Synthesis and Reactions of Some Tris(2-methylphenyl)silanolatometal Compounds. Crystal and Molecular Structures of $[Ta\{OSi(C_6H_4Me\text{-}2)_3\}Cl_4]\cdot 1.5Et_2O$ and $[Ta\{OSi(C_6H_4Me\text{-}2)_3\}Me_3Cl]$†

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The reactions of $HfCl_4$, $NbCl_5$, $TaCl_5$ and WCl_6 with $Li[OSi(C_6H_4Me\text{-}2)_3]$ in 1:1 molar ratios afforded the compounds $[Hf\{OSi(C_6H_4Me\text{-}2)_3\}Cl_4]\cdot Li(Et_2O)_2$ **1**, $[Nb\{OSi(C_6H_4Me\text{-}2)_3\}Cl_4]\cdot 1.5Et_2O$ **2**, $[Ta\{OSi(C_6H_4Me\text{-}2)_3\}Cl_4]\cdot 1.5Et_2O$ **3** and $Si(C_6H_4Me\text{-}2)_3Cl$ respectively. The reactions of **3** with MgMeX (X = Cl or I) under a range of conditions were explored. Thus the compounds $[Ta\{OSi(C_6H_4Me\text{-}2)_3\}Me_3X]$ **4** (X = Cl), and the corresponding isomorphous mixture **4a** having chloride and iodide present in the ratio 2:1, $[\{Ta[OSi(C_6H_4Me\text{-}2)_3]Me_3\}_2]$ **5** and $[Ta\{OSi(C_6H_4Me\text{-}2)_3\}_2Me_2Cl]$ **6** have been prepared and characterised. Compound **6** was also prepared from $[Ta\{OSi(C_6H_4Me\text{-}2)_3\}_2Cl_3]$ **7**. X-Ray structures of compound **3**, and the isomorphous mixture **4a** have been determined. Compound **3** is octahedral with the siloxy and ether groups mutually *trans* with Ta–O distances of 1.812(3) (siloxy) and 2.263(3) Å (ether); Ta–Cl 2.328–2.356(1). Compound **4a** is five-co-ordinate trigonal bipyramidal with the siloxy and halide axial: Ta–O 1.856(5), Ta–Cl/I 2.37(1)/2.674(6), and equatorial Ta–C 2.11–2.17(1) Å.

A diverse range of chemical reactions have been reported for transition-metal compounds having bulky alkoxy, aryloxy or

indicated for $[Ta\{OSiMe_2C(SiMe_3)_3\}Cl_4]$. The triarylsiloxy ligand may be reasonably assumed to be a weaker π donor than

