

The Chemistry of Niobium and Tantalum Dithiocarbamato-complexes. Part 3.¹ Protonation of $[\text{Nb}(\text{NNMeR})(\text{S}_2\text{CNEt}_2)_3]$ (R = Me or Ph)

Richard A. Henderson* and Kay E. Oglieve

AFRC Institute of Plant Science Research, Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ

The reactions of $[\text{Nb}(\text{NNMeR})(\text{S}_2\text{CNEt}_2)_3]$ (R = Me or Ph) with an excess of anhydrous HBr have been studied in MeCN. The reactions, which yield $[\text{NbBr}_2(\text{S}_2\text{CNEt}_2)_3]$ and the corresponding substituted hydrazine, occur in two stages: the first is the initial rapid formation of $[\text{Nb}(\text{NHNHMeR})(\text{S}_2\text{CNEt}_2)_3]^{2+}$, and the second the slow decomposition of this species to yield the products. The sites of protonation of the hydrazide residue have been established by comparison of the rates of protonation of the species with methyl or phenyl substituents. The introduction of methanol into these systems inhibits the rate of protonation due to specific solvation of the monoprotonated complex.

The preparation of the complexes $[\text{Nb}(\text{NNMeR})(\text{S}_2\text{CNEt}_2)_3]$ (R = Me or Ph) was described some time ago,² wherein it was reported that these complexes are reversibly protonated by acids, but pure products could not be isolated. However, the proportion of acid to complex was not reported nor was the solvent. During our studies, developing the protonation chemistry of nitrogenous residues at a 'M(S₂CNEt₂)₃' site (M = Nb or Ta), we reinvestigated the protonation of these hydrazido(2-)-complexes and report herein that, with an excess of anhydrous HBr in MeCN, they react irreversibly to form $[\text{NbBr}_2(\text{S}_2\text{CNEt}_2)_3]$ and the corresponding hydrazine. Furthermore we have detected, spectroscopically, $[\text{Nb}(\text{NHNMeR})(\text{S}_2\text{CNEt}_2)_3]^+$ and $[\text{Nb}(\text{NHNHMeR})(\text{S}_2\text{CNEt}_2)_3]^{2+}$, as intermediates in these reactions, and show that only the first of these can be the species formed by reversible protonation of the hydrazido(2-)-complex alluded to previously.²

Experimental

All manipulations in both the preparative and kinetic aspects of this work were routinely performed under an atmosphere of dinitrogen using standard Schlenk or syringe techniques as appropriate. The solvents were freshly distilled from appropriate drying agents immediately prior to use. The reagents NbCl₅, MePhNNH₂, and Me₂NNH₂ (Aldrich) were used as received. The compounds $[\text{Nb}(\text{NNMe}_2)(\text{S}_2\text{CNEt}_2)_3]$ and $[\text{Nb}(\text{NNMePh})(\text{S}_2\text{CNEt}_2)_3]$ were prepared by the literature method,² and were characterised by elemental analysis and ¹H n.m.r. spectroscopy as shown in Table 1. However we found that these compounds when pure are pale yellow rather than the orange-to-red reported originally.

Product Analysis.—The reaction of either $[\text{Nb}(\text{NNMe}_2)(\text{S}_2\text{CNEt}_2)_3]$ or $[\text{Nb}(\text{NNMePh})(\text{S}_2\text{CNEt}_2)_3]$ with an excess of anhydrous HBr gave $[\text{NbBr}_2(\text{S}_2\text{CNEt}_2)_3]$, as established by elemental analysis and ⁹³Nb n.m.r. spectroscopy.

