The Chemistry of Niobium and Tantalum Dithiocarbamato-complexes. Part 2.†
Trimethylhydrazido(1 −)-complexes: the Reactivity and X-Ray Crystal Structure of [Ta(NMeNMe₂)(S₂CNEt₂)₃]Br·CHCl₃‡

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The synthesis and characterisation of [TaCl₃(NMeNMe₂)₂], [TaCl₃(NMeNMe₂)(S₂CNEt₂)], and [Ta(NMeNMe₂)(S₂CNEt₂)₃]Br are described. The X-ray crystal structure of [Ta(NMeNMe₂)-(S₂CNEt₂)₃]Br shows the cation to contain a side-on co-ordinated trimethylhydrazido(1 −)-ligand with distances Ta–NMe 1.932, Ta–NMe₂ 2.209 Å, and Ta–S in the range 2.542–2.573 Å. The reactivity of the trimethylhydrazido(1 −)-ligand towards protonation and substitution is discussed.

The chemistry of the substituted hydrazido(1 −)-ligand has recently been studied in some depth both from the structural viewpoint [1–3] and in the context of its role as an intermediate in the conversion of hydrazido(2 −)-complexes to yield amines or hydrazines.[3–5] We report herein studies on the synthesis and reactivity of some complexes of tantalum containing the trimethylhydrazido(1 −)-ligand, which further complement our studies on the reactivity of nitrogenous residues bound to the 'M(S₂CNEt₂)₃' site (M = Nb or Ta).

Results and Discussion

Our ultimate goal in this work, to prepare [Ta(NMeNMe₂)-(S₂CNEt₂)₃]⁺, can, in principle, be achieved by two strategies: either initial co-ordination of the NMeNMe₂ moiety to tantalum followed by binding of the S₂CNEt₂ ligands, or the introduction of the NMeNMe₂ residue at a pre-formed 'Ta(S₂CNEt₂)₃' core. Both approaches have been investigated, but only the latter route yields the desired compound.

Preparation and Reactivity of [TaCl₃(NMeNMe₂)₂].—The reaction of TaCl₅ with an excess of Me₃SiNMeNMe₂ in dichloromethane gives [TaCl₃(NMeNMe₂)₂] as a white, microcrystalline solid which is poorly soluble in all common aprotic solvents. Although microanalytical data and limited ¹H n.m.r. spectroscopy (Table 1) are consistent with the formulation given, its poor solubility does not allow us to assign a mononuclear structure with confidence. We were unable to grow crystals of this material suitable for X-ray crystallographic analysis.

Treatment of [TaCl₃(NMeNMe₂)₂] with an excess of SiMe₃-(S₂CNEt₂) in dichloromethane produces [TaCl₃(NMeNMe₂)-(S₂CNEt₂)] as yellow needles. Clearly a hydrazide residue in the parent compound has been replaced by the S₂CNEt₂ ligand, rather than the desired displacement of a chloro-group. This type of reactivity is amplified in the reaction of [TaCl₃-(NMeNMe₂)₂] with a slight excess of Na(S₂CNEt₂), where now both hydrazide residues are displaced to yield [TaCl₃-(S₂CNEt₂)₂], a complex which can be prepared more directly from the reactions of TaCl₅ with Na(S₂CNEt₂)[6] or SiMe₃-(S₂CNEt₂) in dichloromethane.

The ¹H n.m.r. spectrum of [TaCl₃(NMeNMe₂)(S₂CNEt₂)] shows two sets of signals attributable to the S₂CNEt₂ ligand, and each methyl group on the hydrazido(1 −)-residue shows a separate signal (Table 1). These spectroscopic characteristics
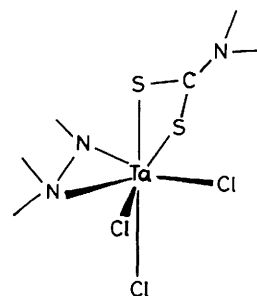

Figure 1. Proposed structure of [TaCl₃(NMeNMe₂)(S₂CNEt₂)] in which the S₂CNEt₂ ligand spans axial and equatorial positions of a pentagonal bipyramid

are consistent with the static pentagonal-bipyramidal structure shown in Figure 1, or its isomer in which the dithiocarbamate ligand spans two equatorial positions.

