. However, the dimensions of the pyrazole rings are virtually the same, and give no indications of any differences between the rings in electron density. Further, there is no marked alternation in bond lengths around the rings, each of which has a delocalized electron system. Consequently the effect would seem to be due to *trans* ligands. The dimethylpyrazole itself has bond lengths systematically slightly shorter around the nitrogen atoms than in the pyrazolyls, but still characteristic of ring delocalization.

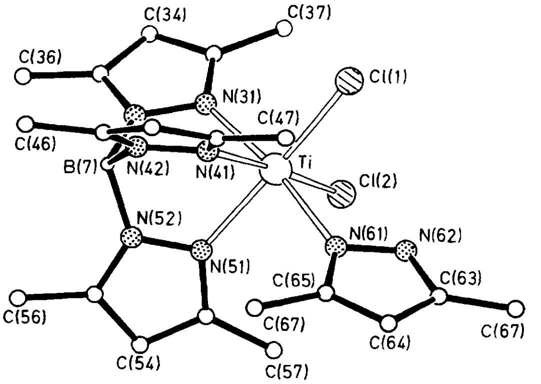

Figure 1. Representation of the molecular structure of $[Ti\{BH(C_3HMe_2N_2)_3\}Cl_2(C_3H_2Me_2N_2)]$

There are no short intermolecular contacts, and the crystal packing appears to be dictated by steric factors and by van der Waals forces.

A view of the complex $[Ti\{BH(C_3HMe_2N_2)_3\}Cl_3]^-$ and of an adjacent $[NHMe_2NHMe]^+$ is given in Figure 2, selected bond lengths and angles in Table 3, and fractional atomic co-ordinates in Table 4.

The complex anion has pseudo-octahedral structure with a

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† Part 4, I. A. Latham and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1986, 399.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Selected molecular dimensions (lengths in Å, angles in °) in $[Ti\{BH(C_3HMe_2N_2)_3\}Cl_2(C_3H_2Me_2N_2)]\cdot 0.5CH_2Cl_2$. Estimated standard deviations (e.s.d.s) are in parentheses

