Organoimido-complexes of Tantalum(V). Preparation and *X*-Ray Crystal Structure of Bis[bis(trimethylsilyl)amido]chloro(t-butylimido)-tantalum(V) and Bis[bis(trimethylsilyl)amido]-di-μ-bromo-dibromobis-(trimethylsilylimido)ditantalum(V) †

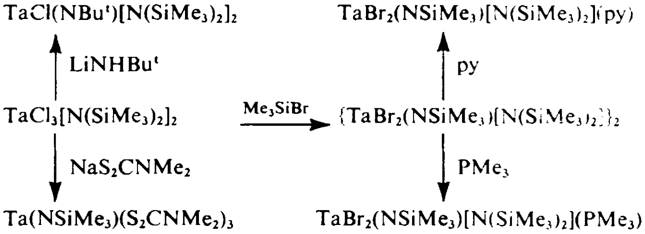
Donald C. Bradley,* Michael B. Hursthouse,* K. M. Abdul Malik, Alistair J. Nielson, and George B. Chota Vuru
Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS

Some novel organoimido-complexes of tantalum have been obtained from reactions of $TaCl_3[N(SiMe_3)_2]_2$ with various reagents. Thus addition of $LiNHBu^t$ gave the monomeric complex $TaCl(NBu^t)[N(SiMe_3)_2]_2$ (molecular geometry parameters: Ta=N 1.763, Ta–N 1.988 and 2.029, Ta–Cl 2.322 Å; Ta=NC 165.8°, from crystal structure analysis) corresponding to replacement of two chlorines. Reaction with Me_3SiBr led to the formation of the centrosymmetric five-co-ordinated dimer $[Ta_2(\mu\text{-}Br)_2Br_2(NSiMe_3)_2\{N(SiMe_3)_2\}_2]$ (for which *X*-ray structure analysis gave Ta=N 1.761, Ta–N 1.965, Ta–Br 2.502; Ta–μ-Br 2.655 and 2.713 Å; Ta=NSi 166.1°) where two chlorines were replaced by bromines and one $N(SiMe_3)_2$ ligand was cleaved to generate the $Ta=NSiMe_3$ moiety. The unsymmetrical bromine bridge was readily disrupted by addition of neutral donor ligands which produced the compounds $TaBr_2(NSiMe_3)[N(SiMe_3)_2](C_5H_5N)$ and $TaBr_2(NSiMe_3)[N(SiMe_3)_2](PMe_3)$. Reaction of $TaCl_3[N(SiMe_3)_2]_2$ with NaS_2CNMe_2 gave the adduct $Ta(NSiMe_3)(S_2CNMe_2)_3(CH_2Cl_2)$ which may involve a seven-co-ordinated tantalum imido-complex.

The organoimido-group RN^{2-} is a versatile ligand which can function in various bonding modes. Thus, non-bridging (linear four-electron donor or bent two-electron donor) and bridging (double or triple) modes have all been recognised in recent structural determinations.[1]

We originally isolated some alkylimidotris(dialkylamido)-tantalum compounds $Ta(NR)(NR_2)_3$ from reactions involving $TaCl_5$ and lithium dialkylamides,[2] and Nugent and Harlow[3] have recently determined the *X*-ray crystal structure of the related compound $Ta(NBu^t)(NMe_2)_3$ and shown that it contains a linear non-bridging t-butylimido-group in a four-co-ordinated tantalum compound. Octahedral tantalum(V) organoimido-complexes of the type $TaCl_3(NR)L_2$ [L = tetrahydrofuran (thf) or PR_3] were recently obtained by Rocklage and Schrock[4] using the novel reactions of the neopentylidene complex $Ta(CHBu^t)Cl_3$ with an imine (RN=CHPh). An *X*-ray crystal structure analysis of $[TaCl_3(NPh)(PEt_3)(thf)]$ showed that it also contained a linear four-electron imido-ligand.[5]

During the course of our investigation of the reactions of the compound $TaCl_3[N(SiMe_3)_2]_2$[6] we have isolated a number of new organoimidotantalum(V) compounds (see Scheme) which we now describe in detail.



