

The isolation and chemistry of tantalum dimethylamides containing resolved 3,3'-disubstituted-1,1'-bi-2,2'-naphthoxide ligands †

Au Ji Ru Son, Scott W. Schweiger, Matthew G. Thorn, John E. Moses, Phillip E. Fanwick and Ian P. Rothwell*

Purdue University, Department of Chemistry, 560 Oval Drive, West Lafayette, IN 47907-2038, USA. E-mail: rothwell@purdue.edu

Received 3rd January 2003, Accepted 31st January 2003

First published as an Advance Article on the web 10th March 2003

Reaction of the tantalum dimethylamide substrates $[\text{Ta}(\text{NMe}_2)_5]$ or *mer,cis*- $[\text{Ta}(\text{NMe}_2)_2\text{Cl}_3(\text{HNMe}_2)]$ with one equivalent of the 3,3'-disubstituted-2,2'-dihydroxy-1,1'-binaphthyl $[\text{H}_2\text{O}_2\text{C}_{20}\text{H}_{10}(\text{R})_2-3,3']$ (R = SiMe₃, **1**; SiMe₂Ph, **2**; SiMePh₂, **3**; SiPh₃, **4**) leads to the series of amine adducts $[\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\text{R}_2-3,3')(\text{NHMe}_2)(\text{NMe}_2)_3]$ (R = SiMe₃, **5**; SiMe₂Ph, **6**; SiMePh₂, **7**; SiPh₃, **8**) and $[\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\text{R}_2-3,3')(\text{NHMe}_2)(\text{NMe}_2)\text{Cl}_2]$ (R = SiMe₃, **9**; SiMe₂Ph, **10**; SiMePh₂, **11**; SiPh₃, **12**). Structural analyses by X-ray diffraction of (*S*)-**5**, (*R*)-**7** and (*R,S*)-**8** show a pseudo-octahedral geometry about tantalum with the coordinated dimethylamine ligand located *cis* to the two naphthoxide oxygen atoms. In the case of (*S*)-**9**, (*R*)-**10** and (*S*)-**12**, the solid-state structure consists of both chloride ligands being located *trans* to the two naphthoxide oxygen atoms. Solution NMR spectroscopic properties of **5–12** are consistent with an identical structure being adopted in solution with the amine ligands being strongly bound in all cases. When (*S*)-**5** is heated under vacuum the dimethylamine ligand is lost leading to $[\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_2-3,3')(\text{NMe}_2)_3]$ (*S*)-**13**. Reaction of (*S*)-**5** with SiCl₄ leads to a mixture of $[\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_2-3,3')(\text{NHMe}_2)\text{Cl}_3]$ (*S*)-**14** and $[\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_2-3,3')\text{Cl}_4][\text{Me}_2\text{NH}_2]$ (*S*)-**15**. The solid-state structure of (*S*)-**15** was determined. The amine/amide ligands in (*S*)-**12** undergo insertion of CS₂ leading to the dimethyldithiocarbamate, (*S*)- $[\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}-3,3'-\{\text{SiPh}_3\}_2)(\text{CS}_2\text{NMe}_2)_2\text{Cl}]$ (*S*)-**16**. The solid state structure of (*S*)-**16** consists of a pentagonal bipyramidal geometry about Ta with an axial oxygen and chloride ligand.

Introduction

The inorganic and organometallic chemistry of niobium and tantalum supported by simple aryloxy ligands continues to be an area of research interest.^{1–5} A number of interesting stoichiometric and catalytic reactions have been developed using these substrates. We have recently begun an exploration of the chemistry of these metals associated with the chiral 3,3'-disubstituted-2,2'-dihydroxy-1,1'-binaphthyl ligands $[\text{H}_2\text{O}_2\text{C}_{20}\text{H}_{10}(\text{R})_2-3,3']$ (R = SiMe₃, **1**; SiMe₂Ph, **2**; SiMePh₂, **3**; SiPh₃, **4**) with the expectation of uncovering asymmetric examples of the reactivity previously established. In this paper we report an investigation of the reaction chemistry of the compounds $[\text{Ta}(\text{NMe}_2)_5]$ ⁶ and *mer,cis*- $[\text{Ta}(\text{NMe}_2)_2\text{Cl}_3(\text{HNMe}_2)]$ ^{7,8} with predominantly resolved examples of these ligands.^{9,10} We have recently reported on the related reactivity of the dimeric $[(\text{Et}_2\text{N})_2\text{Cl}_2\text{Ta}(\mu\text{-Cl})_2\text{TaCl}_2(\text{NEt}_2)_2]$ ¹¹ with these ligands, which leads to a series of chiral compounds containing two of these resolved ligands.¹²