Ti–Cl(1)	2.365(1)	Ti–Cl(2)	2.365(1)
Ti–N(31)	2.146(3)	Ti–N(41)	2.194(3)
Ti–N(51)	2.181(3)	Ti–N(61)	2.187(2)
N(31)–N(32)	1.376(4)	N(41)–N(42)	1.384(4)
N(32)–C(33)	1.352(4)	N(42)–C(43)	1.343(4)
C(33)–C(34)	1.374(6)	C(43)–C(44)	1.367(5)
C(34)–C(35)	1.371(5)	C(44)–C(45)	1.386(5)
N(31)–C(35)	1.345(4)	N(41)–C(45)	1.351(4)
C(33)–C(36)	1.491(7)	C(43)–C(46)	1.505(6)
C(35)–C(37)	1.485(7)	C(45)–C(47)	1.477(6)
N(32)–B(7)	1.536(5)	N(42)–B(7)	1.542(5)
N(51)–N(52)	1.375(4)	N(61)–N(62)	1.359(4)
N(52)–C(53)	1.350(4)	N(62)–C(63)	1.329(4)
C(53)–C(54)	1.372(6)	C(63)–C(64)	1.357(5)
C(54)–C(55)	1.383(5)	C(64)–C(65)	1.381(5)
N(51)–C(55)	1.349(4)	N(61)–C(65)	1.340(4)
C(53)–C(56)	1.480(7)	C(63)–C(66)	1.495(6)
C(55)–C(57)	1.499(6)	C(65)–C(67)	1.499(6)
N(52)–B(7)	1.534(5)		
Cl(81)–C(8)	1.737(8)		
Cl(1)–Ti–Cl(2)	94.7(1)		
Cl(1)–Ti–N(31)	94.4(1)	Cl(1)–Ti–N(41)	89.6(1)
Cl(2)–Ti–N(31)	92.8(1)	Cl(2)–Ti–N(41)	175.5(1)
Cl(1)–Ti–N(51)	174.2(1)	Cl(1)–Ti–N(61)	92.2(1)
Cl(2)–Ti–N(51)	91.1(1)	Cl(2)–Ti–N(61)	88.8(1)
N(31)–Ti–N(41)	85.7(1)	N(41)–Ti–N(51)	84.6(1)
N(31)–Ti–N(51)	85.8(1)	N(41)–Ti–N(61)	92.2(1)
N(31)–Ti–N(61)	173.0(1)	N(51)–Ti–N(61)	87.3(1)
Ti–N(31)–N(32)	118.0(2)	Ti–N(41)–N(42)	117.1(2)
Ti–N(31)–C(35)	134.9(2)	Ti–N(41)–C(45)	136.4(2)
N(32)–N(31)–C(35)	106.7(3)	N(42)–N(41)–C(45)	106.4(3)
N(31)–N(32)–C(33)	109.2(3)	N(41)–N(42)–C(43)	109.3(2)
N(31)–N(32)–B(7)	120.3(2)	N(41)–N(42)–B(7)	119.9(3)
C(33)–N(32)–B(7)	130.5(3)	C(43)–N(42)–B(7)	130.5(3)
N(32)–C(33)–C(34)	107.5(3)	N(42)–C(43)–C(44)	108.4(3)
N(32)–C(33)–C(36)	122.4(4)	N(42)–C(43)–C(46)	123.2(3)
C(34)–C(33)–C(36)	130.0(4)	C(44)–C(43)–C(46)	128.3(4)
C(33)–C(34)–C(35)	107.1(3)	C(43)–C(44)–C(45)	106.6(3)
N(31)–C(35)–C(34)	109.5(3)	N(41)–C(45)–C(44)	109.3(3)
N(31)–C(35)–C(37)	121.6(3)	N(41)–C(45)–C(47)	123.5(4)
C(34)–C(35)–C(37)	128.9(4)	C(44)–C(45)–C(47)	127.2(4)
Ti–N(51)–N(52)	117.6(2)	Ti–N(61)–N(62)	117.8(2)
Ti–N(51)–C(55)	135.7(2)	Ti–N(61)–C(65)	138.0(2)
N(52)–N(51)–C(55)	106.3(3)	N(62)–N(61)–C(65)	104.2(2)
N(51)–N(52)–C(53)	109.6(3)	N(61)–N(62)–C(63)	113.1(3)
N(51)–N(52)–B(7)	120.0(3)		
C(53)–N(52)–B(7)	130.3(3)		
N(52)–C(53)–C(54)	107.9(3)	N(62)–C(63)–C(64)	105.4(3)
N(52)–C(53)–C(56)	123.4(4)	N(62)–C(63)–C(66)	122.3(4)
C(54)–C(53)–C(56)	128.7(4)	C(64)–C(63)–C(66)	132.3(3)
C(53)–C(54)–C(55)	106.5(3)	C(63)–C(64)–C(65)	107.7(3)
N(51)–C(55)–C(54)	109.6(3)	N(61)–C(65)–C(64)	109.6(3)
N(51)–C(55)–C(57)	122.9(3)	N(61)–C(65)–C(67)	122.5(3)
C(54)–C(55)–C(57)	127.5(4)	C(64)–C(65)–C(67)	127.8(3)
N(32)–B(7)–N(42)	109.8(3)		
N(32)–B(7)–N(52)	109.5(3)		
N(42)–B(7)–N(52)	108.3(3)		
Cl(81)–C(8)–Cl(81′)	111.5(8)		

Table 2. Final atomic co-ordinates (fractional × 10^4) in $[Ti\{BH(C_3HMe_2N_2)_3\}Cl_2(C_3H_2Me_2N_2)]\cdot 0.5CH_2Cl_2$. E.s.d.s are in parentheses