Dibromotris(diethylthiocarbamato)niobium. To a solution of $[\text{Nb}(\text{NNMe}_2)(\text{S}_2\text{CNEt}_2)_3]$ (0.17 g, 0.29 mmol) in dichloromethane or acetonitrile (ca. 20 cm³) was added MeOH (0.09 cm³, 2.9 mmol) then SiMe₃Br (0.44 cm³, 2.9 mmol). The solution was stirred at room temperature for 10 min, during which time the colour of the solution changed from yellow to an olive green. The solvent was removed *in vacuo*, the brown residue dissolved in the minimum volume of dichloromethane, and the product crystallised slowly by the careful addition of

diethyl ether to yield $[\text{NbBr}_2(\text{S}_2\text{CNEt}_2)_3]$ as a yellow-brown solid (0.12 g, 0.19 mmol, 63%).

The ⁹³Nb n.m.r. spectra of the product isolated from the reactions of HBr with $[\text{Nb}(\text{NNMe}_2)(\text{S}_2\text{CNEt}_2)_3]$, $[\text{Nb}(\text{NNMePh})(\text{S}_2\text{CNEt}_2)_3]$, or $[\{\text{Nb}(\text{S}_2\text{CNEt}_2)_3\}_2(\mu\text{-N}_2)]^3$ were identical and with the spectrum of an authentic sample of $[\text{NbBr}_2(\text{S}_2\text{CNEt}_2)_3]$ prepared from the reaction of NbBr₅ with SiMe₃(S₂CNEt₂),⁴ as shown in Table 1. Furthermore ⁹³Nb n.m.r. spectra of the crude reaction mixtures (without work-up) also showed the same signal at -540 p.p.m., Δν₃ = 3 kHz (relative to $[\text{NbCl}_6]^-$), demonstrating that the identity of the niobium product had not been perturbed during the work-up procedure.

Isolation of 1-methyl-1-phenylhydrazine. To a solution of $[\text{Nb}(\text{NNMePh})(\text{S}_2\text{CNEt}_2)_3]$ (3.15 g, 4.79 mmol) in dichloromethane was added MeOH (1.53 cm³, 47.9 mmol), then SiMe₃Br (7.42 cm³, 47.9 mmol). After stirring the solution for about 15 min HBF₄·OEt₂ (7.0 cm³, 43.5 mmol) was added to precipitate the white microcrystalline $[\text{PhMeNHNH}_3][\text{BF}_4]_2$. This material was characterised by elemental analysis, and comparison of its ¹H n.m.r. and i.r. spectra with an authentic sample prepared from PhMeNNH₂ and HBF₄·OEt₂ in dichloromethane (Table 1).

The formation of Me₂NNH₂ from the reaction of acid with $[\text{Nb}(\text{NNMe}_2)(\text{S}_2\text{CNEt}_2)_3]$ could not be established in the same manner as for PhMeNNH₂ because of the solubility of $[\text{Me}_2\text{NHNH}_3][\text{BF}_4]_2$. Its formation can only be implied from the identification of the niobium product.

Niobium-93 n.m.r. spectroscopy. All ⁹³Nb n.m.r. spectra were recorded by Mr. C. Macdonald in these laboratories, using the parameters and conditions described before.³

Kinetic Studies.—All kinetic studies were performed on an Aminco-Morrow stopped-flow apparatus modified for handling air-sensitive compounds as described before.⁵ The apparatus was interfaced to a B.B.C. microcomputer (Acorn Computers, Cambridge) via an analogue-to-digital converter operating at 3 kHz. Data were subsequently transferred to a PDP113A computer for analysis, by standard curve-fitting procedures. Analysis of the results was by the necessary straight-line graphs, and errors on the slopes and intercepts of such graphs were established by a linear least-squares analysis. Solutions of anhydrous HBr (25.0 mmol dm⁻³) were prepared in MeCN using MeOH (25.0 mmol) and SiMe₃Br (25.0 mmol). This stock was used to prepare the more dilute solutions, all of which were used within 1 h of their preparation.