Results and discussion

Synthesis and characterization of dimethylamido compounds

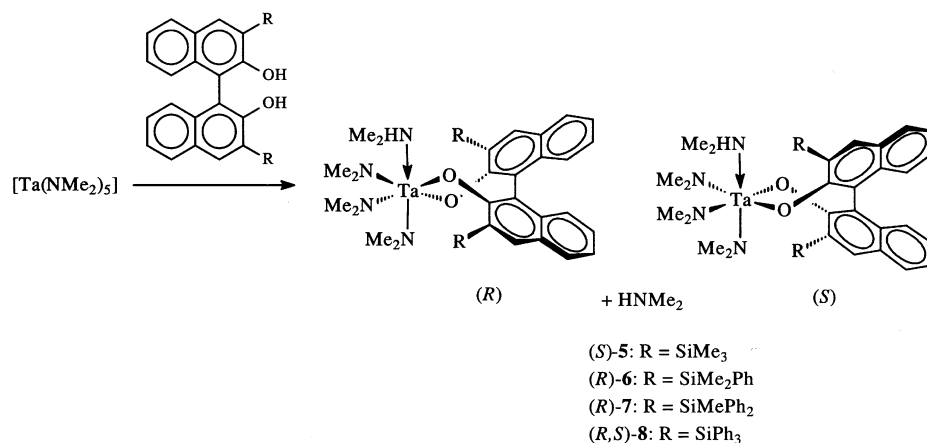
The treatment of hydrocarbon solutions of the compound $[\text{Ta}(\text{NMe}_2)_5]$ with 3,3'-disubstituted-2,2'-dihydroxy-1,1'-binaphthyl ligands **1–4** leads to the rapid (NMR) formation of a series of new tantalum compounds **5–8** which contain only one binaphthoxide ligand in the metal coordination sphere (Scheme 1). The solution NMR spectroscopic properties of **5–8** indicate the presence of a coordinated Me₂NH, formed during the protonolysis reaction, as well as a single resonance for the three

Ta–NMe₂ groups. The equivalence of the three dimethylamido ligands in the ¹H NMR spectra of **5–8** implies that dissociation/re-coordination of the HNMe₂ group occurs on the NMR timescale.