Atom	*x*	*y*	*z*
Ti	1 200.0(2)	2 865.2(5)	1 406.0(2)
Cl(1)	1 350.6(5)	678.2(8)	1 436.9(4)
Cl(2)	167.4(4)	2 809.2(9)	1 744.6(4)
N(31)	770(1)	2 879(3)	578(1)
N(32)	964(1)	3 798(3)	242(1)
C(33)	586(2)	3 745(4)	−240(1)
C(34)	160(2)	2 764(4)	−216(2)
C(35)	278(2)	2 257(4)	293(1)
C(36)	653(3)	4 655(7)	−685(2)
C(37)	−55(3)	1 193(6)	532(2)
N(41)	2 141(1)	3 067(2)	1 072(1)
N(42)	2 152(1)	3 831(2)	623(1)
C(43)	2 753(2)	3 802(3)	457(1)
C(44)	3 137(2)	3 017(3)	790(2)
C(45)	2 747(2)	2 571(3)	1 170(1)
C(46)	2 935(3)	4 521(5)	−26(2)
C(47)	2 938(3)	1 688(5)	1 616(2)
N(51)	1 162(1)	4 895(2)	1 354(1)
N(52)	1 386(1)	5 445(2)	908(1)
C(53)	1 395(2)	6 696(3)	971(2)
C(54)	1 171(2)	6 964(3)	1 459(2)
C(55)	1 028(2)	5 833(3)	1 687(1)
C(56)	1 618(3)	7 568(5)	566(2)
C(57)	769(3)	5 616(5)	2 222(2)
B(7)	1 551(2)	4 639(4)	430(2)
N(61)	1 660(1)	3 093(2)	2 238(1)
N(62)	1 413(2)	2 425(3)	2 634(1)
C(63)	1 749(2)	2 574(3)	3 119(1)
C(64)	2 238(2)	3 382(3)	3 040(2)
C(65)	2 172(2)	3 702(3)	2 497(1)
C(66)	1 565(3)	1 924(6)	3 614(2)
C(67)	2 576(2)	4 610(4)	2 216(2)
Cl(81)	502(1)	8 963(3)	2 951(2)
C(8)	0	9 876(13)	2 500

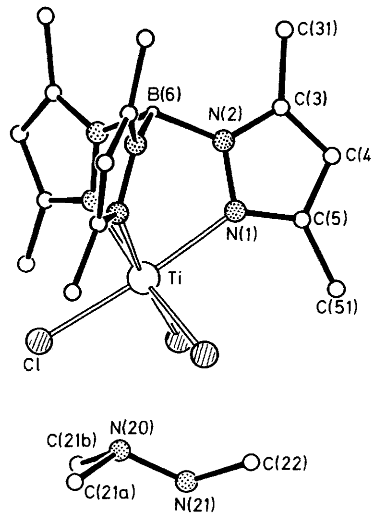

Figure 2. Representation of the structures of the ionic species in $[NHMe_2NHMe][Ti\{BH(C_3HMe_2N_2)_3\}Cl_3]$

precise three-fold rotational axis of symmetry about the B(6)–Ti axis. The pyrazolyl rings are again planar, with dimensions very similar to those described above for the previous complex, and hence they possess delocalized electron systems. The titanium–nitrogen separation [2.179(4) Å] is of the order of the titanium–nitrogen(pyrazolyl) separations of nitrogen *trans* to chlorine in the pyrazole complex. However, the titanium–chlorine separ-

Table 3. Selected molecular dimensions (lengths in Å, angles in °) in $[NHMe_2NHMe][Ti\{BH(C_3HMe_2N_2)_3\}Cl_3]$. E.s.d.s are in parentheses