Preparation and Structure of [Ta(NMeNMe₂)-(S₂CNEt₂)₃]Br.—The lability of the trimethylhydrazido(1 −)-ligand in [TaCl₃(NMeNMe₂)₂] precludes the use of this complex as a precursor to the desired [Ta(NMeNMe₂)-(S₂CNEt₂)₃]⁺. However, our previous studies on the protonation of [{Ta(S₂CNEt₂)₃}₂(μ-N₂)] have resulted in the preparation of the previously unknown [Ta(S₂CNEt₂)₃X₂] (X = Cl, Br, or I), and in particular the bromo-complex whose X-ray structure has been reported.[7]

The reaction of an excess of Me₃SiNMeNMe₂ with [TaBr₂(S₂CNEt₂)₃] in dichloromethane rapidly gives [Ta(NMeNMe₂)(S₂CNEt₂)₃]Br whose structure we have established by X-ray crystallography, as the chloroform solvate. The crystals comprise discrete [Ta(NMeNMe₂)(S₂CNEt₂)₃]⁺ cations, bromide anions, and chloroform (solvent) molecules, separated by normal van der Waals interactions. Atomic co-ordinates are listed in Table 2, and selected molecular dimensions in Table 3.

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† Part 1 is ref. 7.
‡ Tris(diethyldithiocarbamato-SS′)[trimethylhydrazido(1 −)-NN′]-tantalum bromide–chloroform (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix–xxii.

Table 1. Elemental and spectroscopic analysis of complexes

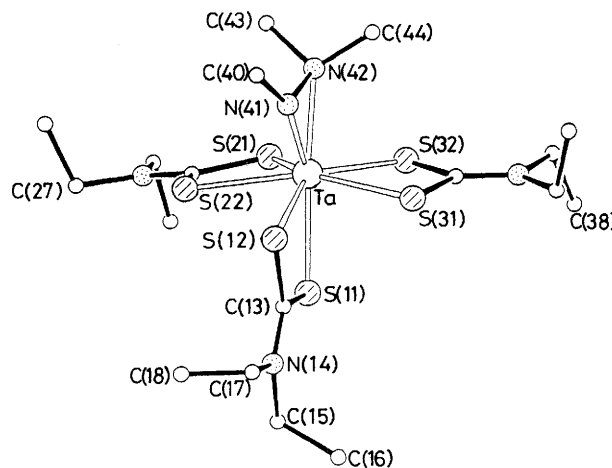| Compound | Colour | Analysis ^{a}/% | | | ^{1}H N.m.r.^{b} |
		C	H	N	
[TaCl$_3$(NMeNMe$_2$)$_2$]	White	16.5 (16.6)	4.0 (4.2)	13.1 (12.9)	2.19(6) (s, NMe$_2$), 3.91(3) (s, NMe)
[TaCl$_3$(NMeNMe$_2$)(S$_2$CNEt$_2$)]	Yellow	18.7 (18.9)	3.7 (3.8)	8.0 (8.0)	1.23(3) (t, Me, J_{HH} = 6.8), 1.35(3) (t, Me, J_{HH} = 6.9), 2.62(3), 3.02(3), 3.35(3) (s, NMe), 3.72(4) (m, CH$_2$)
[Ta(NMeNMe$_2$)(S$_2$CNEt$_2$)$_3$]Br·0.5CH$_2$Cl$_2$	Yellow	26.9 (27.0)	4.7 (4.9)	8.4 (8.5)	1.31(18) (t, Me, J_{HH} = 7.1), 2.16(6) (s, NMe$_2$), 3.73(12) (q, CH$_2$, J_{HH} = 7.3), 3.79(3) (s, NMe), 5.27(1) (s, CH$_2$Cl$_2$)

^{a} Calculated percentages in parentheses. ^{b} All chemical shifts *versus* SiMe$_4$, s = singlet, m = multiplet, q = quartet, and t = triplet. All spectra recorded in CDCl$_3$; variable-temperature ^{1}H n.m.r. revealed no 'freezing out' of the fluxional behaviour even at −60 °C.