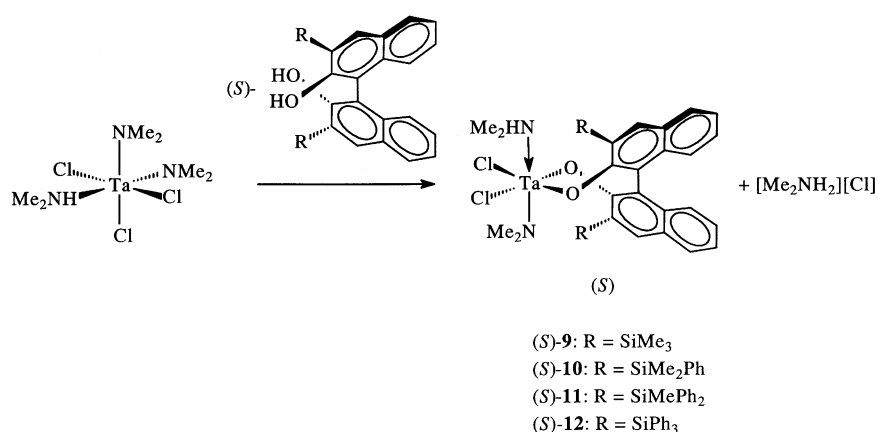
Reaction of the mixed amido–chloride *mer,cis*- $[\text{Ta}(\text{NMe}_2)_2\text{Cl}_3(\text{HNMe}_2)]$ with **1–4** does not lead to protonation of two dimethylamido ligands. Instead the products obtained (**9–12**, Scheme 2) arise *via* the elimination of one chloride ligand (*via* the amine salt) and one amide ligand. A similar reactivity has been reported for both mono(aryloxy) and non-chiral, bis(aryloxy) ligands. The lack of protonation of the second Ta–NMe₂ group has been discussed in detail in a previous study.¹³ In the ¹H NMR spectra of **9–12** the Ta–HNMe₂ group appears as a pair of diastereotopic methyl resonances (well separated doublets) and a broad septet for the amine proton. Hence, dissociation of this ligand does not occur on the NMR timescale, presumably reflecting the more Lewis acidic metal center in **9–12** compared to **5–8**. The strong binding of the dimethylamine ligands in **9–12** leads to a lack of any symmetry elements in the molecules on the NMR time-scale. The spectroscopic details of the dimethylphenylsilyl compound (*S*)-**10** are particularly informative. In the ¹H NMR spectrum (Fig. 1) the non-equivalent, diastereotopic SiMe₂Ph methyl groups appear as three singlets (two singlets overlapping), while four distinct Si–methyl resonances are clearly resolved in the ¹³C NMR spectrum.

The fluxionality difference between the tris-amido compounds **5–8** compared to **9–12** is consistent with the observation that the dimethylamine ligand can be thermally lost from the coordination sphere of **5**. Hence, heating the crude product obtained by adding **1** to $[\text{Ta}(\text{NMe}_2)_5]$, leads to the tris(amide) **13** as shown in Scheme 3. An attempt to thermally remove the dimethylamine ligands from adducts **9–12** failed. It is not unusual for dimethylamine adducts of early transition metals to even sublime in vacuum intact.¹⁴

† Electronic supplementary information (ESI) available: ORTEP views of (*R*)-**7**, (*R,S*)-**8**, (*S*)-**9** and (*S*)-**12**. See <http://www.rsc.org/suppdata/dt/b2/b212910h/>



Scheme 1



Scheme 2

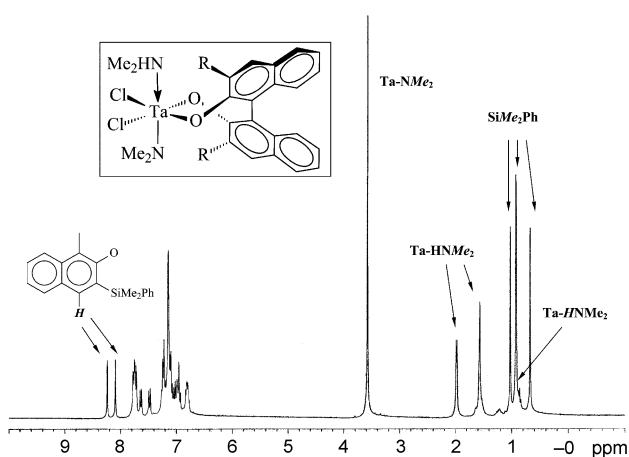


Fig. 1 ¹H NMR spectrum (C₆D₆) of [Ta(O₂C₂₀H₁₀{SiMe₂Ph}₂-3,3') (NHMe₂)(NMe₂)Cl₂] (S)-10.

Structural studies

The compounds (S)-5, (R)-7, (R,S)-8, (S)-9, (S)-10, and (S)-12 have been subjected to single crystal X-ray diffraction analysis. Two representative ORTEPs are shown in Figs. 2 and 3 while selected bond distances and angles are collected in Tables 1–6. All six compounds can be seen to adopt a slightly distorted octahedral geometry about the tantalum metal center. In all cases the dimethylamine ligand is located *cis* to the two, chelated aryloxy oxygen atoms and also is located *trans* to a dimethylamido ligand. In compound 7 there is a disorder involving the position of the tantalum atom along the amido, amine axis. In compounds 5–8 there are two dimethylamido

