The Chemistry of Dinitrogen Residues. Part 4.[1-3] The Decomposition of Hydrazide(1 −) and Hydrazide(2 −) when bound to Titanium(IV)

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Reaction of $[Ti(C_5H_5)Cl_3]$ with both $Me_3SiNHNHSiMe_3$ and $Li(NHNH_2)$ in tetrahydrofuran yields $[Ti(C_5H_5)Cl_2(thf)]$ and N_2 or NH_3, in proportions depending on the stoicheiometric ratio of the reactants. The results are interpreted in terms of a reductive disproportionation of $NHNH^{2-}$ and $N_2H_3^-$.

The previous three papers[1-3] in this series have described how various alkylated and arylated dinitrogen residues bind to the titanium(IV) in $Ti(C_5H_5)Cl_2^+$. There is a considerable tendency for both nitrogens to bind to the metal, to the extent that the phenyldiazenido-complex is apparently unique in this respect among all diazenido-complexes.[1] These papers provide the background to the basic problem this work is designed to solve, which is the mechanism of protonation of dinitrogen to yield ammonia and hydrazine.[4]

The characteristic mode of bonding of substituted dinitrogen residues NNR^-, $NRNR^{2-}$, NNR_2^{2-}, and $NRNR_2^-$, at least with Ti^{IV} in $Ti(C_5H_5)Cl_2^+$, may not hold for the unsubstituted species NNH^-, $NHNH^{2-}$, NNH_2^{2-}, and $NHNH_2^-$. However, there is no information on these rather inaccessible species, and in the circumstances we can do no better than extrapolate from the substituted examples to the unsubstituted. In addition, there is no parent dinitrogen complex $[Ti(C_5H_5)Cl_2(N_2)]$. Consequently, we cannot study the important first step NN $\longrightarrow$ NNH (or NNR) in this series. However, the subsequent steps from NNH (or rather NNPh) through to a hydrazine have been described in earlier papers, and this constitutes one justification for our choice of system. Another is that we should be able to study the chemistry of the appropriate species without complications of redox reactions arising from metal-to-ligand electron transfer. This paper describes our efforts to characterise $NHNH_2^-$ and $NHNH^{2-}$ when bound to $Ti(C_5H_5)Cl_2^+$.

Results and Discussion

The complex $[Ti(C_5H_5)Cl_3]$ reacts with $Li(NHNH_2)$ or with $Me_3SiNHNHSiMe_3$ in tetrahydrofuran (thf) in a molar ratio of 2:1 with a colour change from yellow to green. The desired complex $[\{Ti(C_5H_5)Cl_2\}_2NHNH]$ was not isolated, but rather $[Ti(C_5H_5)Cl_2(thf)]$, and N_2 plus NH_3, with the stoicheiometry as in reaction (1). Good nitrogen balances were obtained for

$$6[Ti(C_5H_5)Cl_3] + 3Me_3SiNHNHSiMe_3 \text{ (or } LiNHNH_2) \xrightarrow{thf} 6[Ti(C_5H_5)Cl_2(thf)] + 2N_2 + 2NH_3 \quad (1)$$

these reactions as shown by the typical examples quoted in Table 1. The presence of the paramagnetic titanium(III) species was confirmed by e.s.r. spectroscopy. No H_2 was found in any of the reactions and the yields of hydrazine are negligible. The molar ratios of products found for the 2:1 stoicheiometry stated are 0.33. The reaction yields are not the same in $Bu^n{}_2O$ as in thf and more hydrazine and less NH_3 and N_2 are produced. The reaction is not catalytic. Addition of a large excess of hydrazine to $[Ti(C_5H_5)Cl_3]$ in thf produced little NH_3 or N_2, and a black uncharacterisable product. However, even where the total recovery of nitrogen was low, as with $L(NHNH_2)$, the ratio of NH_3 to N_2 was always *ca.* 1:1.