Scheme.

Results and Discussion

Bis[bis(trimethylsilyl)amido]chloro(t-butylimido)tantalum-(V).—The compound $TaCl(NBu^t)[N(SiMe_3)_2]_2$ was obtained as pale yellow crystals from the reaction of $TaCl_3[N(SiMe_3)_2]_2$[6] and $LiNHBu^t$ in a 1 : 3 molar ratio in pentane. The ^1H n.m.r. spectrum (C_6D_6) gave singlets corresponding to $NC(CH_3)_3$ (δ 1.48) and $N[Si(CH_3)_3]_2$ (δ 0.45) in the correct ratio of intensities. In the i.r. spectrum bands at 410 and 353 cm^{-1} were assigned to Ta–N and Ta–Cl stretching vibrations respectively (Table 1). A weak band at 1 150 cm^{-1} is believed to be due to the $Ta=NBu^t$ stretching vibration but further work using ^{15}N-labelled ligand is needed to provide definitive assignments. The mass spectrum showed the parent molecular ion (*m/e* 607) together with the species $TaCl[N(SiMe_3)_2]^+$ and $TaCl(NBu^t)[N(SiMe_3)_2]^+$, but the most intense tantalum-containing ion was at *m/e* 592 derived by loss of a methyl group from the parent ion. Another strong peak at *m/e* 431 corresponded to the loss of methane from $TaCl(NBu^t)[N(SiMe_3)_2]$. It is noteworthy that all of these species contain chlorine bonded to tantalum.

A single-crystal *X*-ray structure determination confirmed the mononuclear pseudo-tetrahedral configuration (Figure 1). The t-butylimidotantalum moiety is nearly linear (CNTa 165.8°) consistent with the ligand nitrogen acting as a four-electron donor. Some triple-bond character $N\overset{\rightarrow}{=}Ta$ is conconfirmed by the short bond distance (Ta–N 1.763 Å) which is comparable to that in $Ta(NBu^t)(NMe_2)_3$ (Ta–N 1.77 Å).[3] It is of interest to compare the Ta–Cl, Ta–N, and Si–N bond distances in $TaCl(NBu^t)[N(SiMe_3)_2]_2$ with those in $TaCl_3[N(SiMe_3)_2]_2$.[6] The single Ta–Cl distance is significantly shorter than those in the trichloride (2.322 compared with 2.351, 2.362, and 2.366 Å), whereas the Ta–N distances are considerably longer (1.988 and 2.029 compared with 1.928 and 1.933 Å). In addition the Si–N distances are shorter in the imido-complex (1.774, 1.756, 1.759, and 1.755 compared with 1.785, 1.826, 1.790, and 1.823 Å). The exterior angles of the silylamides are much closer to 120 ° (SiNSi 119.5 and 119.0 compared with 115.5 and 114.8°) and the ligands show less distortion suggesting that there is less steric compression in $TaCl(NBu^t)[N(SiMe_3)_2]_2$. Therefore the longer Ta–N and

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† *Supplementary data available* (No. SUP 23882, 33 pp.): full bond lengths and angles, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Physical properties, i.r. and ^{1}H n.m.r. data