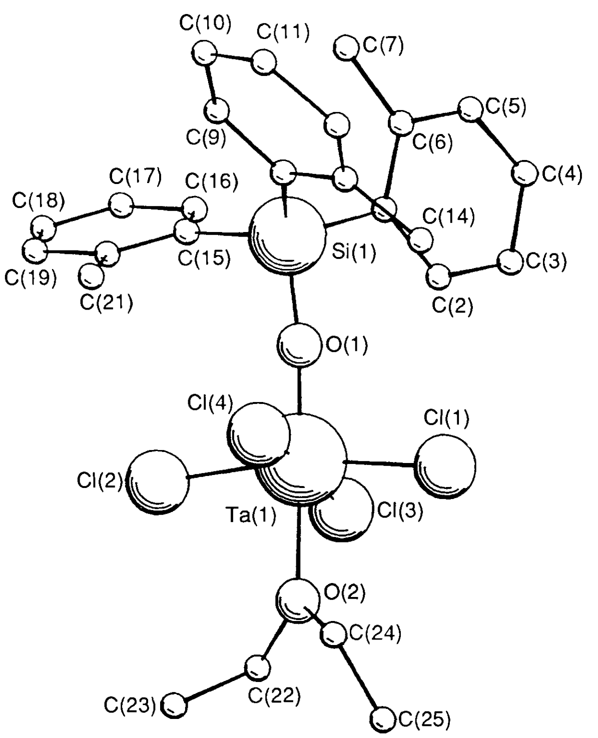

Fig. 1 The molecular structure of compound **3**

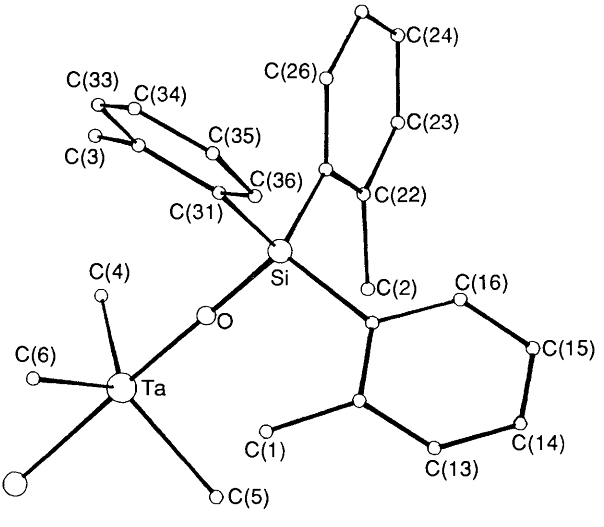

Fig. 2 The molecular structure of compound **4a**

Table 1 Bond lengths (Å) and angles (°) for compound **3**

Ta-Cl(1)	2.353(1)	Ta-Cl(2)	2.328(1)
Ta-Cl(3)	2.356(1)	Ta-Cl(4)	2.351(1)
Ta-O(1)	1.812(3)	Ta-O(2)	2.263(3)
Si-O(1)	1.706(3)	Si-C(1)	1.877(4)
Si-C(8)	1.884(4)	Si-C(15)	1.873(5)
Cl(1)-Ta-Cl(2)	168.64(5)	Cl(1)-Ta-Cl(3)	88.48(5)
Cl(1)-Ta-Cl(4)	90.84(5)	Cl(2)-Ta-Cl(3)	88.42(5)
Cl(2)-Ta-Cl(4)	90.40(5)	Cl(3)-Ta-Cl(4)	170.4(5)
Cl(1)-Ta-O(1)	94.9(1)	Cl(1)-Ta-O(2)	84.71(1)
Cl(2)-Ta-O(1)	96.3(1)	Cl(2)-Ta-O(2)	84.2(1)
Cl(3)-Ta-O(1)	95.7(1)	Cl(3)-Ta-O(2)	86.8(1)
Cl(4)-Ta-O(1)	93.9(1)	Cl(4)-Ta-O(2)	83.7(1)
O(1)-Ta-O(2)	177.5(1)	O(1)-Si-C(8)	108.8(3)
O(1)-Si-C(1)	104.4(3)	C(1)-Si-C(8)	112.6(4)
O(1)-Si-C(15)	104.8(3)	C(8)-Si-C(12)	113.9(2)
C(1)-Si-C(15)	111.5(4)		
Ta-O(1)-Si	172.1(2)		

$[Ta\{OSi(C_6H_4Me\text{-}2)_3\}Me_4]$ **A** and its decomposition product $[\{Ta[OSi(C_6H_4Me\text{-}2)_3]Me_3\}_2]$ **5** were obtained. When left at room temperature for approximately 24 h the solutions were found to be free of the tetramethyl component. Compound **5** and traces of methane were the only species detected in the NMR spectrum. Crystals of **5** suitable for X-ray analysis could not be obtained but an unbridged D_{3h} structure with a Ta–Ta single bond was consistent with ^1H NMR and molecular-weight data. A similar unbridged dimeric tantalum(IV) species was proposed for the compound $[\{Ta(OSiBu^t_3)_2H_2\}_2]$.[5] It is noteworthy that the compound $TaMe_3Cl_2$ is thermally unstable at room temperature while the compound $TaMe_4Cl$ has not been isolated.[13] In an attempt to generate compound **5** by a different route, compound **4** was treated with 1 equivalent of sodium amalgam in tetrahydrofuran (thf) at room temperature. A mixture of products was indicated from the ^1H NMR spectrum of the reaction mixture including peaks due to $[Ta\{OSi(C_6H_4Me\text{-}2)_3\}_2Me_2Cl]$ **6** and compound **5**. Compounds **5** and **6** were also observed among the reaction products when **4** was treated with the ylide $Ph_2MeP{=}CH_2$ but the expected alkylidene product could not be detected. Compound **5** failed to react with excess of dimethylphenylphosphine but NMR samples of **5** treated with iodine were converted into the compound $[Ta\{OSi(C_6H_4Me\text{-}2)_3\}Me_3I]$. If a trigonal-bipyramidal structure obtains in the case of the tetramethyl derivative **A**, then the comparative stability of the trimethyl derivatives **4**, with halide *trans* to the siloxy group, may imply some π interaction between the halide ligand and tantalum.