Table 1. Reactions of $[Ti(C_5H_5)Cl_3]$ with $Li(NHNH_2)$ and $Me_3SiNHNHSiMe_3$ in thf, molar ratio 2:1

	Molar ratio of product to titanium compound			Total N recovered/%
	NH_3	N_2H_4	N_2	
$Me_3SiNHNHSiMe_3$	0.34	0.03	0.35	95.0
	0.36	0.05	0.35	93.8
$Li(NHNH_2)$	0.31	0.01	0.30	92.2
	0.34	0.10	0.26	80.0

Labelling experiments using a 30:70 mixture of $^{15}N_2H_4$ and $^{14}N_2H_4$ converted into the lithium hydrazide showed that the N_2 generated contained $^{15}N_2$ and $^{14}N_2$ only, in the 30:70 ratio, with no $^{14}N^{15}N$.

A plausible reaction sequence, based upon the above observations and the chemistry described in Part 3 of this series,[3] is as in equations (2)—(4). However, this cannot define the detailed

$$2[Ti(C_5H_5)Cl_3] + Me_3SiNHNHSiMe_3 \longrightarrow [\{Ti(C_5H_5)Cl_2\}NHNH\{Ti(C_5H_5)Cl_2\}] \quad (2)$$

$$[\{Ti(C_5H_5)Cl_2\}NHNH\{Ti(C_5H_5)Cl_2\}] \longrightarrow N_2H_2 + [\{Ti(C_5H_5)Cl_2\}_2] \quad (3)$$

$$N_2H_2 \longrightarrow \tfrac{2}{3}N_2 + \tfrac{2}{3}NH_3 \quad (4)$$

mechanism of the reaction. Decomposition of free N_2H_2 to give $N_2 + NH_3$ would be unusual. The two-electron oxidation of N_2H_4 produces N_2 plus N_2H_4 *via* free N_2H_2.[5] The disproportionation of complexed N_2H_2 in $[\{M(C_5H_5)(CO)_2\}_2\text{-}N_2H_2]$ (M = Mn or Re) to yield $[M(C_5H_5)(CO)_2(N_2)]$ and $[M(C_5H_5)(CO)_2(NH_3)]$ has been reported by Sellmann and co-workers.[6,7] Consequently, in our case the N_2H_2 is probably complexed, although whether it is better to represent it as hydrazide (2 −), or as diazene as in the compounds of Sellmann, is perhaps open to question. In view of the preparative route, we provisionally regard it as the former. A significant aspect of the reaction would appear to be the reduction of the Ti^{IV} to Ti^{III}, so that the overall process is represented as in equation (5).

$$6Ti^{IV} + 3NHNH^{2-} \longrightarrow 2N_2 + 2NH_3 + 6Ti^{III} \quad (5)$$

However, the stoicheiometry of the products, but not their nature, is affected by the stoicheiometry of the reactants. If the Ti^{IV}:hydrazide ratio is not 2:1, but rather 1:1, the ratio N_2:NH_3 is not 1:1 but 1:2.

As described earlier, the reaction of $[Ti(C_5H_5)Cl_3]$ with $Me_3SiNHNHSiMe_3$ (1:1) gives rise to an unstable complex

Table 2. Reactions of $[Ti(C_5H_5)Cl_3]$ with $Li(NHNH_2)$ and $Me_3SiNHNHSiMe_3$, molar ratio 1 : 1

	Molar ratio of product to titanium compound			Total N recovered/ %
	NH_3	N_2H_4	N_2	
$Me_3SiNHNHSiMe_3$	0.79	0.01	0.46	88
	0.86	0.02	0.47	93
	0.86	0.01	0.47	93
	0.85	0.000(2)	0.46	90
$Li(NHNH_2)$	1.01	0.01	0.46	>85
	0.98	0.01	0.50	>85
	0.80	0.009	0.46	88