Compound	Colour	M.p. (°C)	Infrared spectra ^{a} (cm^{-1}) ν(Ta≡N)	ν(Ta–N)	ν(Ta–X)	^{1}H N.m.r. spectra ^{b} (δ)
$TaCl_3[N(SiMe_3)_2]_2$	Yellow	146—147	—	415, 400	340, 316 ^{c}	0.44 $[(CH_3)_3Si]_2N$
$TaCl(NBu^t)[N(SiMe_3)_2]_2$	Pale yellow	140—142	1 150	410	353 ^{c}	0.45 $[(CH_3)_3Si]_2N$ 1.48 $(CH_3)_3CN$
$Ta_2Br_4(NSiMe_3)_2[N(SiMe_3)_2]_2$	Yellow	105—107	1 135	400	250 ^{d}	0.22 $(CH_3)_3SiN$ 0.38 $[(CH_3)_3Si]_2N$
$TaBr_2(NSiMe_3)[N(SiMe_3)_2](C_5H_5N)$	Yellow	—	1 135	418	250 ^{d}	—
$TaBr_2(NSiMe_3)[N(SiMe_3)_2](PMe_3)$	White	84—86	1 085	350	—	—
$Ta(NSiMe_3)(S_2CNMe_2)_3(CH_2Cl_2)$	Yellow	240—242	1 140	—	360 ^{e}	0.20 $(CH_3)_3SiN$ ^{f} 3.30 $(CH_3)_2NCS_2$ ^{f} 5.25 CH_2Cl_2 ^{f}

^{a} Nujol mulls. ^{b} In C_6D_6 (δ downfield from $SiMe_4$). ^{c} Ta–Cl. ^{d} Ta–Br. ^{e} Ta–S. ^{f} In $CDCl_3$.

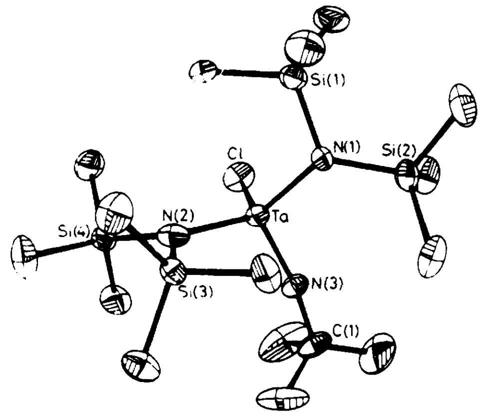

Figure 1. The structure of $TaCl(NBu^t)[N(SiMe_3)_2]_2$. Significant bond lengths (Å) and angles (°) are: Ta–Cl 2.322(2), Ta–N(1) 1.988(5), Ta–N(2) 2.029(5), Ta–N(3) 1.763(6), Si(1)–N(1) 1.774(6), Si(2)–N(1) 1.756(6), Si(3)–N(2) 1.759(6), and Si(4)–N(2) 1.755(5). Ta–N(3)–C(1) 165.8(6), Cl–Ta–N(1) 108.0(2), Cl–Ta–N(2) 111.9(2), Cl–Ta–N(3) 101.8(2), N(1)–Ta–N(2) 117.2(2), N(1)–Ta–N(3) 107.4(3), and N(2)–Ta–N(3) 109.3(2)

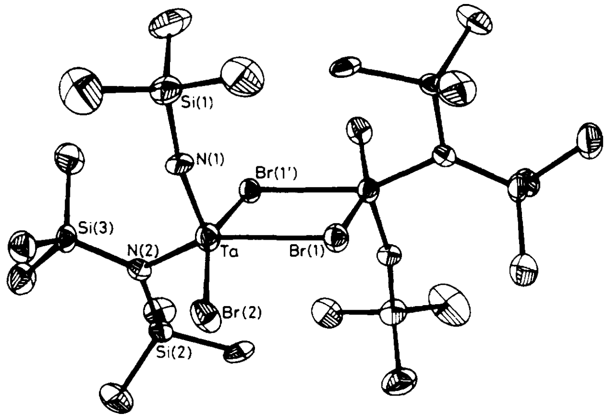

Figure 2. The structure of $\{TaBr(\mu\text{-}Br)(NSiMe_3)[N(SiMe_3)_2]\}_2$. Significant bond lengths (Å) and angles (°) are: Ta–Br(1) 2.713(1), Ta–Br(1′) 2.655(1), Ta–Br(2) 2.502(1), Ta–N(1) 1.761(9), Ta–N(2) 1.965(9), Si(1)–N(1) 1.733(9), Si(2)–N(2) 1.754(10), and Si(3)–N(2) 1.757(11). N(1)–Ta–Br(1) 104.7(3), N(1)–Ta–Br(1′) 97.3(3), N(1)–Ta–Br(2) 100.5(3), N(1)–Ta–N(2) 105.4(4), Br(1)–Ta–Br(1′) 77.3(0), Br(1)–Ta–Br(2) 83.3(0), Br(1)′–Ta–Br(2) 156.4(0), Br(1)–Ta–N(2) 148.6(3), N(2)–Ta–Br(2) 99.7(3), and N(2)–Ta–Br(1′) 90.3(3)