Table 2. Final atom co-ordinates (fractional × 10^4) for [Ta(NMeNMe$_2$)(S$_2$CNEt$_2$)$_3$]Br·CHCl$_3$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
Ta	1 058.6(5)	1 569.4(5)	3 317.7(4)
S(11)	367(4)	3 367(3)	3 774(3)
S(12)	1 579(4)	2 431(3)	1 922(3)
C(13)	925(13)	3 475(12)	2 641(12)
N(14)	873(11)	4 307(11)	2 339(11)
C(15)	276(16)	5 185(15)	2 915(16)
C(16)	1 159(19)	6 410(16)	3 743(21)
C(17)	1 380(16)	4 356(14)	1 345(14)
C(18)	478(24)	3 647(23)	230(18)
S(21)	−822(3)	668(3)	3 922(3)
S(22)	−858(4)	476(4)	1 676(3)
C(23)	−1 681(13)	154(12)	2 572(12)
N(24)	−2 873(11)	−425(11)	2 282(9)
C(25)	−3 526(14)	−656(15)	3 131(13)
C(26)	−3 908(18)	379(19)	3 841(18)
C(27)	−3 597(14)	−940(14)	1 107(12)
C(28)	−3 595(17)	−2 184(17)	348(14)
S(31)	3 138(3)	3 191(3)	4 321(3)
S(32)	1 584(3)	2 268(3)	5 514(3)
C(33)	3 000(14)	3 170(11)	5 610(13)
N(34)	3 840(12)	3 806(11)	6 567(11)
C(35)	5 035(15)	4 580(15)	6 565(17)
C(36)	5 904(17)	3 884(19)	6 211(19)
C(37)	3 700(16)	3 733(15)	7 635(13)
C(38)	3 329(25)	4 679(21)	8 489(21)
C(40)	2 070(16)	−253(16)	1 211(13)
N(41)	1 728(10)	419(10)	2 305(9)
N(42)	1 606(12)	43(11)	3 148(10)
C(43)	716(19)	−1 244(15)	2 683(18)
C(44)	2 733(21)	127(20)	3 776(16)
Br	6 729(2)	2 711(2)	8 521(2)
Cl(61)	2 741(6)	6 049(6)	6 440(5)
Cl(62)*	2 903(8)	7 466(6)	8 873(6)
Cl(64)*	2 358(36)	7 824(36)	8 271(36)
Cl(63)	4 768(7)	8 196(9)	7 861(9)
C(6)	3 196(20)	7 505(21)	7 611(19)

* Site occupancy factors for Cl(62) and Cl(64) are 0.8 and 0.2 respectively.

Figure 2. A view of the cation [Ta(NMeNMe$_2$)(S$_2$CNEt$_2$)$_3$]$^+$

In the cation shown in Figure 2 the Ta atom is co-ordinated by three bidentate S$_2$CNEt$_2$ ligands and a side-on bound hydrazido(1−)-ligand. The co-ordination pattern may be described either as distorted dodecahedral (in which the hydrazide ligand is bidentate), or as distorted pentagonal bipyramidal (where the hydrazide ligand occupies a single site). In the former case, each of the four bidentate ligands span an *m* edge of the interlocking trapezoidal planes which form the dodecahedron.[8] However, because of the small 'bite' of the hydrazide group, the distortions result in Ta–S distances quite different from those in,

for example, the [Ta(S$_2$CNEt$_2$)$_4$]$^+$ cation, where the Ta–S$_B$ distances (S$_B$ is in a B site of the dodecahedron) are distinctly shorter than the Ta–S$_A$ lengths.[9] In our cation, the Ta–S$_B$ distances, to S(11), S(22), and S(31) are 2.562(5), 2.573(4), and 2.542(3) Å, which are, respectively, very similar to, rather longer than, and rather less than the Ta–S$_A$ distances for the same ligand.

Alternatively, we may consider the cation to have pentagonal-bipyramidal co-ordination in which the hydrazide group occupies a single axial site, two S$_2$CNEt$_2$ ligands lie in the equatorial plane, and the third tries to span an equatorial and an axial site. The Ta–S$_{eq}$ distances show a range of 2.543(4)—2.571(4) Å; for the spanning S$_2$CNEt$_2$ ligand, Ta–S(12) (S$_{eq}$) is 2.556(5) Å, and Ta–S(11) (S$_{ax}$) is 2.562(5) Å. According to Drew,[10] this relatively long Ta–S$_{ax}$ bond would indicate the presence of a multiple Ta–X bond to the opposite axial group where, in our cation, there is co-ordination through the two N atoms of the hydrazido-ligand. The Ta–N(41) distance [where N(41) is formally the negatively charged atom] is short, 1.932(12) Å, and Ta–N(42) is longer at 2.209(16) Å. The NMeNMe$_2$ ligand has the dimensions and conformation typical of this group in side-on co-ordination.[2]