Ti–Cl	2.401(1)	Ti–N(1)	2.179(4)
N(1)–N(2)	1.376(5)		
N(1)–C(5)	1.347(6)		
N(2)–C(3)	1.343(5)	N(2)–B(6)	1.535(5)
C(3)–C(4)	1.370(7)	C(3)–C(31)	1.497(7)
C(4)–C(5)	1.375(7)	C(5)–C(51)	1.504(7)
N(20)–C(21a)	1.50(2)	N(20)–C(21b)	1.43(2)
N(20)–N(21)	1.45(2)	N(21)–C(22)	1.43(2)
N(1)–Ti–N(1′)	85.3(1)	N(1)–Ti–Cl	174.5(1)
N(1)–Ti–Cl′	91.8(1)	N(1)–Ti–Cl″	89.8(1)
Cl–Ti–Cl′	92.9(1)		
N(2)–N(1)–Ti	116.5(3)	C(5)–N(1)–Ti	136.1(3)
N(2)–N(1)–C(5)	106.0(4)	N(1)–N(2)–B(6)	119.8(4)
N(1)–N(2)–C(3)	109.8(4)	C(3)–N(2)–B(6)	130.0(4)
N(2)–C(3)–C(4)	107.7(4)	C(4)–C(3)–C(31)	129.4(5)
C(3)–C(4)–C(5)	106.8(4)	N(2)–C(3)–C(31)	123.0(5)
N(1)–C(5)–C(4)	109.7(4)	N(1)–C(5)–C(51)	122.4(5)
		C(4)–C(5)–C(51)	127.9(5)
		N(2)–B(6)–N(2′)	109.1(4)
C(21a)–N(20)–C(21b)	98.0(16)	C(21a)–N(20)–N(21)	118.7(13)
C(21b)–N(20)–N(21)	106.3(16)	N(20)–N(21)–C(22)	125.9(16)

ation [2.401(1) Å] is marginally longer than in the former case [2.365(1) Å]. It is difficult to ascribe with certainty reasons for these small differences. However, they may be related to the hydrogen bonding present in this structure but absent in that of the pyrazolyl complex.

The hydrazinium cation, the dimensions of which have been constrained to normal values, shows three-fold disorder about the same rotational symmetry axis. The N $\cdots$ Cl separations are 3.29(1), 3.35(1), and 3.65(1) Å. It is proposed therefore that there are two N–H $\cdots$ Cl hydrogen bonds associated with the two smaller separations, the relative arrangements of the anion and cation determining which two chlorine atoms of the three partake in hydrogen bonding. On average, each chlorine is hydrogen-bonded to the hydrazinium nitrogen in two cases out of three. Other interatomic distances are consistent with van der Waals contacts.

Discussion

There are few titanium(III) structures with which meaningful comparisons can be made. In chloro[*N,N′*-ethylenebis(salicylideneiminato)]pyridinetitanium(III)–tetrahydrofuran (1/1)[5] the structure is essentially octahedral, with Ti–N(pyridine) 2.279(9) and Ti–N(Schiff-base) 2.137(7) and 2.139(9) Å, the last two being marginally shorter than observed here. The Ti–Cl distance [2.418(4) Å] is, in contrast, slightly longer than our values [2.365(1) Å]. The structure of [*N,N*-bis(6-methyl-2-pyridylmethyl)methylamine]trichlorotitanium(III) has the three chlorine atoms in meridional configuration, rather than facial as in our case, with a mean Ti–Cl separation of 2.36 Å.[6] The significance of these differences is not clear. There is one other pyrazolyl complex of titanium(III), $[\{Ti(C_5H_5)_2\}_2(C_3H_3N_2)_2]$, which has pyrazolyl bridging between titanium atoms.[7] This has a shorter N–N separation than in our compound, 1.312(6) compared to 1.359(4) Å, and all the ring dimensions are slightly shorter. This is presumably due to the bridging, involving electron donation to titanium by both nitrogen atoms rather than by just one.

Table 4. Final atomic co-ordinates (fractional × 10^4) in $[NHMe_2NHMe][Ti\{BH(C_3HMe_2N_2)_3\}Cl_3]$. E.s.d.s are in parentheses

Atom	*x*	*y*	*z*
Ti*	3 333	6 667	2 541(1)
Cl	3 935(2)	5 256(2)	3 544(1)
N(1)	2 875(4)	7 904(4)	1 505(3)
N(2)	3 148(4)	7 850(4)	487(3)
C(3)	3 079(5)	8 850(5)	−25(4)
C(31)	3 341(6)	9 078(7)	−1 148(4)
C(4)	2 733(5)	9 550(5)	661(4)
C(5)	2 615(5)	8 947(5)	1 598(4)
C(51)	2 218(9)	9 309(8)	2 599(5)
B(6)*	3 333	6 667	88(6)