shorter Si–N bonds in the silylamide ligands are indicative of less π donation from N to Ta in $TaCl(NBu^t)[N(SiMe_3)_2]_2$ than in the trichloride. This probably arises from the presence of the strongly π-donating imido-function.

Bis[bis(trimethylsilyl)amido]-di-μ-bromo-dibromobis(trimethylsilylimido)ditantalum.—This compound was unexpectedly obtained in attempting bromine exchange of chlorine in $TaCl_3[N(SiMe_3)_2]_2$ using Me_3SiBr. The yellow crystalline product gave a highest mass peak at *m/e* 588 in the mass spectrum corresponding to $TaBr_2(NSiMe_3)[N(SiMe_3)_2]^+$ and a very intense fragment ion at *m/e* 573 corresponding to loss of a methyl radical. The i.r. spectrum had bands which were assigned to Ta≡N, Ta–N, and Ta–Br stretching frequencies (1 135, 400, and 250 cm^{-1} respectively; Table 1). However, the single-crystal *X*-ray structure determination showed that in the solid state the compound existed as a centrosymmetric bromide-bridged dimer (Figure 2). The trimethylsilylimido-group is near-linear (SiNTa 166.1°) with a short Ta=N bond distance (1.761 Å) implying triple-bond character involving a four-electron nitrogen donor. It is somewhat surprising to find this Ta≡N distance so close to that in the t-butylimido-complex because competition by the silicon atom in Me_3Si–N≡Ta for the nitrogen π electrons would tend to reduce the triple-bond character of the Ta=N bond. In fact the Si–N distance (1.733 Å) in the Me_3Si–N=Ta is significantly shorter than in the silylamide ligand (1.757 and 1.754 Å), but this must be due in part to the *sp* hybridization of nitrogen in the imide compared with sp^2 hybridization in the amide. The silylamide ligand shows angular distortion upon co-ordination (TaNSi 112.3 and 124.0°) but the Si–N bond distances are equal. The Ta–N distance (1.965 Å) is longer than in $TaCl_3[N(SiMe_3)_2]_2$ and shorter than in $TaCl(NBu^t)[N(SiMe_3)_2]_2$. The dimer is based on a significantly unsymmetrical double-bromine bridge (Ta–Br 2.655 and 2.713 Å). This may be indicative of a rather weak bridge bond, and may explain why the mass spectrum contains no dimer species, due to the ease of dissociation into the monomer. The tantalum atoms are five-co-ordinated in a configuration recognisable as a distorted square-based pyramid having the trimethylsilylimido-group in the axial position. The longer Ta–Br bridge distance is virtually *trans* to the terminal Ta–Br (2.502 Å). In solution (C_6D_6) the ^{1}H n.m.r. spectrum gave singlets corresponding to trimethylsilylimide (δ 0.22) and bis(trimethylsilyl)amide (δ 0.38) groups in the correct ratio of intensities, although it was surprising to find the imide chemical shift at higher field than the amide. A molecular weight determination is required to establish whether the dimer persists in solution.

Further evidence for the ready cleavage of the bromide bridge was obtained by adding neutral donor ligands (see Scheme) which produced the adducts $TaBr_2(NSiMe_3)[N(SiMe_3)_2](py)$ (py = pyridine) and $TaBr_2(NSiMe_3)[N(SiMe_3)_2](PMe_3)$ (data in Table 1).