When temperatures of −78 °C were employed in the preparations of compounds **4** and **5** deep green solutions (presumably owing to the generation of Ta^{IV}) were formed resulting in black suspensions at room temperature and mixtures of products from which the compound **4** or **5** could be separated by exploitation of slight solubility differences. At 0 °C however these reactions proceeded cleanly. The compound $[Ta\{OSi(C_6H_4Me\text{-}2)_3\}_2Me_2Cl]$ **6** was also isolated from one reaction carried out at −78 °C, between compound **3** and 3 equivalents of methylmagnesium chloride. This indicated that siloxide displacement is a competitive process at low temperature and is in contrast to the reactivity of related di- or tri-siloxy species $[Ta(OSiBu^t_3)_2Cl_3]$ or $[Ta(OSiBu^t_3)_3Cl_2]$ which undergo halide displacement and reduction without loss of siloxy group.[3,5] It is probable that the siloxide group Bu^t_3SiO is a stronger π donor than is $(2\text{-}MeC_6H_4)_3SiO$ and therefore less readily displaced. This, however, is not reflected in the reported Ta–O and Si–O distances in related species (see below).

Crystal Structures.—The structures of compounds **3** and **4a** are shown in Figs. 1 and 2 with selected bond lengths and angles in Tables 1 and 2. Incorporation of one ether molecule into the co-ordination sphere of compound **3** results in the observed octahedral geometry with the chloride groups in the equatorial plane. A second disordered ether molecule is also present in each unit cell, effectively trapped within the cavity generated by the tris(2-methylphenyl)silyl umbrellas of adjacent molecules. In this complex the Ta atom has a formal electron count of 12, and the shortness of the Ta–O(siloxy) bond [1.812(3) Å] together with the near linearity of the Ta–O–Si [172.1(2) Å] chain clearly reflects the presence of significant O–Ta p_π–d_π interaction as a means of increasing the electron count. Some π donation from the chloride ligands may also occur, and it is pertinent to note that the Ta–Cl distances here are on average a little shorter than those in a similar equatorial arrangement in the tantalum(V) complex $[Ta(\eta^5\text{-}C_5Me_5)Cl_4(CH{=}PMePh_2)]$.[14] One of the Ta–Cl distances in compound **3** is slightly shorter than the other three but there is no obvious reason for this; none