$[Ti(C_5H_5)Cl_2(NHNHSiMe_3)]$.[2] In solution in thf decomposition is complete within a matter of hours, compared with weeks in the solid state. With $Li(NHNH_2)$ the reaction is also rapid, but there is no sign of an intermediate. The gaseous product is N_2 (no H_2), and $[\{Ti(C_5H_5)Cl_2\}_2]$ (or its thf adduct) and NH_3 were also identified. There was little hydrazine. The observations are illustrated by typical data presented in Table 2. The reproducibility of these results is high. The metal-containing product is paramagnetic (e.s.r.) but always contained some nitrogen before hydrolysis to release the ammonia. Conceivably, therefore, nitrido-, amido-, or imido-species are primary products. The yield of ammonia (but not of N_2) in the reactions with $Li(NHNH_2)$ shows a dependence upon reaction time. After 18 h of reaction we recovered *ca.* 20% of the expected amount of NH_3; after 40 h the recovery was 100%. This is further evidence for the formation of a nitrogen-containing titanium complex which releases ammonia rather slowly. Nitrogen-labelling experiments as detailed above showed that no new N–N bonds were formed upon generating the N_2.

Decomposition of the complex formulated as $[Ti(C_5H_5)Cl_2(NHNHSiMe_3)]$[2] in thf produces N_2 and NH_3 in ratios approaching 1 : 2. The material also breaks down in the presence of 1 mol equivalent of $[Ti(C_5H_5)Cl_3]$, though the $N_2 : NH_3$ ratio was not reproducible.

These data are best accommodated by equation (6). This

$$2Ti^{IV} + 2NHNH_2^- \longrightarrow N_2 + 2NH_3 + 2Ti^{III} \qquad (6)$$

summarises several mechanistic steps and a hydrolysis, and is a purely formal representation. The immediate conclusion from these data is that both $NHNH^{2-}$ and $NHNH_2^-$ are unstable when bound to titanium(IV) and that they break down by a route which involves reduction to titanium(II) and some kind of multimolecular disproportionation of the dinitrogen residue.

The relevance of these observations to nitrogen-fixation reactions, and to the field of hydrazine chemistry, is considerable. Disproportionations have been invoked by Schrauzer and co-workers [8] to explain their observations on the conversion of N_2 into N_2H_4 and NH_3 *via* N_2H_2 (diazene), and N_2H_2 has been shown independently[9] to react with itself to generate $N_2 + N_2H_4$. However, what we observe here is rather different.

It is well established that the protonation of terminally co-ordinated N_2 to yield ammonia passes through a hydrazido-(2−)-stage, *viz.* $=NNH_2$.[10] Little is known about the intermediates between NNH_2 and NH_3. George and co-workers[11] have demonstrated that $[Mo(NNH_2)Br(PPh_3)\{(Ph_2PCH_2CH_2)_2PPh\}]^+$, a formal molybdenum(IV) complex, reacts with acid to yield $[MoBr_3\{(Ph_2PCH_2CH_2)_2PPh\}]$, and N_2 and NH_3 in the molar ratio 1 : 2. Richards[12] has shown by labelling experiments that there is no N–N bond making in the protonation of $[Mo(NNH_2)Br_2(PMe_2Ph)_3]$, which produces N_2 and NH_3 in the same ratio, and also generates a molybdenum(III) product. The analogy with our titanium systems is very obvious and constitutes strong circumstantial evidence for $NHNH_2$ as the intermediate which succeeds NNH_2 in the protonation sequence.

The N-labelling experiments of George and co-workers[11] on $[Mo(N_2)_2(PPh_3)\{(Ph_2PCH_2CH_2)_2PPh\}]$ and the data of Richards[13] concerning the amounts of N_2 and NH_3 produced upon protonation of molybdenum and tungsten bis(dinitrogen) species all suggest that the protonation of N_2 on Mo follows a path involving disproportionation of $NHNH_2$. Complexes of tungsten are clearly different, for where NNH_2 can be converted into NH_3, the yield of NH_3 approaches 2 mol equivalents.[14] This suggests an alternative pathway, perhaps related to the reluctance of tungsten to undergo a reduction, $W^{IV} \longrightarrow W^{III}$. Consistent with this, we find that reactions of $[MoCl_4(PPh_3)_2]$ with $Li(NHNH_2)$ in molar ratios of 2 : 1 and 1 : 1 produce N_2 and NH_3 in the same molar proportions as observed with $[Ti(C_5H_5)Cl_3]$, and with excellent recovery of nitrogen (100%), essentially no other nitrogen products being formed. In contrast, $[WCl_4(PPh_3)_2]$ yields ammonia and little N_2, and considerable quantities of N_2H_4. Presumably a stable hydrazide-(1−) complex is involved. Work on these reactions is still in progress.