Tris(dimethyldithiocarbamato)trimethylsilylimidotantalum(v)–*Dichloromethane* (1/1).—Another imidotantalum compound was generated by the reaction of $TaCl_3[N(SiMe_3)_2]_2$ with NaS_2CNMe_2 in 1 : 3 molar ratio in dichloromethane. The complex $Ta(NSiMe_3)(S_2CNMe_2)_3(CH_2Cl_2)$ (data in Table 1) had an i.r. band at 1 140 cm^{-1} corresponding to the Ta=N stretching vibration, and bands at 987 and 1 515 cm^{-1} due to the dithiocarbamate ligands. Its mass spectrum gave a strong peak at *m/e* 628 due to the parent ion of the unsolvated complex $Ta(NSiMe_3)(S_2CNMe_2)_3$, and a very strong peak at *m/e* 508 corresponding to $Ta(NSiMe_3)(S_2CNMe_2)_2^+$. The ^1H n.m.r. spectrum of the CH_2Cl_2 solvate in $CDCl_3$ gave peaks due to CH_2Cl_2, Me_2NCS_2, and Me_3SiN (δ 5.25, 3.30, and 0.20) in the correct ratios for the formula $Ta(NSiMe_3)(S_2CNMe_2)_3(CH_2Cl_2)$ but the data did not provide definitive structural information. The i.r. spectra suggested that the dithiocarbamate ligands were bidentate and a seven-coordinated tantalum seems a reasonable proposal.

Experimental

All preparations and manipulations were carried under dry oxygen-free nitrogen using Schlenk tubes and a vacuum line.

Tantalum pentachloride (Specpure grade) was obtained in sealed ampoules from Johnson Matthey Chemicals Ltd. and halogen-free $LiBu^n$ from Metallgesellschaft A.G., Frankfurt as a 1.56 mol dm^{-3} solution in mixed hydrocarbons (b.p. 35—37 °C). The lithium bis(trimethylsilyl)amide was prepared by dropwise addition of excess of $(Me_3Si)_2NH$ to a measured volume of $LiBu^n$ solution at 0 °C.

Micro-analyses (C, H, N, and S) were by the Microanalytical Laboratory of University College, London. Analyses for Ta and Cl were carried out gravimetrically (Ta_2O_5 and AgCl) on the macro-scale.

Infrared spectra were obtained as Nujol mulls using Perkin-Elmer 577 or 255 spectrophotometers covering the range 4 000—200 cm^{-1} using KBr or CsI plates as required. Raman spectra were obtained on the SPEX 1401 laser Raman equipment at Imperial College under the auspices of the University of London Intercollegiate Research Services. Powdered samples were sealed under nitrogen in capillary tubes.

Mass spectra were obtained at 70 eV (*ca.* 1.12×10^{-17} J) using an AEI MS-902 spectrometer by direct insertion. Accurate mass measurements were carried out on certain peaks to establish the elemental constitution of the positively charged species.

N.m.r. spectra were obtained using a Bruker WH80 FT spectrometer usually in C_6D_6 or $C_6D_5CD_3$ with $SiMe_4$ as internal reference.

Bis[bis(trimethylsilyl)amido]chloro(t-butylimido)tantalum(v).—Lithium *t*-butylamide (0.82 g, 0.0104 mol) was added to a stirred solution of $TaCl_3[N(SiMe_3)_2]_2$ (2.1 g, 0.0035 mol) in pentane (50 cm^3). After stirring for 15 h the mixture was filtered, concentrated under reduced pressure, and then cooled to −25 °C. Light yellow crystals were deposited which were recrystallized from pentane giving 1.5 g (71% yield, m.p. 140—142 °C) {Found: C, 32.25; H, 7.45; Cl, 5.65; N, 6.65; Ta, 30.35. $TaCl(NBu^t)[N(SiMe_3)_2]_2$ requires C, 31.6; H, 7.45; Cl, 5.85; N, 6.90; Ta, 29.75%}. Accurate mass measurement on the parent ion gave 607.184 555; calc. for $TaCl(NBu^t)[N(SiMe_3)_2]_2$ 607.185 770. The main tantalum-containing peaks in the mass spectrum (intensities relative to $HNSi_2Me_5^+$ at *m/e* 146 as 100%, in parentheses) at 101 °C were *m/e* 607 (5.6), 592 (62.7), 536 (7.8), 447 (3.4), 432 (5.8), and 431 (26.2). The i.r. bands below 1 300 cm^{-1} were 1 250vs, 1 215s, 1 150w, 925 (sh), 850s (br), 790s, 765w, 710s, 673s, 623w, 505s, 410br, and 353s cm^{-1}.