Table 2 Bond lengths (Å) and angles (°) for compound **4a**

I–Ta	2.674(6)	Cl–Ta	2.368(10)
O–Ta	1.856(5)	C(4)–Ta	2.169(8)
C(5)–Ta	2.143(8)	C(6)–Ta	2.107(7)
Cl–I	0.343(10)	O–Si	1.655(5)
C(11)–Si	1.875(7)	C(21)–Si	1.869(7)
C(31)–Si	1.874(7)	C(12)–C(11)	1.425(7)
C(16)–C(11)	1.390(9)	C(13)–C(12)	1.380(9)
C(1)–C(12)	1.522(10)	C(14)–C(13)	1.389(11)
C(15)–C(14)	1.372(11)	C(16)–C(15)	1.380(9)
C(22)–C(21)	1.382(9)	C(26)–C(21)	1.431(9)
C(23)–C(22)	1.413(10)	C(2)–C(22)	1.488(11)
C(24)–C(23)	1.432(15)	C(25)–C(24)	1.366(14)
C(26)–C(25)	1.392(9)	C(32)–C(31)	1.398(8)
C(36)–C(31)	1.390(8)	C(33)–C(32)	1.407(9)
C(3)–C(32)	1.504(11)	C(34)–C(33)	1.403(12)
C(35)–C(34)	1.395(11)	C(36)–C(35)	1.391(9)
O–Ta–Cl	177.8(2)	O–Ta–I	177.1(1)
C(4)–Ta–Cl	87.9(4)	C(4)–Ta–I	91.1(3)
C(5)–Ta–I	86.8(3)	C(4)–Ta–O	91.6(3)
C(5)–Ta–O	91.0(3)	C(5)–Ta–Cl	87.5(4)
C(6)–Ta–I	86.9(3)	C(5)–Ta–C(4)	122.3(4)
C(6)–Ta–O	92.5(3)	C(6)–Ta–Cl	89.6(4)
C(6)–Ta–C(5)	120.9(4)	C(6)–Ta–C(4)	116.5(4)
C(21)–Si–O	108.2(3)	C(11)–Si–O	108.5(3)
C(31)–Si–O	106.7(3)	C(21)–Si–C(11)	109.6(3)
C(31)–Si–C(21)	111.3(3)	C(31)–Si–C(11)	112.3(3)
C(12)–C(11)–Si	124.2(5)	Si–O–Ta	177.9(2)
C(16)–C(11)–C(12)	117.9(6)	C(16)–C(11)–Si	117.9(5)
C(1)–C(12)–C(11)	121.2(6)	C(13)–C(12)–C(11)	118.8(6)
C(14)–C(13)–C(12)	122.8(7)	C(1)–C(12)–C(13)	120.1(6)
C(16)–C(15)–C(14)	121.5(7)	C(15)–C(14)–C(13)	117.8(7)
C(22)–C(21)–Si	124.6(5)	C(15)–C(16)–C(11)	121.3(6)
C(26)–C(21)–C(22)	119.1(6)	C(26)–C(21)–Si	116.2(5)
C(2)–C(22)–C(21)	122.1(6)	C(23)–C(22)–C(21)	119.7(8)
C(24)–C(23)–C(22)	119.1(10)	C(2)–C(22)–C(23)	118.2(8)
C(26)–C(25)–C(24)	118.3(9)	C(25)–C(24)–C(23)	121.7(8)
C(32)–C(31)–Si	122.5(5)	C(25)–C(26)–C(21)	121.9(8)
C(36)–C(31)–C(32)	119.2(6)	C(36)–C(31)–Si	118.3(5)
C(3)–C(32)–C(31)	123.6(6)	C(33)–C(32)–C(31)	119.5(7)
C(34)–C(33)–C(32)	120.2(7)	C(3)–C(32)–C(33)	116.9(7)
C(36)–C(35)–C(34)	118.8(7)	C(35)–C(34)–C(33)	120.1(7)
		C(35)–C(36)–C(31)	122.1(7)

of the three chlorides with the longer bonds is involved in significant intermolecular interactions. Coincidentally, one of the four Ta–Cl bonds in the ylide complex just mentioned was also found to be considerably shorter than the other three and was in an eclipsed position relative to a C–Me bond on the cyclopentadienyl function. No feature of this kind is present in our complex however.

Compound **4a** has distorted trigonal-bipyramidal geometry with the methyl groups in the equatorial sites. The refinement revealed isomorphous random distribution of chloride and iodide at one of the axial sites with occupancies in the approximate ratio 2:1. The Ta–O(siloxy) bond is slightly longer than that in compound **3**, possibly as a result of some competition from the potentially weakly π-donating *trans* halide. This feature may also reflect the nature of the axial bonding in this trigonal-bipyramidal structure. However the Ta–O–Si chain is essentially linear and the Ta–O distance is considerably shorter than the Ta–O(axial) distances in the closely related trigonal-bipyramidal complexes [Ta(OR)(OR′)-Me$_3$] (OR = OR′ = 2,6-di-*tert*-butylphenoxide; OR = 4-methoxy-2,5-di-*tert*-butylphenoxide, OR′ = methoxide) which are > 1.925 Å,[15] but where these π-donating ligands are mutually *trans*. The Ta–C(methyl) distances in **4a** are similar to those in the aryl oxides in spite of the assumed significant steric