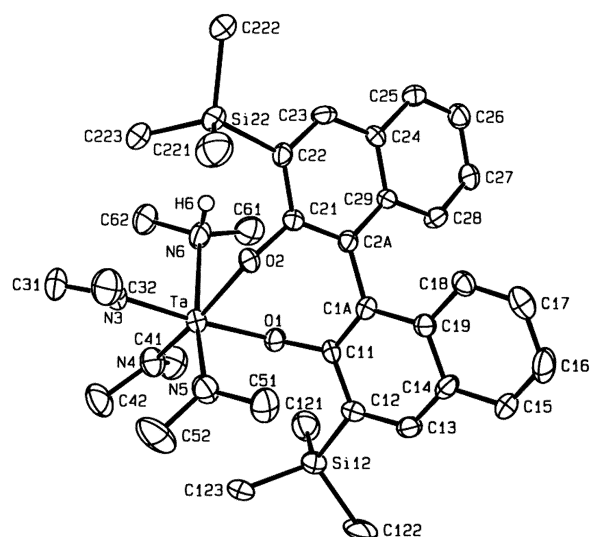
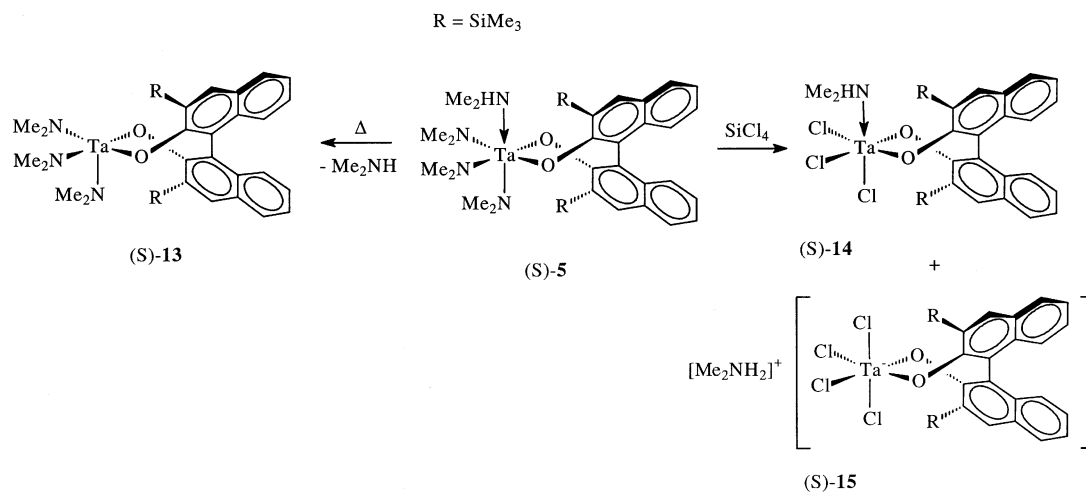


Fig. 2 Molecular structure of [Ta(O₂C₂₀H₁₀{SiMe₃}₂-3,3') (NHMe₂)(NMe₂)₃] (S)-5.

ligands positioned *trans* to the binaphthoxide oxygens whereas in 9–12 two chloride ligands occupy these positions. The replacement of two amide ligands by chlorides would be predicted to lead to an increase in the electron deficiency (Lewis acidity) of the metal center. Dialkylamido ligands are well known to be able to π-donate to metal centers to which they are bound, with demonstrable structural effects and chemical consequences.¹⁵ The structural parameters for those compounds studied do show the effect of the chloride for amide