Bis[bis(trimethylsilyl)amido]-di-μ-bromo-dibromobis(trimethylsilylimido)ditantalum(v).—A solution of $TaCl_3[N(SiMe_3)_2]_2$ (2.1 g, 0.0035 mol) in toluene (50 cm^3) was refluxed with a slight excess of Me_3SiBr (1.4 cm^3) for 6 h. After concentration under reduced pressure and cooling to −25 °C yellow crystals (1.0 g, 25% yield; m.p. 105—107 °C) were obtained {Found: C, 18.05; H, 4.95; Br, 26.75; N, 4.80; Ta, 31.05. $TaBr_2(NSiMe_3)[N(SiMe_3)_2]$ requires C, 18.35; H, 4.65. Br, 27.15; N, 4.75; Ta, 30.75%}. Accurate mass measurement on the parent ion gave 587.950 412; calc. for $TaBr_2(NSiMe_3)[N(SiMe_3)_2]$ 587.948 319. The main Ta-containing peaks in the mass spectrum at 101 °C (relative to *m/e* 573 as 100%) were *m/e* 588 (9.0), 573 (100), 543 (3.7), 528 (3.5), and 483 (2.5). The i.r. bands below 1 300 cm^{-1} were 1 280 (sh), 1 248vs, 1 135s (br), 840s (br), 755m, 690w, 670w, 643w, 400s, and 250w (br) cm^{-1}.

[Bis(trimethylsilyl)amido]dibromo(trimethylsilylimido)tantalum(v)–*Pyridine* (1/1).— Pyridine (0.4 cm^3, 0.0051 mol) was added to a stirred solution of $Ta_2Br_4(NSiMe_3)_2[N(SiMe_3)_2]_2$ (3.0 g, 0.0026 mol) in pentane (50 cm^3) and a yellow solid was precipitated {Found: C, 24.4; H, 5.15; Br, 25.35; N, 6.10; Ta, 27.0. $TaBr_2(NSiMe_3)[(NSiMe_3)_2](C_5H_5N)$ requires C, 25.2; H, 4.85; Br, 23.95; N, 6.35; Ta, 27.1%}. The i.r. spectrum gave a pyridine band at 1 604vs cm^{-1} and the following bands below 1 300 cm^{-1}: 1 250vs, 1 220s, 1 135vs (br), 915m, 880 (sh), 840s (br), 800m, 760s, 715w, 695m, 680 (sh), 640s, 442w, 418m, 356w, and 250w cm^{-1}.

[Bis(trimethylsilyl)amido]dibromo(trimethylsilylimido)tantalum(v)–*Trimethylphosphine* (1/1).—Trimethylphosphine was added in excess to $Ta_2Br_4(NSiMe_3)_2[N(SiMe_3)_2]_2$ in pentane and gave white crystals (m.p. 84—86 °C) {Found: C, 21.1; H, 5.65; Br, 24.1; N, 4.15; Ta, 27.3. $TaBr_2(NSiMe_3)[N(SiMe_3)_2](PMe_3)$ requires C, 21.7; H, 5.45; Br, 24.05; N, 4.20; Ta, 27.25%}. The i.r. spectrum showed the following bands below 1 300 cm^{-1}: 1 250vs, 1 085 (sh), 1 015 (sh), 975w, 915s, 845s, 795m, 755m, 720 (sh), 690 (sh), 605w, 510w, 450br, 350w, and 330 (sh) cm^{-1}.