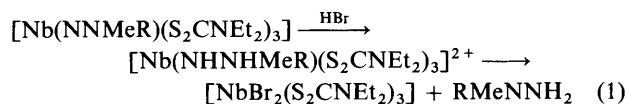
Table 1. Analytical and spectroscopic characterisation of compounds

| Compound | Analysis ^a /% | | | ¹ H N.m.r. ^b | ⁹³ Nb N.m.r. ^c (p.p.m.) |
|---|--------------------------|--------------|----------------|--|---|
| | C | H | N | | |
| [Nb(NNMe ₂)(S ₂ CNEt ₂) ₃] | 34.3 (34.2) | 6.1 (6.0) | 11.8 (11.7) | 2.85(6) (s, NMe ₂) ^d | <i>e</i> |
| [Nb(NNMePh)(S ₂ CNEt ₂) ₃] | 40.4 (40.1) | 6.1 (5.8) | 10.3 (10.6) | 3.38(3) (s, NMe), <i>ca.</i> 7.0(5) (m, NPh) ^d | <i>e</i> |
| [NbBr ₂ (S ₂ CNEt ₂) ₃] | 26.2 (25.8) | 4.3 (4.3) | 5.8 (6.0) | 1.35(3) (t, Me, <i>J</i> _{HH} = 7.0), 3.85(2) (q, CH ₂ , <i>J</i> _{HH} = 7.1) | -545 ($\Delta\nu_{1/2} \approx 2.5$ kHz) |
| [PhMeNHNH ₃][BF ₄] ₂ | 28.4 (28.2) | 4.4 (4.0) | 9.2 (9.4) | 3.26(3) (s, Me) ^f , 7.25–7.53(5) (m, Ph), 8.33(3) (br, NH ₃), 9.13(1) (br, NH) | |

^a Calculated values shown in parentheses. ^b All chemical shifts *versus* SiMe₄, *J* values in Hz; s = singlet, m = multiplet, t = triplet, q = quartet, and br = broad. Spectra recorded in CD₂Cl₂. ^c Spectra recorded in CH₂Cl₂. Chemical shifts *versus* [NbCl₆]⁻ in MeCN, $\delta \pm 4$ p.p.m. ^d Signals attributable to S₂CNEt₂ at 1.24(18) (t, Me, *J*_{HH} = 7.0) and 3.85(12) (q, CH₂, *J*_{HH} = 7.0 Hz). ^e No ⁹³Nb n.m.r. spectrum observed. ^f Spectrum recorded in CD₃CN.

Results and Discussion

The reactions between [Nb(NNMeR)(S₂CNEt₂)₃] (R = Me or Ph) and an excess of HBr occur in two distinct stages: the initial rapid protonation of the hydrazido(2-)-complex to generate [Nb(NHNHMeR)(S₂CNEt₂)₃]²⁺, followed by decomposition of this intermediate to yield [NbBr₂(S₂CNEt₂)₃] and the corresponding hydrazine, as summarised in equation (1). It is thus most convenient to discuss the results in sections corresponding to these two stages.



Protonation of [Nb(NNMeR)(S₂CNEt₂)₃].—Although both the dimethylhydrazide and the methylphenylhydrazide react with HBr in the manner described above, the protonation of [Nb(NNMe₂)(S₂CNEt₂)₃] to form [Nb(NHNHMe₂)(S₂CNEt₂)₃]²⁺ is too rapid to be studied by stopped-flow spectrophotometry, only with [Nb(NNMePh)(S₂CNEt₂)₃] is the reaction to form the diprotonated intermediate sufficiently slow to be studied by this technique.