Hydrazinium cation, disordered about a three-fold symmetry axis; each atom has a site occupancy factor of 0.3333

N(20)	6 888(16)	3 729(12)	4 352(7)
C(21a)	7 664(22)	3 079(24)	3 918(16)
C(21b)	7 818(27)	5 119(22)	4 049(21)
N(21)	5 567(18)	3 372(20)	3 917(14)
C(22)	4 254(22)	2 320(24)	4 282(19)

* Atom on a three-fold symmetry axis.

There are few poly(pyrazolyl)borato-complexes of titanium(III) or titanium(II) with which we can make comparison.[8] The vast majority of poly(pyrazolyl)borato-complexes are of molybdenum,[2] and a particularly interesting one is $[NEt_4][Mo\{BH(C_3HMe_2N_2)_3\}Cl_3]$.[9] This complex has distorted near-octahedral geometry. The radii of Mo^{III} and Ti^{III} are unlikely to be very different because the corresponding ionic radii are 0.66 (Mo^{4+}) and 0.77 Å (Ti^{3+}).[10] The molybdenum–chlorine [2.433(1) Å] and molybdenum–nitrogen separations [2.198(5) Å], both slightly longer than in the titanium complexes, suggest tighter binding to titanium than molybdenum, especially since the metal radii are probably in the opposite sense. This is unexpected.

More intriguing is the observed reduction of titanium(IV) to titanium(III) by hydrazines. It is puzzling because we were able to isolate a titanium(IV) hydrazido(1−)-complex from the reaction of NMe₂NMeH and $[Ti\{BH(C_3H_3N_2)_3\}_3Cl_3]$.[4] One might have expected a pyrazolylborato-complex to be less electron-rich than the corresponding dimethylpyrazolylborato-complex and consequently easier to reduce. This is clearly not the case. We were actually able to synthesize the titanium(III) pyrazole complex from the reaction of $TiCl_3$, $K[BH(C_3HMe_2N_2)_3]$, and $C_3H_2Me_2N_2$ in tetrahydrofuran (thf), so this complex is reasonably stable, and not a kinetic accident of the reaction conditions. Similarly, we synthesized $[Ti\{BH(C_3HMe_2N_2)_3\}Cl_2(C_3H_4N_2)]$ and $[Ti\{BH(C_3H_3N_2)_3\}Cl_2(C_3H_4N_2)]$.

A further interesting problem concerns the origin of the co-ordinated dimethylpyrazole in the dimethylpyrazoletitanium(III) complex. The reaction of $[Ti\{BH(C_3HMe_2N_2)_3\}Cl_3]$ with $NMePhNH_2$ gives a mixture, one component of which is the purple dimethylpyrazole complex, but this is accompanied by white material which we were unable to characterize. In fact, we were forced to separate the purple crystals of the pyrazole complex mechanically. The breakdown of pyrazolylborates during reactions of complexes has been observed in other circumstances. For example, $[Mo\{BH(C_3HMe_2N_2)_3\}(NO)I_2]$ reacts with acetone to yield an organic material identified[11] as $\text{CMe=CHCMe=N}^{+}\text{CMe}_2\text{CH}_2\text{CMe(OH)N}$, which is clearly a degradation product of 1,3-dimethylpyrazole. The same complex reacts with catechol to yield $[Mo(C_3H_2Me_2N_2)_3(NO)$-

$(OC_6H_4O)]I_3$, which has been characterized structurally.[11] In this case, boron has been abstracted from the tris(pyrazolyl)borate.