1.878(9) Å, Si–O 1.68(3) Å, and Ta–O–Si 170(3)° (all average values). It is also noteworthy that the Ta–O distances are very similar to those reported for the dialkoxytantalum species $[Ta(CH_2Bu^t)_3L_2]$ 1.869(9) Å, L = 9-oxytriptycene,[6] and in the diaryloxytantalum species $[Ta(OC_6H_3Bu^t{}_2\text{-}2,6)_2Cl_3]$, 1.836(4) Å and 1.872(5) Å (axial), where the aryl oxide groups are mutually *cis*.[16] No significant differences in the π-donor abilities of these oxo-ligating groups is detectable from these data and we must presume that this property is therefore not significantly affected by any O–Si p_π–d_π bonding which might occur in the siloxy function, particularly in the arylsiloxides despite the fact that these ligands are apparently more readily displaced than alkylsiloxides by anionic basic reagents.

Experimental

Standard Schlenk techniques were employed throughout this work. Melting points were recorded on samples sealed in capillaries under nitrogen. Elemental analyses were from University College London Analytical Service. Spectrometers: NMR, Bruker (80 and 250 MHz) in [$^2H_6$]benzene; mass, Kratos MS 50RF (at 70 eV, 1.12 × 10^{-17} J).

Bis(diethyl ether)lithium–Tetrachlorotris(2-methylphenyl)silanolatohafnium (1/1) **1**.—A slurry of hafnium tetrachloride (2.99 g, 8.4 mmol) in thf (40 cm^3) at −78 °C was treated with tris(2-methylphenyl)silanolatolithium (8.4 mmol) in diethyl ether (30 cm^3). The resultant yellow solution was brought to room temperature and stirred overnight. The ethers were removed and toluene (40 cm^3) was added to the gummy residue. A clear solution was obtained when the mixture was heated to 90 °C and on cooling to room temperature a pale pink crystalline solid was deposited (4.2 g, 63%), m.p. 170–175 °C (Found: C, 43.0; H, 5.1. Calc. for $C_{29}H_{41}Cl_4HfLiO_3Si$: C, 43.9, H, 5.2%); *m*/*z* 602 (0.3) {$[M - LiCl(Et_2O)_2]^+$} and 510 (4.5%) ($[602 - C_7H_8]^+$). ^{1}H NMR (C_6D_6): δ 1.14 (m, 12 H, Et$_2$O), 2.65 (s, 9 H, *o*-Me), 3.93 (m, 8 H, Et$_2$O), 7.1 (m, aryl) and 8.1 (m, *p*-H).

Tetrachlorotris(2-methylphenyl)silanolatoniobium–Diethyl Ether (1/1.5) **2**.—A slurry of niobium pentachloride (2.37 g, 8.8 mmol) in toluene (30 cm^3) at −78 °C was treated with tris(2-methylphenyl)silanolatolithium (8.8 mmol) in diethyl ether (30 cm^3). The yellow suspension was warmed to room temperature, stirred overnight, and then filtered. The filtrate was concentrated and then diluted with pentane until a yellow precipitate began to appear. Filtration followed by cooling to −20 °C afforded bright yellow needles of the product (2.1 g, 36.2%), m.p. 86 °C (decomp.) (Found: C, 49.1; H, 5.3. Calc. for $C_{27}H_{36}Cl_4NbO_{2.5}Si$: C, 48.9; H, 5.5%). ^{1}H NMR (C_6D_6): δ 1.0 (t, 9 H, Et$_2$O), 2.57 (s, 9 H, *o*-Me), 4.12 (q, 6 H, Et$_2$O), 6.7–7.2 (m, aryl H) and 8.0–8.2 (m, *p*-H).

Tetrachlorotris(2-methylphenyl)silanolatotantalum–Diethyl Ether (1:1.5) **3**.—To a suspension of $TaCl_5$ (0.62 g, 1.73 mmol) in toluene (30 cm^3) was added dropwise, at −78 °C, a solution of tris(2-methylphenyl)silanolatolithium (1.73 mmol), in toluene (40 cm^3). The yellow suspension slowly decolourised and after stirring for 2 h at low temperature was allowed to warm to room temperature overnight. The solvent was removed and fresh toluene added to the residual off-white solid. Filtration of the hot toluene extract followed by concentration and cooling gave a mass of colourless cubes (1.12 g, 86%), m.p. 75 °C (Found: C, 42.9; H, 4.6. Calc. for $C_{27}H_{36}Cl_4O_{2.5}SiTa$: C, 43.2; H, 4.8%). ^{1}H NMR ($CDCl_3$): δ 1.39 (t, 9 H, Et$_2$O), 2.27 (s, 9 H, *o*-Me), 4.59 (q, 6 H, Et$_2$O) and 7.23–7.86 (m, aryl H).