Tris(dimethyldithiocarbamato)trimethylsilylimidotantalum(v)–*Dichloromethane* (1/1).—Sodium dimethyldithiocarbamate (1.45 g, 0.0101 mol) was added to a stirred solution of $TaCl_3[N(SiMe_3)_2]_2$ (2.0 g, 0.0033 mol) in dichloromethane (35 cm^3). After stirring for 12 h followed by filtration, the filtrate was concentrated under reduced pressure and cooled to −25 °C. Yellow crystals (m.p. 240—242 °C) sparingly soluble in pentane, diethyl ether, and benzene but soluble in dichloromethane and chloroform were deposited {Found: C, 22.05; H, 4.35; Cl, 9.15; N, 7.90; S, 27.1; Ta, 25.2. $Ta(NSiMe_3)(S_2CNMe_2)_3(CH_2Cl_2)$ requires C, 21.9; H, 4.10; Cl, 9.95; N, 7.85; S, 26.95; Ta, 25.35%}. Accurate mass measurement on the parent ion gave 627.978 767; $Ta(NSiMe_3)(S_2CNMe_2)_3$ requires 627.980 803. The major tantalum-containing peak in the mass spectrum (181 °C) was at *m/e* 508 corresponding to $Ta(NSiMe_3)(S_2CNMe_2)_2^+$ (accurate mass: found, 507.985 724; calc., 507.986 632). Other species (relative to *m/e* 508, 100%)

Table 2. Fractional atomic co-ordinates for the chloro-complex

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ta	0.245 66(2)	0.140 31(1)	0.233 30(2)	C(11)	0.497 6(6)	0.140 2(5)	0.341 7(7)
Cl	0.240 6(2)	0.247 3(1)	0.323 7(2)	C(12)	0.558 1(8)	0.236 2(6)	0.164 6(10)
Si(1)	0.495 0(2)	0.149 1(1)	0.188 5(2)	C(13)	0.580 1(8)	0.075 7(6)	0.142 0(9)
Si(2)	0.332 7(2)	0.164 0(1)	−0.014 5(2)	C(21)	0.274 9(9)	0.254 1(5)	−0.028 0(8)
Si(3)	0.261 9(2)	−0.026 8(1)	0.288 1(2)	C(22)	0.239 0(8)	0.098 3(5)	−0.085 8(6)
Si(4)	0.221 3(2)	0.070 3(1)	0.477 4(2)	C(23)	0.458 8(9)	0.162 6(6)	−0.090 7(8)
N(1)	0.359 3(4)	0.145 8(3)	0.127 1(4)	C(31)	0.136 6(7)	−0.079 7(5)	0.306 6(8)
N(2)	0.254 2(4)	0.058 7(3)	0.340 8(4)	C(32)	0.385 4(8)	−0.073 0(5)	0.353 6(8)
N(3)	0.118 4(5)	0.139 2(3)	0.155 3(5)	C(33)	0.276 3(8)	−0.025 6(4)	0.137 1(6)
C(1)	0.002 9(6)	0.140 2(4)	0.117 6(7)	C(41)	0.310 0(8)	0.138 4(5)	0.554 7(7)
C(2)	−0.017 5(9)	0.161 3(10)	0.000 0(11)	C(42)	0.078 7(7)	0.098 2(6)	0.476 1(8)
C(3)	−0.044 0(10)	0.068 9(6)	0.133 9(14)	C(43)	0.238 1(11)	−0.010 7(6)	0.564 0(7)
C(4)	−0.050 9(10)	0.191 7(9)	0.190 2(13)				