It has been noted[9,10] that where there are two coplanar S$_2$CNEt$_2$ ligands, as in each trapezoidal plane of dodecahedral [M(S$_2$CNEt$_2$)$_4$] complexes, and in the equatorial plane of pentagonal-bipyramidal [M(S$_2$CNEt$_2$)$_3$X] complexes, the interligand S $\cdots$ S distance is short, suggesting attractive forces between the two S atoms. In our complex, S(21) $\cdots$ S(32) is 2.973(5) Å (*cf.* the van der Waals distance of 3.7 Å) and rather shorter than all the other interligand S $\cdots$ S contacts. For example, the next shortest is S(12) $\cdots$ S(31) at 3.113(5) Å. The N(41) $\cdots$ S(12) distance 2.954(12) Å is also rather shorter than
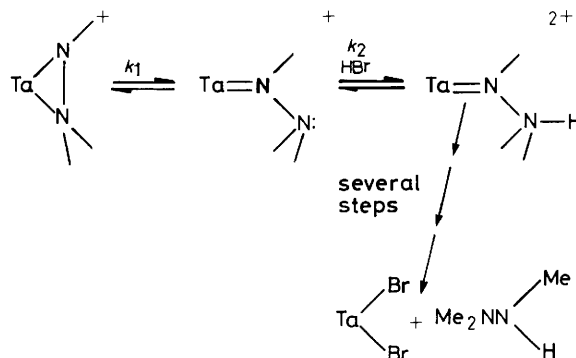
Table 3. Molecular dimensions (lengths in Å, angles in °) with e.s.d.s in parentheses

(a) About the Ta atom

Ta–S(11)	2.562(5)	Ta–S(31)	2.542(3)
Ta–S(12)	2.556(5)	Ta–S(32)	2.571(4)
Ta–S(21)	2.543(4)	Ta–N(41)	1.932(12)
Ta–S(22)	2.573(4)	Ta–N(42)	2.209(16)
S(11)–Ta–S(12)	68.2(1)	S(31)–Ta–S(32)	67.1(1)
S(11)–Ta–S(21)	87.5(1)	S(11)–Ta–N(41)	149.1(5)
S(12)–Ta–S(21)	138.1(1)	S(12)–Ta–N(41)	81.0(5)
S(11)–Ta–S(22)	82.3(1)	S(21)–Ta–N(41)	114.7(4)
S(12)–Ta–S(22)	75.8(1)	S(22)–Ta–N(41)	86.9(3)
S(21)–Ta–S(22)	67.2(1)	S(31)–Ta–N(41)	92.8(3)
S(11)–Ta–S(31)	83.2(1)	S(32)–Ta–N(41)	117.7(4)
S(12)–Ta–S(31)	75.3(1)	S(11)–Ta–N(42)	172.5(4)
S(21)–Ta–S(31)	137.2(1)	S(12)–Ta–N(42)	119.1(4)
S(22)–Ta–S(31)	150.8(2)	S(21)–Ta–N(42)	87.4(4)
S(11)–Ta–S(32)	89.0(1)	S(22)–Ta–N(42)	100.8(3)
S(12)–Ta–S(32)	138.1(1)	S(31)–Ta–N(42)	96.9(3)
S(21)–Ta–S(32)	71.1(1)	S(32)–Ta–N(42)	84.1(3)
S(22)–Ta–S(32)	137.6(1)	N(41)–Ta–N(42)	38.5(6)