The reaction between [Nb(NNMePh)(S₂CNEt₂)₃] and an excess of HBr is best studied at $\lambda = 420$ nm, where the absorbance changes are maximised. However, identical behaviour (and rate constants) are observed at all wavelengths studied in the range $\lambda = 350$ –550 nm. Upon mixing [Nb(NNMePh)(S₂CNEt₂)₃] ($\epsilon_{420} = 1.1 \times 10^3$ dm³ mol⁻¹ cm⁻¹) and an excess of HBr there is an initial rapid absorbance jump to yield a species ($\epsilon_{420} = 1.8 \times 10^3$ dm³ mol⁻¹ cm⁻¹) within the dead-time of the stopped-flow apparatus (3.3 ms), followed by a slow further rise in absorbance to give a species ($\epsilon_{420} = 3.7 \times 10^3$ dm³ mol⁻¹ cm⁻¹) which is stable for about 3–5 s at 25.0 °C before decomposing to [NbBr₂(S₂CNEt₂)₃] and PhMeNNH₂ (see below). We propose that the two detected intermediates are [Nb(NHNMePh)(S₂CNEt₂)₃]⁺ and [Nb(NHNHMePh)(S₂CNEt₂)₃]²⁺ respectively. The kinetics of the conversion of [Nb(NHNMePh)(S₂CNEt₂)₃]⁺ into [Nb(NHNHMePh)(S₂CNEt₂)₃]²⁺ exhibit a first-order dependence on the concentration of [Nb(NHNMePh)(S₂CNEt₂)₃]⁺ and an apparent first-order dependence on the concentration of HBr as shown in Table 2. In a more rigorous analysis of these data we have calculated the concentration of HBr allowing for (i) the acid dissociation ($K_a = 3.16 \times 10^{-6}$) and homoconjugation equilibria ($K_{Br} = 2.51 \times 10^2$ dm³ mol⁻¹) in MeCN⁶ shown in equations (2) and (3) respectively and, (ii) the 1 mol equivalent of HBr which we presume to have been consumed during the initial absorbance jump to form [Nb-

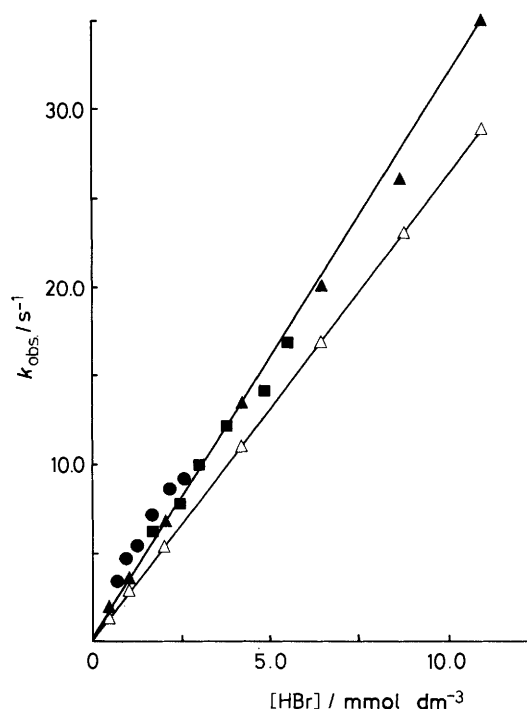
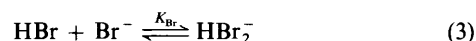


Figure 1. Graph of k_{obs} against the concentration of HBr for the reaction between [Nb(NNMePh)(S₂CNEt₂)₃] and HBr to form [Nb(NHNHMePh)(S₂CNEt₂)₃]²⁺. Data points correspond to those studied in HBr (▲) or DBr (△) alone, or when [HBr] = 6.25, [Br⁻] = 1.25–15.0 (■) and [HBr] = 3.125, [Br⁻] = 1.25–15.0 mmol dm⁻³ (●). All concentrations plotted have been corrected for the equilibria shown in equations (2) and (3), and the initial rapid protonation of [Nb(NNMePh)(S₂CNEt₂)₃]. Data are those shown in Table 2