Scheme 3

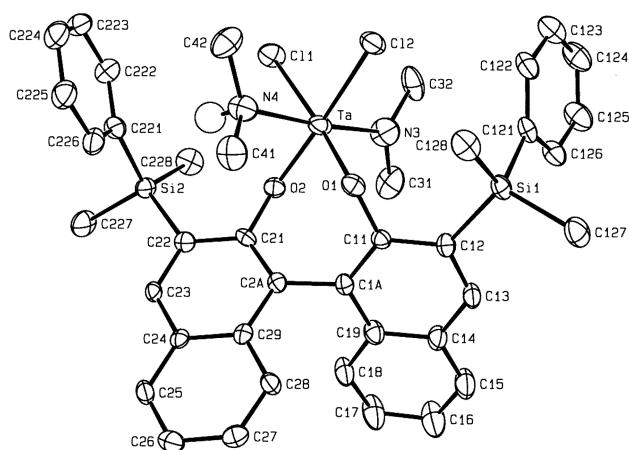


Fig. 3 Molecular structure of [Ta(O₂C₂₀H₁₀{SiMe₂Ph}_{2-3,3'})(NHMe₂)(NMe₂)Cl₂] (*S*)-10.

Table 1 Selected bond distances (Å) and angles (°) for [Ta(O₂C₂₀H₁₀{SiMe₃}_{2-3,3'})(NHMe₂)(NMe₂)₂] (*S*)-5

Ta–O(1)	2.036(4)	Ta–N(4)	2.009(5)
Ta–O(2)	2.039(3)	Ta–N(5)	2.000(5)
Ta–N(3)	2.006(5)	Ta–N(6)	2.456(5)
Ta–O(1)–C(11)	130.3(4)	O(2)–Ta–N(5)	91.5(2)
Ta–O(2)–C(21)	132.5(3)	O(2)–Ta–N(6)	79.2(2)
O(1)–Ta–O(2)	84.9(2)	N(3)–Ta–N(4)	90.5(3)
O(1)–Ta–N(3)	175.1(2)	N(3)–Ta–N(5)	89.9(3)
O(1)–Ta–N(4)	89.2(2)	N(3)–Ta–N(6)	93.2(2)
O(1)–Ta–N(5)	94.9(2)	N(4)–Ta–N(5)	103.1(2)
O(1)–Ta–N(6)	81.9(2)	N(4)–Ta–N(6)	86.0(2)
O(2)–Ta–N(3)	94.1(2)	N(5)–Ta–N(6)	170.3(2)
O(2)–Ta–N(4)	164.7(2)		

replacement. This is particularly evident in the Ta–HNMe₂ distances (Tables 1–6). In tris-amides (*S*)-5, (*R*)-7 and (*R,S*)-8, the Ta–N(amine) distances are 2.456(5), 2.428(4) and 2.441(3) Å respectively. These are among the longest distances so far reported for amine adducts of this metal. Comparable or longer Ta–N(dative) bonds are typically found in TMEDA and related adducts such as in [(Et₂NCH₂CH₂NET₂)(Cl)₂Ta(μ-Cl)₂Ta(Cl)₂(Et₂NCH₂CH₂NET₂)], 2.464(8) Å.¹⁶ Distances of 2.48–2.53 Å are reported in a series of cyclometallated adducts.¹⁷ A distance of 2.487(5) Å is reported for the central Ta–N(donor) bond in [N(CH₂CH₂NSiMe₃)₃]TaTe.¹⁸ Banaszak Holl and Wolczanski reported a Ta–NH₃ distance of 2.508(28) Å for an interesting ammonia cluster of tantalum.¹⁹ Perhaps the most dramatic examples are the TMEDA adducts [(C₆H₃Prⁱ_{2-2,6-N})Ta(X)₃₋

Table 2 Selected bond distances (Å) and angles (°) for [Ta(O₂C₂₀H₁₀{SiMePh₂}_{2-3,3'})(NHMe₂)(NMe₂)₃] (*R*)-7

Ta–O(1)	2.043(3)	Ta–N(4)	2.005(3)
Ta–O(1')	2.061(3)	Ta–N(3')	2.038(3)
Ta–N(3)	1.995(3)	Ta–N(4')	2.428(4)
Ta–O(1)–C(1)	133.6(2)	O(1')–Ta–N(3')	90.1(1)
Ta–O(1')–C(1')	125.0(2)	O(1')–Ta–N(4')	79.3(1)
O(1)–Ta–O(1')	86.4(1)	N(3)–Ta–N(4)	97.4(2)
O(1)–Ta–N(3)	91.8(1)	N(3)–Ta–N(3')	89.5(2)
O(1)–Ta–N(4)	90.7(1)	N(3)–Ta–N(4')	104.4(2)
O(1)–Ta–N(3')	164.6(2)	N(4)–Ta–N(3')	92.0(2)
O(1)–Ta–N(4')	80.6(1)	N(4)–Ta–N(4')	167.4(2)
O(1')–Ta–N(3)	171.3(2)	N(3')–Ta–N(4')	84.0(2)
O(1')–Ta–N(4)	91.2(1)		