(b) In the ligands

S(11)–C(13)	1.701(18)	S(31)–C(33)	1.712(18)
S(12)–C(13)	1.713(17)	S(32)–C(33)	1.710(15)
C(13)–N(14)	1.332(26)	C(33)–N(34)	1.306(18)
N(14)–C(15)	1.472(24)	N(34)–C(35)	1.484(22)
N(14)–C(17)	1.480(24)	N(34)–C(37)	1.454(25)
C(15)–C(16)	1.498(20)	C(35)–C(36)	1.52(3)
C(17)–C(18)	1.476(25)	C(37)–C(38)	1.47(3)
S(21)–C(23)	1.714(15)	C(40)–N(41)	1.469(20)
S(22)–C(23)	1.682(17)	N(41)–N(42)	1.389(22)
C(23)–N(24)	1.329(18)	N(42)–C(43)	1.535(20)
N(24)–C(25)	1.476(23)	N(42)–C(44)	1.465(30)
N(24)–C(27)	1.464(18)		
C(25)–C(26)	1.491(29)		
C(27)–C(28)	1.503(26)		
Ta–S(11)–C(13)	88.7(6)	Ta–S(31)–C(33)	91.0(5)
Ta–S(12)–C(13)	88.6(6)	Ta–S(32)–C(33)	90.0(6)
S(11)–C(13)–S(12)	114.5(11)	S(31)–C(33)–S(32)	111.3(8)
S(11)–C(13)–N(14)	123.1(12)	S(31)–C(33)–N(34)	124.9(13)
S(12)–C(13)–N(14)	122.4(13)	S(32)–C(33)–N(34)	123.7(14)
C(13)–N(14)–C(15)	123.4(16)	C(33)–N(34)–C(35)	119.5(16)
C(13)–N(14)–C(17)	120.5(14)	C(33)–N(34)–C(37)	123.1(14)
C(15)–N(14)–C(17)	116.0(17)	C(35)–N(34)–C(37)	117.2(13)
N(14)–C(15)–C(16)	113.0(15)	N(34)–C(35)–C(36)	111.2(16)
N(14)–C(17)–C(18)	113.0(16)	N(34)–C(37)–C(38)	114.8(20)
Ta–S(21)–C(23)	90.1(5)	Ta–N(41)–C(40)	154.9(14)
Ta–S(22)–C(23)	89.8(5)	Ta–N(41)–N(42)	81.6(8)
S(21)–C(23)–S(22)	112.9(8)	C(40)–N(41)–N(42)	122.4(15)
S(21)–C(23)–N(24)	122.9(13)	Ta–N(42)–N(41)	59.9(8)
S(22)–C(23)–N(24)	124.2(12)	Ta–N(42)–C(43)	124.1(12)
C(23)–N(24)–C(25)	120.5(12)	N(41)–N(42)–C(43)	113.6(12)
C(23)–N(24)–C(27)	123.1(13)	Ta–N(42)–C(44)	126.0(11)
C(25)–N(24)–C(27)	116.2(11)	N(41)–N(42)–C(44)	115.9(14)
N(24)–C(25)–C(26)	110.0(18)	C(43)–N(42)–C(44)	107.2(17)
N(24)–C(27)–C(28)	111.3(17)		

(c) In the CHCl₃ solvent molecule

Cl(61)–C(6)	1.752(20)	Cl(61)–C(6)–Cl(62)	110.7(16)
Cl(62)–C(6)	1.725(29)	Cl(61)–C(6)–Cl(64)	117.9(19)
Cl(64)–C(6)	1.39(5)	Cl(61)–C(6)–Cl(63)	109.5(14)
Cl(63)–C(6)	1.750(23)	Cl(62)–C(6)–Cl(63)	106.5(13)
		Cl(64)–C(6)–Cl(63)	131.5(18)

any other $N \cdots S$ distance and we infer that the hydrazide group, through its sp^2 N(41) atom, is attracted in a similar

Table 4. Kinetic data for the reaction of $[\overline{Ta(NMeNMe_2)}$-$(S_2CNEt_2)_3]^+$ with HBr in MeCN (24.0 °C, $\lambda = 400$ nm)

[Ta]/mmol dm⁻³	[HBr]/mmol dm⁻³	$10^3\,k_{obs.}/s^{-1}$
0.50	5.0	7.3
	10.0	6.8
	20.0	7.1
	30.0	7.3
	40.0	6.8
	50.0	7.0
0.25	10.0	6.9
1.00	10.0	7.1

Scheme. The mechanism for the formation of Me_2NNHMe and $[TaBr_2$-$(S_2CNEt_2)_3]$ from the reaction of $[\overline{Ta(NMeNMe_2)}(S_2CNEt_2)_3]^+$ with HBr in MeCN, dithiocarbamate ligands omitted for clarity

(though rather weaker) coplanar interaction with the S_2CNEt_2 ligand of S(12). This would account for the alignment of the hydrazido(1 −)-ligand in this direction; we see no steric advantage for this arrangement.