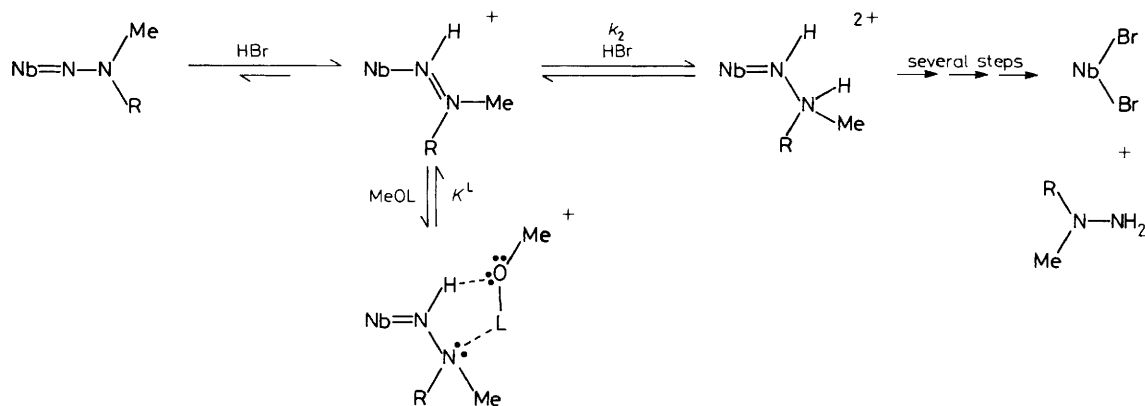
(NHNMePh)(S₂CNEt₂)₃]⁺. Here (and throughout this series of papers), $K_a = [\text{MeCNH}^+][\text{Br}^-]/[\text{MeCN}][\text{HBr}]$.

The derived dependence of k_{obs} (where k_{obs} throughout this paper is the observed rate constant measured under pseudo-first-order conditions) on the concentration of HBr is shown in Figure 1 which also includes the data for the same reactions in the presence of [NBu₄]⁺Br⁻. The fact that the data from these latter studies also define the same straight line graph as the

Table 2. Kinetic data for the reactions between $[\text{Nb}(\text{NNMeR})(\text{S}_2\text{CNEt}_2)_3]$ ($\text{R} = \text{Me}$ or Ph) and HBr in MeCN (25.0°C , $\lambda = 420 \text{ nm}$)

| $[\text{Nb}]/\text{mmol dm}^{-3}$ | $[\text{HBr}]/\text{mmol dm}^{-3}$ | $[\text{Br}^-]/\text{mmol dm}^{-3}$ | $k_{\text{obs.}}/\text{s}^{-1}$ (fast phase) | $10^2 k_{\text{obs.}}/\text{s}^{-1}$ (slow phase) | |
|-----------------------------------|------------------------------------|-------------------------------------|---|--|-----|
| R = Me | | | | | |
| 0.1 | 2.0 | | <i>a</i> | 1.0 | |
| | 4.0 | | | 0.9 | |
| | 10.0 | | | 1.0 | |
| | 15.0 | | | 1.0 | |
| | 20.0 | | | 1.0 | |
| 0.2 | 20.0 | | | 0.9 | |
| 0.05 | 20.0 | | | 0.9 | |
| R = Ph | | | | | |
| 0.1 | 0.625 | | 1.9 (1.7) ^b | | |
| | 1.25 | | 3.6 (3.0) | | |
| | 2.50 | | 6.9 (5.6) | 1.3 | |
| | 5.00 | | 13.6 (11.2) | 1.3 | |
| | 7.50 | | 20.0 (17.0) | 1.5 | |
| | 10.0 | | 26.0 (23.3) | 1.6 | |
| | 12.5 | | 34.9 (29.0) | 1.5 | |
| | 0.2 | 12.5 | | 34.6 | 1.5 |
| | 0.05 | 12.5 | | 34.6 | 1.5 |
| | 0.1 | 6.25 | 1.25 | 16.8 | |
| 2.50 | | | 14.2 | 1.5 | |
| 5.00 | | | 12.3 | | |
| 7.50 | | | 10.2 | 1.5 | |
| 10.00 | | | 7.9 | | |
| 3.125 | | 1.25 | 9.4 | | |
| | | 2.50 | 8.7 | 1.5 | |
| | | 5.00 | 7.3 | | |
| | | 7.50 | 5.7 | 1.3 | |
| | | 10.00 | 4.9 | | |
| 15.00 | | 1.25 | 6.3 | 1.5 | |
| | | 2.50 | 9.4 | | |
| | | 5.00 | 8.7 | 1.5 | |
| | | 7.50 | 7.3 | | |
| | | 10.00 | 5.7 | 1.3 | |
| 15.00 | 1.25 | 4.9 | | | |
| | 2.50 | 3.5 | 1.3 | | |
| | 5.00 | | | | |
| | 7.50 | | | | |
| | 10.00 | | | | |

^a Fast phase complete within dead-time of stopped-flow apparatus. ^b Values in parentheses were obtained using DBr.