One may write a series of all formal reactions [equations (7)—(11)] to describe the reductive breakdown of all the

$$N_2^{4-} \longrightarrow N_2 + 4e \qquad (7)$$

$$N_2H^{3-} \longrightarrow \tfrac{1}{3}NH_3 + \tfrac{5}{6}N_2 + 3e \qquad (8)$$

$$N_2H_2^{2-} \longrightarrow \tfrac{2}{3}NH_3 + \tfrac{2}{3}N_2 + 2e \qquad (9)$$

$$N_2H_3^- \longrightarrow NH_3 + \tfrac{1}{2}N_2 + e \qquad (10)$$

$$N_2H_4 \longrightarrow NH_3 + \tfrac{1}{2}N_2 + \tfrac{1}{2}H_2 \qquad (11)$$

dinitrogen hydride residues derived from hydrazine. The driving force for all is presumably the formation of the strong triple bond of N_2. Of these reactions, (7) has been observed by Dilworth *et al.*[15] in the reaction of $[MoCl_4(thf)_2]$ with $(Me_3Si)_2NN(SiMe_3)_2$. Reactions (9) and (10) have been described above and may also be involved in reactions such as the synthesis of $[Ru(NH_3)_5(N_2)]^{2+}$ from $RuCl_3{\cdot}3H_2O$ and hydrazine.[16] Reaction (11) is photo-catalysed over platinum-doped rutile.[17] We attempted to demonstrate (8), but $[Ti(C_5H_5)Cl_3]$ in thf reacts with neither $(Me_3Si)_2NNHSiMe_3$ nor $(Me_3Si)_2NN(SiMe_3)_2$; N_2 and NH_3 are produced by the former and $[MoCl_4(PPh_3)_2]$, but the results are not yet reproducible. Uncomplexed NNH_2 has recently been shown to disproportionate to give N_2 and NH_3,[18] although the mechanism is probably different from that observed here.

Such reactions presumably also account for the scarcity of $NHNH_2^-$ transition-metal complexes described in the literature. To our knowledge, there are only two,* and they have not been unequivocally characterised.[19] In fact, it is only when bound to transition metals in oxidation states not easily reduced (or to Main Group elements) that one would expect hydrazide(1−) to be stable.

Disproportionation has also been invoked in reduction reactions by hydrazine itself. These have been investigated in some detail, and have yet to be completely clarified (see ref. 5). However, the generalised mechanism in equations (12)—(14) appears to hold. The stoicheiometry is consistent with the

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

$$M^{n+} + N_2H_4 \xrightarrow{\text{outer sphere}} M^{(n-1)+} + N_2H_3 + H^+ \quad (12)$$

$$2N_2H_3 \longrightarrow N_4H_6 \quad (13)$$

$$N_4H_6 \longrightarrow 2NH_3 + N_2 \quad (14)$$

known decomposition of N_4H_6.[20] Isotopic labelling at N shows that 50% of the N_2 generated in this process arises from N–N bond formation. In the reaction of Ti^{IV} with $NHNH_2^-$ described above no new N–N bonds are formed which suggests that the interaction of Ti^{IV} with $NHNH_2^-$ does not generate unbound N_2H_3 radicals.