A similar observation concerns diethyldipyrazolylborate, which forms complexes apparently less stable than those of dipyrazolylborate.[12] Attempts to prepare $[Mo\{B(C_3H_3N_2)_2Et_2\}(CO)_2(C_3H_5)]$ from $K[B(C_3H_3N_2)_2Et_2]$, $[Mo(CO)_6]$, and allyl bromide in tetrahydrofuran led to the isolation of $[Mo\{B(C_3H_3N_2)_2Et_2\}(CO)_2(C_3H_5)(C_3H_4N_2)]$, in which the pyrazole undoubtedly arises by decomposition of the pyrazolylborate.[12] This may be due to the presence of water, as suggested for the formation of pyrazole from poly(pyrazolyl)borate in other systems,[13] and we cannot exclude the possibility that traces of water are involved in our systems. In addition, it is conceivable that the oxygen-containing solvents used in these reactions may provoke decomposition because of the strong affinity of boron for oxygen. We have succeeded[4] in isolating $[Ti\{BH(C_3H_3N_2)_3\}Cl_2(NMeNMe_2)]$ from trichloro[tris(pyrazolyl)borate]titanium(IV) and trimethylhydrazine, but this is a far from general reaction for all tris(pyrazolyl)borate derivatives. Clearly, it should not be assumed that tris(pyrazolyl)borates will retain their integrity in reactions of their titanium complexes.

A final noteworthy feature of the observations reported here is the isolation of a salt containing the anion $[Ti\{BH(C_3HMe_2N_2)_3\}Cl_3]^-$. This might have been expected to lose a chloride rather rapidly to yield $Ti\{BH(C_3HMe_2N_2)_3\}Cl_2$, possibly dinuclear through halogen bridging or solvated, giving $[Ti\{BH(C_3H_3N_2)_3\}Cl_2(thf)]$.[8] Indeed, e.s.r. studies at 77 K show that $[Ti(C_5H_5)Cl_3]^-$ produced by ^{60}Co γ-irradiation of $[Ti(C_5H_5)Cl_3]$ in methyltetrahydrofuran loses a chloride rapidly and irreversibly on annealing to yield $[Ti(C_5H_5)Cl_2]$,[14] [*cf.* $Ti(C_5H_5)Cl_2$, which forms adducts containing one or two thf molecules].[15] Clearly a comparison of the reductions of $[Ti(C_5H_5)Cl_3]$, $[Ti\{BH(C_3HMe_2N_2)_3\}Cl_3]$, and $[Ti\{BH(C_3H_3N_2)_3\}Cl_3]$ under similar conditions might help to rationalize these different observations. We are currently undertaking an electrochemical study of these systems.[16]

Experimental

Reactions were carried out under dry dinitrogen using standard Schlenk-tube techniques. The following spectrometers were used: i.r., Pye Unicam SP-3, Nujol mulls; n.m.r., JEOL FX-90Q; m.s., Kratos MS80RF/DS55M with fast atom bombardment (f.a.b.) mode; e.s.r., Bruker 200D, in CH_2Cl_2 at 130 K. Trichloro[tris(3,5-dimethylpyrazolyl)borato]titanium(IV)[3] and trimethylhydrazine[17] were prepared according to the literature. All other compounds used were obtained commercially.

Trimethylhydrazinium Trichloro[tris(3,5-dimethylpyrazolyl)borato]titanate(III).—Trimethylhydrazine (0.60 cm^3, 6.2 mmol) was added dropwise with stirring to trichloro[tris(3,5-dimethylpyrazolylborato)]titanium(IV) (1.41 g, 3.1 mmol) dissolved in tetrahydrofuran (25 cm^3). This produced a blue solution which was taken to dryness. The residue was redissolved in CH_2Cl_2 and layered with hexane, producing chunky blue *crystals* at the interface. Yield 1.38 g, 87% (Found: C, 39.2; H, 6.20; Cl, 21.4; N, 20.7. $C_{18}H_{33}BCl_3N_8Ti$ requires C, 41.0; H, 6.25; Cl, 20.3; N, 21.3%). The n.m.r. spectrum in solution in $CDCl_3$ is characteristic of a paramagnetic species. The f.a.b. mass spectrum shows no parent ion, but a strong signal at $m/e = 75$, corresponding to $NHMe_2NHMe^+$. Principal i.r. bands: 2 543 [ν(BH)], 3 129, 3 272 [ν(NH)] cm^{-1}.