Scheme. The mechanism of the reaction between $[\text{Nb}(\text{NNMeR})(\text{S}_2\text{CNEt}_2)_3]$ ($\text{R} = \text{Me}$ or Ph) and HBr in MeCN . Dithiocarbamate ligands omitted for clarity

studies in the presence of HBr alone establishes that the protonation is specifically performed by HBr .

This kinetic behaviour, and in particular the first-order dependence on the concentration of HBr , is consistent with the mechanism shown in the Scheme. Initial rapid protonation of $[\text{Nb}(\text{NNMeR})(\text{S}_2\text{CNEt}_2)_3]$ by HBr generated the species $[\text{Nb}(\text{NHNMeR})(\text{S}_2\text{CNEt}_2)_3]^+$ within the dead-time of the stopped-flow apparatus. Subsequent protonation of this species by another molecule of HBr generates $[\text{Nb}(\text{NHNHMeR})(\text{S}_2\text{CNEt}_2)_3]^{2+}$ and for $\text{R} = \text{Ph}$ protonation at the remote nitrogen atom is sufficiently slow to be measured [$k_2 = (3.2 \pm 0.2) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$]. Consistent with this inter-

pretation a primary isotope effect ($k_2^{\text{H}}/k_2^{\text{D}} = 1.21$) has been measured for the protonation step. Furthermore the order in which the two nitrogen atoms are protonated is strongly indicated by the relative protonation rates of $[\text{Nb}(\text{NNMe}_2)(\text{S}_2\text{CNEt}_2)_3]$ and $[\text{Nb}(\text{NNMePh})(\text{S}_2\text{CNEt}_2)_3]$. With the phenyl substituent on the remote nitrogen atom in the latter complex, protonation is much slower at this position than the analogous site containing the more electron-releasing methyl groups. This use of alkyl and aryl substituents to act as probes for the sites of protonation of hydrazido(2-)-ligands has been employed in the reactions of *cis*- $[\text{Mo}(\text{NNRPh})_2(\text{S}_2\text{CNEt}_2)_2]$ ($\text{R} = \text{Me}$ or Ph).⁷

The addition of even small amounts of methanol (although

Table 3. Inhibition, by methanol, of the reaction between $[\text{Nb}(\text{NNMePh})(\text{S}_2\text{CNET}_2)_3]$ and HBr in MeCN (25.0°C , $\lambda = 420\text{ nm}$, $[\text{Nb}] = 1 \times 10^{-4}\text{ mol dm}^{-3}$)

| $[\text{HBr}]/\text{mmol dm}^{-3}$ | $[\text{MeOH}]/\text{mmol dm}^{-3}$ | $k_{\text{obs.}}/\text{s}^{-1}$ (fast phase) |
|------------------------------------|-------------------------------------|--|
| 12.5 | 3.0 | 33.0 |
| | 6.0 | 30.6 |
| | 9.0 | 29.0 |
| | 12.0 | 27.0 |
| | 18.0 | 23.9 |
| | 33.0 | 22.9 |
| | 63.0 | 16.2 |
| | 94.0 | 14.5 |
| | 125.0 | 12.2 |
| | 158.0 | 11.0 |
| 6.25 | 18.0 | 11.6 (13.2)* |
| | 33.0 | 9.8 (12.0) |
| | 63.0 | 7.8 (9.7) |
| | 94.0 | 6.6 (8.2) |
| | 125.0 | 5.6 (7.4) |
| | 158.0 | 5.2 (6.5) |

* Values in parentheses are for studies using MeOD with DBr .