Within each S_2CNEt_2 ligand the dimensions are as expected and the S_2CNC_2 group is virtually planar, with a very small rotation, *ca.* 1—3°, about the C(n3)–N(n4) bond. The two end methyl groups are directed almost straight out from the S_2CNC_2 plane, one to each side; the C(n3)–N(n4)–C–C torsion angles are all close to 90°, lying in the range 86(2)—103(2)°.

Protonation of $[\overline{Ta(NMeNMe_2)}(S_2CNEt_2)_3]^+$.—The reaction of an excess of HBr with $[\overline{Ta(NMeNMe_2)}(S_2CNEt_2)_3]^+$ in MeCN rapidly yields $[TaBr_2(S_2CNEt_2)_3]$ and trimethylhydrazine as described by equation (1). Both products were

$$[\overline{Ta(NMeNMe_2)}(S_2CNEt_2)_3]^+ + 2HBr \longrightarrow$$
$$[TaBr_2(S_2CNEt_2)_3] + Me_2NHNHMe^+ \quad (1)$$
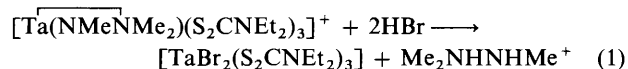
isolated and characterised by elemental analysis and ¹H n.m.r. spectroscopy.

Kinetic studies on reaction (1) show that in the range [HBr] = 5—50 mmol dm⁻³ the rate of the reaction exhibits a first-order dependence on the concentration of hydrazide complex, but is independent of the acid concentration, $k_{obs.} = k_1 = (7.0 \pm 0.3) \times 10^{-3}$ s⁻¹ ($k_{obs.}$ is the observed rate constant measured under pseudo-first-order conditions). The kinetic data are shown in Table 4. This rate law, together with the monophasic reaction time course, is consistent with the mechanism shown in the Scheme in which rate-limiting ring opening of the hydrazide ligand allows subsequent rapid protonation of this residue, and formation of products by a pathway which is kinetically hidden from us. This mechanism is identical to that observed in the only other study on the

protonation of side-on hydrazido(1 −)-ligands, where again ring opening of the hydrazide in [Mo(NHNMePh)(NNMePh)-(S₂CNEt₂)₂]⁺ must precede protonation of this complex.[3] The reason why the protonation of the ligand does not occur when both nitrogen atoms are bound must be a consequence of the lack of a stereochemical lone pair of electrons on the nitrogen atoms, as is clear when it is appreciated that the angle between the normals of the planes defined by Ta, N(41), N(42) and N(41), N(42), C(40) is only 7.9°. It is only upon ring opening that a lone pair of electrons becomes available for protic attack.

Experimental

All manipulations in both the synthetic and kinetic studies were routinely performed under an atmosphere of dinitrogen using *Schlenk* or syringe techniques as appropriate.

I.r. spectra were recorded on a Perkin-Elmer SP3-200 spectrometer and n.m.r. spectra on a JEOL FX90Q instrument. Microanalyses were performed in these laboratories by Mr. C. J. Macdonald.

The compounds, [TaBr₂(S₂CNEt₂)₃],[7] SiMe₃(S₂CNEt₂),[11] and Me₃SiNMeNMe₂[12] were prepared by the literature methods.

Trichlorobis[trimethylhydrazido(1 −)]tantalum.—To a slurry of TaCl₅ (3.6 g, 10.0 mmol) in dichloromethane (*ca.* 30 cm³) was added Me₃SiNMeNMe₂ (4.5 cm³, 30.0 mmol) with vigorous stirring. The slurry was heated under reflux for 1 h during which time the solid dissolved and yielded a pale yellow solution. The solution was allowed to cool, filtered to remove any solid, then concentrated to about 15 cm³ *in vacuo.* Addition of diethyl ether yielded [TaCl₃(NMeNMe₂)₂] as a white microcrystalline solid (3.5 g, 8.1 mmol, 81%).

Trichloro(diethyldithiocarbamato)[trimethylhydrazido(1 −)]-tantalum.—To a slurry of [TaCl₃(NMeNMe₂)₂] (0.65 g, 1.5 mmol) in dichloromethane (*ca.* 30 cm³) was added SiMe₃-(S₂CNEt₂) (1.7 g, 7.5 mmol). The solution was stirred for 1 h, filtered to remove any solid, then the solvent removed *in vacuo.* Addition of diethyl ether and stirring produced a yellow solid which was removed by filtration and recrystallised slowly from dichloromethane–diethyl ether[10] as orange needles of [TaCl₃(NMeNMe₂)(S₂CNEt₂)] (0.4 g, 0.78 mmol, 52%).