Dichloro(dimethylpyrazole)[tris(3,5-dimethylpyrazolyl)borato]titanium(III)*-Dichloromethane* (1/0.5).—(*a*) To $TiCl_3$ (1.13 g, 7.3 mmol) and $K[BH(C_3HMe_2N_2)_3]$ (2.46 g, 7.3 mmol) in thf (20 cm^3) was added $C_3H_2Me_2N_2$ (0.70 g, 7.3 mmol) and the solution stirred for 2 h. The solution was then taken to dryness *in vacuo* and CH_2Cl_2 (10 cm^3) added. The mixture was filtered and then layered with hexane to produce a crop of large purple *crystals* which were separated mechanically from a white impurity (Found: C, 44.4; H, 5.50; N, 19.6. $C_{20.5}H_{31}BCl_3N_8Ti$ requires C, 44.3; H, 5.60; N, 20.2%).

(*b*) To trichloro[tris(3,5-dimethylpyrazolyl)borato]titanium (1.97 g, 4.4 mmol) in thf (50 cm^3) was added 1,1-methylphenylhydrazine (1.02 cm^3, 8.8 mmol) and the mixture stirred for 1 h. The solvent was removed *in vacuo* and CH_2Cl_2 (20 cm^3) was added, giving a purple solution, which yielded a mixture of purple *crystals* and a white solid. The purple crystals were separated mechanically (Found: C, 43.8; H, 5.90; N, 17.9. $C_{20.5}H_{31}BCl_3N_8Ti$ requires C, 44.3; H, 5.60; N, 20.2%).

The ^1H n.m.r. spectrum seemed typical of a paramagnetic species, and only a resonance assignable to CH_2Cl_2 was clearly identified. ν(BH) 2 540 cm^{-1}. E.s.r. (CH_2Cl_2, 130 K): $g_{\parallel} = 1.985$, $g_{\perp} = 1.877$.

Dichloro(pyrazole)[tris(3,5-dimethylpyrazolyl)borato]titanium(III)*-Dichloromethane* (1/0.5).—To $TiCl_3$ (0.43 g, 2.8 mmol), $K[BH(C_3HMe_2N_2)_3]$ (0.94 g, 2.8 mmol), and $C_3H_4N_2$ (0.19 g, 2.8 mmol) was added thf (20 cm^3). The mixture was stirred for 3 h, evaporated to dryness, dissolved in CH_2Cl_2 (10 cm^3), and filtered, and the filtrate layered with hexane (40 cm^3). Purple *crystals* separated over 3 d. These were separated mechanically, washed with hexane, and dried (Found: C, 41.9; H, 5.25; N, 20.5. $C_{18.5}H_{27}BCl_3N_8Ti$ requires C, 42.1; H, 5.10; N, 21.3%). ^1H N.m.r., paramagnetic. ν(BH) 2 540 cm^{-1}. E.s.r. (CH_2Cl_2, 130 K): $g_{\parallel} = 1.982$, $g_{\perp} = 1.884$.

Dichloro(pyrazole)[tris(pyrazolyl)borato]titanium(III)*-Dichloromethane* (1/0.5).—This was prepared as above, on a scale of 10.4 mmol, as purple *crystals* (Found: C, 33.0; H, 3.00; N, 25.3. $C_{12.5}H_{15}BCl_3N_8Ti$ requires C, 33.9; H, 3.40; N, 25.3%). ^1H N.m.r., paramagnetic. ν(BH) 2 530 cm^{-1}. E.s.r. (CH_2Cl_2, 130 K): $g_{\parallel} = 1.968$, $g_{\perp} = 1.888$.

X-Ray Structure Analyses.—$[Ti\{BH(C_3HMe_2N_2)_3\}Cl_2(C_3H_2Me_2N_2)]\cdot 0.5CH_2Cl_2$. Preliminary *X*-ray photographic studies on a single crystal of the purple moderately air-stable product established approximate cell dimensions and the crystal system. Accurate cell dimensions (by refinement from the settings of 25 reflections having $\theta = 10$—$11°$) and intensity data were measured for this crystal (*ca.* 0.21 × 0.17 × 0.38 mm) mounted on a glass fibre and coated with epoxy resin, on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo-K_α radiation.