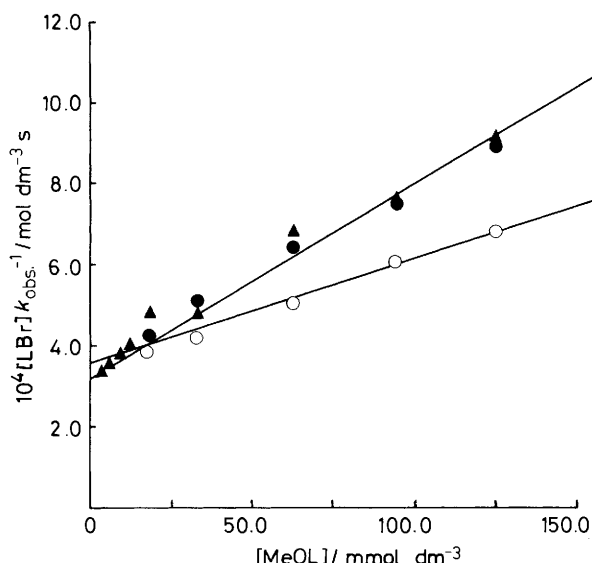


Figure 2. Graph of $[\text{LBr}]_{\text{free}}/k_{\text{obs.}}$ against the concentration of MeOL ($\text{L} = \text{H}$ or D) showing the inhibition by methanol of the reaction between $[\text{Nb}(\text{NNMePh})(\text{S}_2\text{CNET}_2)_3]$ and HBr to form $[\text{Nb}(\text{NHNHMePh})(\text{S}_2\text{CNET}_2)_3]^{2+}$. Data points correspond to: $[\text{HBr}] = 12.5$ (\blacktriangle), $[\text{HBr}] = 6.25$ (\bullet), and $[\text{DBr}] = 6.25\text{ mmol dm}^{-3}$ (\circ). Data are those shown in Table 3

always in a large excess over the concentration of complex) to the reaction between $[\text{Nb}(\text{NNMePh})(\text{S}_2\text{CNET}_2)_3]$ and HBr inhibits the rate of protonation of this species as shown by the data in Table 3 and illustrated in Figure 2. Furthermore MeOD inhibits the reaction less than MeOH . This inhibition is associated with the specific solvation of $[\text{Nb}(\text{NHNMePh})(\text{S}_2\text{CNET}_2)_3]^+$ since even under conditions where the concentration of methanol is less than that of HBr , but still greater than that of the niobium complex, the mathematical form of the inhibition is that illustrated in Figure 2 and given by the expression (4). When

$$k_{\text{obs.}} = \frac{k_2^1 [\text{LBr}]}{1 + K^1 [\text{MeOL}]} \quad (4)$$

$\text{L} = \text{H}$, $k_2^{\text{H}} = 3.1 \times 10^3\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1}$ and $K^{\text{H}} = 1.48 \times 10^{-2}$

$\text{dm}^3\text{ mol}^{-1}$; when $\text{L} = \text{D}$, $k_2^{\text{D}} = 2.7 \times 10^3\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1}$ and $K^{\text{D}} = 7.14 \times 10^{-3}\text{ dm}^3\text{ mol}^{-1}$, giving $K^{\text{H}}/K^{\text{D}} = 2.07$.

It seems likely that the specific solvation by methanol is as shown in the Scheme and that the hydrogen bonding of the methanolic proton to the remote nitrogen atom does not allow the close approach of HBr to this site.