Tris(diethyldithiocarbamato)[trimethylhydrazido(1 −)]tantalum Bromide.—To a solution of [TaBr₂(S₂CNEt₂)₃] (0.5 g, 0.64 mmol) in dichloromethane (*ca.* 30 cm³) was added Me₃SiNMeNMe₂ (0.8 g, 6.0 mmol). After stirring at room temperature for several minutes the solution became pale yellow, and was stirred for a further 40 min. The solvent was removed *in vacuo* to yield a pale yellow solid which was dissolved in the minimum of dichloromethane, filtered to remove any solid, and then slowly crystallised by the addition of diethyl ether to give yellow prisms of [Ta(NMeNMe₂)-(S₂CNEt₂)₃]Br·CH₂Cl₂ (0.43 g, 0.5 mmol, 78%). This material loses the solvent of crystallisation over 24 h at room temperature, and is thus best stored at −20 °C.

Kinetic Studies.—All kinetic studies were performed on a Philips-Scientific SP1800 spectrophotometer, equipped with a thermostatted cell holder. The temperature in the cell holder was maintained at 25.0 °C by recirculating water from a Grant SE10 thermostatted tank.

The reactions were monitored at λ = 400 nm and were initiated by injecting an aliquot of HBr of known concentration in MeCN through a Subaseal into a known volume of the complex solution, also in MeCN that had previously been

equilibrated to the correct temperature. Stock solutions of anhydrous HBr were prepared and handled as described before.[13]

The rate constants were determined from the normal semilogarithmic plots.[14] Such plots were linear for at least two half-lives.

Crystal Structure Analysis of [Ta(NMeNMe₂)-(S₂CNEt₂)₃]Br·CHCl₃.—*Crystal data.* C₁₈H₃₉BrN₅S₆Ta·CHCl₃, *M* = 898.1, triclinic, space group *P*1̄ (no. 2), *a* = 11.764(6), *b* = 13.182(6), *c* = 13.059(4) Å, α = 115.78(3), β = 93.56(3), γ = 106.52(4)°, *U* = 1 707.2 Å³, *Z* = 2, *D*𝒸 = 1.747 g cm⁻³, *F*(000) = 888, μ(Mo-*K*ₐ) = 49.5 cm⁻¹, λ(Mo-*K*ₐ) = 0.710 69 Å.

Crystals of the compound recrystallised from dichloromethane–ether were clear yellow rectangular prisms stable only under dinitrogen and below *ca.* 0 °C. However, when recrystallised from a chloroform–ether mixture the crystals are small, brighter yellow prisms and much more stable. The sample taken for crystal analysis (0.12 × 0.17 × 0.30 mm) was mounted, in air, on a glass fibre and coated in epoxy resin. After a photograph to confirm crystal quality, the sample was transferred to our Enraf-Nonius CAD4 diffractometer for measurement of accurate cell dimensions (by refinement from the settings of 25 centred reflections with θ *ca.* 11°) and diffraction intensities (to θ_{max.} = 20°). After processing and correction for Lorentz-polarisation effects, absorption (by semiempirical ψ-scan methods), and for negative intensities (by Bayesian statistics), intensity data for 3 195 unique reflections were entered into the SHELX program;[15] no deterioration correction was necessary.

The structure was readily determined by the heavy-atom method and was refined by full-matrix least-squares methods to convergence at *R* = 0.058, *R'* = 0.063[15] for the 2 952 reflections having *I* > σ_{I}, and weighted *w* = (σ_{F}² + 0.005 91 *F*²)⁻¹. Hydrogen atoms were included in idealised positions, with the methyl groups in staggered arrangements; most H atoms were set to ride on their bonded C atoms, but some methyl groups were refined as rigid groups. The chloroform solvent molecule was found to be disordered in two orientations (with occupancy ratio 4/1), pivoting about two of the Cl atoms. Except for the single minor-occupancy Cl atom, all non-hydrogen atoms were allowed anisotropic thermal parameters.

Scattering factors for the neutral atoms (Ta, C, H, N, S, and Cl) and for Br⁻ were from ref. 16. Computer programs used in this analysis have been listed in Table 4 of ref. 17, and were run on the AFRC's VAX 11/750 machine at IHR-Glasshouse Crops Research Institute, Littlehampton.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

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