Chlorotrimethyltris(2-methylphenyl)silanolatotantalum **4**.—To a cooled solution (0 °C), of compound **3** (1.5 g, 1.99 mmol) in diethyl ether (20 cm^3) was added dropwise a solution of

Table 3 Fractional atomic coordinates for compound **3**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ta	2377.3(1)	1792.2(1)	323.4(1)
Cl(1)	39(1)	1739(1)	464(1)
Cl(2)	4736(1)	1636(1)	−76(1)
Cl(3)	2020(1)	−26(1)	1310(1)
Cl(4)	2795(2)	3483(1)	−925(1)
Si	2129(1)	2975.5(9)	2587.3(9)
O(1)	2125(3)	2385(3)	1522(3)
C(1)	636(5)	2254(4)	3793(4)
C(2)	−53(5)	1367(4)	3666(4)
C(3)	−1151(6)	795(6)	4534(5)
C(4)	−1558(7)	1062(7)	5552(6)
C(5)	−902(7)	1964(6)	5656(5)
C(6)	191(7)	2566(5)	4815(4)
C(7)	891(12)	3536(7)	5011(7)
C(8)	1920(5)	4471(4)	2190(4)
C(9)	2830(6)	5191(4)	2353(5)
C(10)	2761(7)	6317(5)	2079(5)
C(11)	1710(7)	6689(4)	1676(5)
C(12)	813(7)	5999(5)	1512(5)

Table 4 Fractional atomic coordinates (× 10^4) for compound **4a**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ta	7712.0(2)	6 893.9(2)	−280.5(1)
I	8774(3)	5 789(3)	1726(3)
Cl	8693(9)	5 802(9)	1441(6)
Si	6335(1)	8 523(1)	−2852(1)
O	7005(3)	7 740(3)	−1652(3)
C(11)	7294(5)	10 001(5)	−3134(4)
C(12)	7554(5)	10 932(5)	−2358(5)
C(13)	8280(6)	11 978(6)	−2661(6)
C(14)	8755(8)	12 172(7)	−3697(7)
C(15)	8508(7)	11 261(7)	−4431(6)
C(16)	7793(6)	10 196(6)	−4162(5)
C(21)	6500(6)	7 434(5)	−3979(4)
C(22)	7698(7)	6 835(6)	−4188(5)
C(23)	7713(12)	6 075(8)	−5095(7)
C(24)	6495(13)	5 996(9)	−5818(8)
C(25)	5305(10)	6 588(8)	−5624(6)
C(26)	5301(8)	7 300(6)	−4707(5)
C(31)	4523(5)	8 932(5)	−2698(4)
C(32)	3658(6)	8 005(6)	−2335(4)

were solved *via* standard heavy-atom procedures and refined using full-matrix least-squares methods[18] with scattering factors calculated using data from ref. 19. The hydrogen atoms were generated geometrically and were not refined.

Crystal data for compound **3**, C[illegible]H[illegible]Cl[illegible]O[illegible]SiTa, *M* =

2 L. R. Chamberlain, I. Rothwell, K. Folting and J. C. Huffman, *J. Chem. Soc., Dalton Trans.*, 1987, 155.
3 R. E. Lapointe, P. T. Wolczanski and J. F. Mitchell, *J. Am. Chem. Soc.*, 1987, **108**, 6382.
4 F. Preuss and W. Towae, *Z. Naturforsch., Teil B*, 1981, **36**, 1130; H. Pesel, C. Pierrard and M. Wiedenbruch, *Z. Naturforsch., Teil B*, 1978, **33**, 1468; R. Harlow and W. A. Nugent, *Inorg. Chem.*, 1980, **19**,