Finally, we note that disproportionations are significant even where N_2 is not an ultimate product. For example, the reaction of $[MoO_2(S_2CNMe_2)_2]$ with phenylhydrazine produces $[Mo(NNPh)(NHNHPh)(S_2CNMe_2)_2]$ rather than $[Mo(NNHPh)_2(S_2CNMe_2)_2]$ as might have been expected.[21] The complex $[ReCl_4(PMe_2Ph)_2]$ with $PhNHNH_2$ produces a high yield (*ca.* 80%) of $[ReCl_2(NNPh)(NH_3)(PMe_2Ph)_2]$ together with aniline, presumably *via* $[ReCl_2(NHNHPh)_2(PMe_2Ph)_2]$.[22] The data cited here and elsewhere[10] suggest that although disproportionations occur in the dinitrogen protonation chemistry of Mo and Ti, they do not necessarily apply to W. We are attempting to determine whether they might not occur during nitrogenase function.

Experimental

All manipulations were carried out using standard dry-box and vacuum-line techniques. The complexes $[Ti(C_5H_5)Cl_3]$,[23] $[MoCl_4(PPh_3)_2]$,[24] and $[WCl_4(PPh_3)_2]$[25] were prepared as described in the literature. Silylhydrazines were prepared as described elsewhere, and $Li(NHNH_2)$ was obtained *in situ* by reaction of anhydrous N_2H_4 with a solution of 1 mol equivalent of $LiBu^n$. Reactions of metal complexes and hydrazides were carried out in evacuated vessels. Gas evolved was removed by a Toepler pump system and then checked by mass spectrometry (AEI MS10C). After hydrolyses and distillation, ammonia was determined by the indophenol test.[26] Hydrazine was determined using *p*-dimethylaminobenzaldehyde.[27] Appropriate blanks and checks for interference were run. The e.s.r. spectrometer was a Bruker ER 200-D instrument.

Reactions of $[Ti(C_5H_5)Cl_3]$ *with* $Li(NHNH_2)$ *or* $Me_3SiNHNHSiMe_3$.—2:1 *Stoicheiometry.* The hydrazide $Me_3SiNHNHSiMe_3$ or $Li(NHNH_2)$ [generated from $LiBu^n$ and N_2H_4 (0.11 mmol)] was dissolved in thf (25 cm^3) in flasks with greaseless taps. Each flask contained a bent side tube capable of holding solid. In this was placed $[Ti(C_5H_5)Cl_3]$ (0.5 g, 2.3 mmol). The solution was degassed by the freeze–thaw technique, and after three such exercises the reactants were mixed *in vacuo*. The yellow solutions were allowed to stand overnight. The reaction mixture gradually turned green and produced small amounts of green $[Ti(C_5H_5)Cl_2(thf)]$. The gases were removed using the Toepler system, the gas volume determined, and the gas analysed by mass spectroscopy.

The green solution was analysed for hydrazine and ammonia. Aliquots (1 cm^3) of the thf solution were diluted with water to 10 cm^3, and then diluted as necessary to give final concentrations in the range 1—6 $\mu g\ cm^{-3}$. The e.s.r. spectrum of the residual solution in the flask was determined.

1:1 *Stoicheiometry.* These reactions were carried out as above. However, longer times were necessary (*ca.* 2 d) to ensure completeness of reaction.

Reactions with Labelled Hydrazines.—Reactions using commercially available $[^{15}N_2H_6]SO_4$ converted into the lithium hydrazide gave no N_2 or NH_3. It is still not clear why, though sulphate apparently interferes. Consequently, the sulphate salt was converted into $^{15}N_2H_4$ as follows. The hydrazine $[^{15}N_2H_6]SO_4$ (1.1 g, 8.45 mmol) was placed in a micro-Soxhlet apparatus (sinter coarseness no. 3), and the sulphate extracted with liquid ammonia (*ca.* 20 cm^3) under reflux from a solid CO_2–methanol cold-finger. After 2 h the cold-finger was allowed to warm up and the NH_3 allowed to escape under a stream of N_2. Tetrahydrofuran (25 cm^3) was added to the residual $^{15}N_2H_4$–NH_3 (*ca.* 1 cm^3) and stirred under a slow stream of N_2 for 36 h. The hydrazine and residual ammonia contents of the thf solutions were then determined in the usual way. The solution always contained a small amount of ammonia, and the amounts of ammonia determined in the reactions were always corrected for this.

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