Decomposition of $[\text{Nb}(\text{NHNHMeR})(\text{S}_2\text{CNET}_2)_3]^{2+}$.—The relatively slow decomposition of $[\text{Nb}(\text{NHNHMeR})(\text{S}_2\text{CNET}_2)_3]^{2+}$ occurs in the presence of an excess of HBr at a rate which exhibits a first-order dependence on the concentration of the niobium species but is independent of the concentration of acid and only slightly dependent on the substituents of the nitrogenous residue: when $\text{R} = \text{Me}$, $k_3 = (1.0 \pm 0.1) \times 10^{-2}\text{ s}^{-1}$ and when $\text{R} = \text{Ph}$, $k_3 = (1.6 \pm 0.1) \times 10^{-2}\text{ s}^{-1}$. This behaviour is consistent with rate-limiting dissociation of the nitrogen ligand, but all the intimate details of the conversion from $[\text{Nb}(\text{NHNHMeR})(\text{S}_2\text{CNET}_2)_3]^{2+}$ to $[\text{NbBr}_2(\text{S}_2\text{CNET}_2)_3]$ are hidden from us because of the simplicity of the rate law for this stage.

Conclusion

We have shown that in the presence of an excess of HBr the reaction with $[\text{Nb}(\text{NNMeR})(\text{S}_2\text{CNET}_2)_3]$ is irreversible, giving rise to $[\text{NbBr}_2(\text{S}_2\text{CNET}_2)_3]$ and RMeNNH_2 via the protonated species $[\text{Nb}(\text{NHNMeR})(\text{S}_2\text{CNET}_2)_3]^+$ and $[\text{Nb}(\text{NHNHMeR})(\text{S}_2\text{CNET}_2)_3]^{2+}$. Furthermore it is now clear from these studies that the previously reported reversible protonation of the hydrazido(2-)-complexes² must involve the reaction with only 1 mol equivalent of acid, since the addition of any larger excess than this would involve the formation of $[\text{Nb}(\text{NHNHMeR})(\text{S}_2\text{CNET}_2)_3]^{2+}$ which loses hydrazine with a half-life of about 1 min. We also have attempted to isolate the monoprotonated species but have been unsuccessful.

Although many of the factors involved in activating mononuclear dinitrogen complexes towards protonation have been defined,^{8,9} a major gap in our understanding, until recently, has been the sites of protonation of hydrazido(2-)-species. The work described herein is the third study on the protonation of substituted hydrazido(2-)-complexes. In common with the other two systems, *cis*- $[\text{Mo}(\text{NNR-Ph})_2(\text{S}_2\text{CNET}_2)_2]$ (gives hydrazines upon protonation)⁷ and $[\text{Mo}\{\text{NN}(\text{CH}_2)_4\text{CH}_2\}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ {gives $\text{NH}(\text{CH}_2)_4\text{CH}_2$ and *trans*- $[\text{MoN}(\text{NCMe})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^+$ upon protonation},¹⁰ protonation of both nitrogen atoms are essential for rapid activation of the nitrogenous residue.

References

- Part 2, F. P. O'Flaherty, R. A. Henderson, and D. L. Hughes, preceding paper.
- L. Seng Tan, G. V. Goeden, and B. L. Haymore, *Inorg. Chem.*, 1983, **22**, 1744.
- J. R. Dilworth, R. A. Henderson, A. Hills, D. L. Hughes, C. Macdonald, A. N. Stephens, and D. R. M. Walton, *J. Chem. Soc., Dalton Trans.*, 1990, 1077.
- P. R. Heckley, D. G. Holah, and D. Brown, *Can. J. Chem.*, 1971, **49**, 1151.
- R. A. Henderson, *J. Chem. Soc., Dalton Trans.*, 1982, 917.
- J. F. Coetzee, *Prog. Phys. Org. Chem.*, 1967, **4**, 45.
- J. R. Dilworth, R. A. Henderson, P. Dahlstrom, T. Nicholson, and J. A. Zubieta, *J. Chem. Soc., Dalton Trans.*, 1987, 529.
- R. A. Henderson, G. J. Leigh, and C. J. Pickett, *Adv. Inorg. Chem. Radiochem.*, 1983, **27**, 197 and refs. therein.
- R. A. Henderson, *J. Chem. Soc., Dalton Trans.*, 1984, 2259.
- R. A. Henderson, G. J. Leigh, and C. J. Pickett, *J. Chem. Soc., Dalton Trans.*, 1989, 425.

Received 12th May 1989; Paper 9/01990A