Table 3. Fractional atomic co-ordinates for the bromo-complex

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ta	0.063 05(5)	0.014 96(5)	0.329 60(4)	C(12)	0.536 8(20)	0.177 8(25)	0.405 0(20)
Br(1)	−0.077 0(1)	0.145 7(1)	0.489 3(1)	C(13)	0.500 1(31)	0.289 7(32)	0.166 8(18)
Br(2)	−0.050 3(2)	0.167 0(2)	0.204 0(1)	C(21)	−0.244 2(13)	−0.195 0(17)	0.345 7(13)
Si(1)	0.411 8(4)	0.248 9(5)	0.308 4(4)	C(22)	−0.188 4(22)	−0.303 7(19)	0.124 2(15)
Si(2)	−0.110 6(4)	−0.278 9(4)	0.256 1(3)	C(23)	−0.102 5(21)	−0.456 2(16)	0.326 4(16)
Si(3)	0.219 9(4)	−0.183 0(4)	0.157 3(3)	C(31)	0.380 4(20)	−0.182 5(20)	0.236 9(14)
N(1)	0.248 7(10)	0.115 5(10)	0.313 6(9)	C(32)	0.266 4(19)	−0.031 4(19)	0.043 0(12)
N(2)	0.063 6(11)	−0.156 2(11)	0.241 7(8)	C(33)	0.178 3(22)	−0.368 1(20)	0.091 7(16)
C(11)	0.356 6(26)	0.416 2(18)	0.366 7(18)				

present were *m/e* 628 (37.2), 613 (2.3), 568 (5.4), and 388 (3.0%). The i.r. bands below 1 600 cm^{-1} were 1 560 (sh), 1 540 (sh), 1 515s (br), 1 250s, 1 140 (sh), 1 105vs, 1 000 (sh), 987m, 915br, 835vs, 750w, 735m, 633, 578s, 447s, and 360s (br) cm^{-1}.

Crystallography.—Crystals of both compounds were sealed in Lindemann capillaries for *X*-ray study. Unit-cell parameters were determined, and intensity data recorded at 295 K, using an Enraf–Nonius CAD4 diffractometer and graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) in the ω–2θ scan mode in a manner previously described in detail.[7] The intensity data were corrected for absorption.

Crystal data. $TaCl(NBu^t)[N(SiMe_3)_2]_2$, $C_{16}H_{45}ClN_3Si_4Ta$, M = 608.32, monoclinic, a = 12.343(2), b = 19.089(3), c = 12.135(3) Å, β = 94.98(3)°, U = 2 848.4 Å^3, space group $P2_1/n$, Z = 4, D_c = 1.42 g cm^{-3}, μ(Mo-K_α) = 45.8 cm^{-1}.

$Ta_2Br_4(NSiMe_3)_2[N(SiMe_3)_2]_2$, $C_{18}H_{54}Br_4N_4Si_6Ta_2$, M = 1 176.7, triclinic, a = 9.254(4), b = 9.340(4), c = 12.287(5) Å, α = 87.57(4), β = 84.04(4), γ = 102.30(4)°, U = 1 025.5 Å^3, space group $P\bar{1}$, Z = 1, D_c = 1.905 g cm^{-3}, μ = 92.9 cm^{-1}.

The structures were solved routinely *via* the heavy-atom method and refined by full-matrix least squares using standard computer programs and scattering-factor data.[7] In both cases, non-hydrogen atoms were assigned anisotropic thermal parameters and hydrogen atoms included in idealized positions with common isotropic thermal parameters.

The final R (= $\Sigma|\Delta F|/\Sigma|F|$) and R' (= $\Sigma w^{\frac{1}{2}}|\Delta F|/\Sigma w^{\frac{1}{2}}|F|$) values were 0.041 and 0.037 for the chloro-compound {3 826 observed data [$I > 2\sigma(I)$], 5 008 measured, weights = $1/(\sigma^2F_o + 0.0004F_o^2)$} and 0.053 and 0.053 for the bromo-compound {2 658 observed data [$I > 2\sigma(I)$], 3 221 measured, weights = $1/(\sigma^2F + 0.0012F_o^2)$}.

Fractional atomic co-ordinates are given in Tables 2 and 3.

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