Crystal data. $C_{20.5}H_{31}BCl_3N_8Ti$, $M = 554.5$, monoclinic, $a = 20.531(8)$, $b = 10.722(4)$, $c = 24.801(9)$ Å, $\beta = 96.25(3)°$, $U = 5\,426.7$ Å^3, space group $C2/c$ (no. 15), $Z = 8$, $D_c = 1.357$ g cm^{-3}, $F(000) = 2\,304$, $\mu(\text{Mo-}K_\alpha) = 6.3$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å.

4 770 Unique reflections with $\theta_{max.} = 25°$ were measured. Corrections for slight crystal deterioration (5.3% overall), Lorentz and polarization effects, absorption (by semiempirical ψ-scan methods), and negative intensities (by Bayesian statistical methods) were applied. Structure analysis was by direct methods with the SHELX program;[18] the routine TANG generated a convergence map and four 'starting' reflections which were then used in the automated EEES routine. *E* Maps showing two superimposed molecular images were produced; an electron-density map, phased by 20 atoms at the midpoints between the two images showed most of the complex molecule. The remaining atoms, including hydrogen atoms, were located in subsequent electron-density and difference Fourier syntheses.

In the full-matrix least-squares refinement, all the non-hydrogen atoms of the complex molecule were refined anisotropically, and the hydrogen atoms isotropically. The solvent dichloromethane lies about a two-fold symmetry axis. The (unique) chlorine atom was refined anisotropically, and the carbon atom isotropically. The final R and R' values were 0.060 and 0.064 for the 4 150 reflections with $I > \sigma_I$ and a refined weighting scheme, $w = [\sigma(F_o)^2 + 0.002\,05F_o^2]^{-1}$. A final difference synthesis showed all the features in the range -0.39 to $+0.63$ e Å^{-3}, the strongest of which is close to the titanium atom.

$[NHMe_2NHMe][Ti\{BH(C_3HMe_2N_2)_3\}Cl_3]$. The analysis was carried out similarly to that described above. The crystal had dimensions of *ca.* 0.4 × 0.2 × 0.2 mm. Intensity data ($2 < \theta < 25°$) were recorded using a ω—θ scan mode.

Crystal data. $C_{18}H_{33}BCl_3N_8Ti$, $M = 526.6$, trigonal, $a = b = 11.225(2)$, $c = 13.099(4)$ Å, $U = 1\,429.2$ Å^3, space group $P\bar{3}$ (no. 147), $Z = 2$, $D_c = 1.22$ g cm^{-3}, $F(000) = 550$, μ(Mo-K_α) = 6.0 cm^{-1}.

1 683 Unique reflections were measured. Corrections for slight crystal deterioration (*ca.* 6% overall) and otherwise as above were applied. The structure was solved using the automatic Patterson method in SHELXS,[19] refinement giving the positions of all the non-hydrogen atoms of the complex anion. The hydrazinium ion (located in subsequent difference Fourier maps) is disordered over three possible sites about a three-fold symmetry axis. The C, N skeleton of one cation position was used to generate those at the two other symmetry-related sites, each site having an occupancy of 1/3. The C–N bond lengths in the cation were constrained to ideal values and no attempt was made to include hydrazinium hydrogen atoms. The non-hydrogen atoms of the anion were refined anisotropically and the hydrogen atoms isotropically, by repeated full-matrix least-squares methods, the CH_3 groups being restrained to ideal geometries. The cation carbon and nitrogen atoms were refined isotropically. At convergence, with all reflections weighted equally, $R = 0.083$. The final difference map showed all features in the range -0.35 to $+0.35$ e Å^{-3}, the strongest peak being located near the hydrazinium cation.

Details of programs (run on the AFRC VAX 11/750 computer at G.C.R.I., Littlehampton) are in Table 4 of ref. 20, and sources of scattering factors are in ref. 21.

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

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