Table 3 Selected bond distances (Å) and angles (°) for [Ta(O₂C₂₀H₁₀{SiPh₃}_{2-3,3'})(NHMe₂)(NMe₂)₃] (*R,S*)-8

Ta–O(1)	2.021(2)	Ta–N(4)	2.010(3)
Ta–O(2)	2.075(2)	Ta–N(5)	1.983(3)
Ta–N(3)	1.991(3)	Ta–N(6)	2.441(3)
Ta–O(1)–C(11)	139.2(2)	O(2)–Ta–N(5)	97.3(1)
Ta–O(2)–C(21)	123.7(2)	O(2)–Ta–N(6)	81.1(1)
O(1)–Ta–O(2)	86.75(9)	N(3)–Ta–N(4)	89.6(1)
O(1)–Ta–N(3)	166.0(1)	N(3)–Ta–N(5)	104.3(1)
O(1)–Ta–N(4)	94.3(1)	N(3)–Ta–N(6)	88.7(1)
O(1)–Ta–N(5)	89.0(1)	N(4)–Ta–N(5)	91.8(1)
O(1)–Ta–N(6)	77.9(1)	N(4)–Ta–N(6)	90.2(1)
O(2)–Ta–N(3)	87.3(1)	N(5)–Ta–N(6)	166.9(1)
O(2)–Ta–N(4)	170.9(1)		

Table 4 Selected bond distances (Å) and angles (°) for [Ta(O₂C₂₀H₁₀{SiMe₃}_{2-3,3'})(NHMe₂)(NMe₂)Cl₂] (*S*)-9

Ta–O(2)	1.938(5)	Ta–O(1)	1.916(5)
Ta–N(3)	2.027(6)	Ta–N(4)	2.318(7)
Ta–Cl(2)	2.364(2)	Ta–Cl(1)	2.390(2)
O(2)–Ta–O(1)	86.4(2)	O(2)–Ta–N(3)	93.0(2)
O(1)–Ta–N(3)	98.9(3)	O(2)–Ta–N(4)	88.1(2)
O(1)–Ta–N(4)	87.0(3)	N(3)–Ta–N(4)	174.1(3)
O(2)–Ta–Cl(2)	172.3(2)	O(1)–Ta–Cl(2)	90.5(2)
N(3)–Ta–Cl(2)	94.5(2)	N(4)–Ta–Cl(2)	84.7(2)
O(2)–Ta–Cl(1)	91.7(2)	O(1)–Ta–Cl(1)	172.5(2)
N(3)–Ta–Cl(1)	88.4(2)	N(4)–Ta–Cl(1)	85.7(3)
Cl(2)–Ta–Cl(1)	90.41(7)	C(11)–O(1)–Ta	136.2(4)
C(21)–O(2)–Ta	131.0(4)		

(TMEDA)] (X = Cl, Br) where the NMe₂ group *trans* to the Ta-imido bond is elongated to 2.561(7) and 2.544(11) Å respectively.²⁰ In the chloro compounds (*S*)-9, (*S*)-10, and (*S*)-12 the

Table 5 Selected bond distances (Å) and angles (°) for [Ta(O₂C₂₀H₁₀{SiMe₂Ph}₂-3,3')-(NHMe₂)(NMe₂)Cl₂] (*S*)-**10**

Ta–O(2)	1.914(4)	Ta–O(1)	1.928(4)
Ta–N(3)	2.069(6)	Ta–N(4)	2.246(5)
Ta–Cl(2)	2.379(2)	Ta–Cl(1)	2.390(2)
O(2)–Ta–O(1)	87.5(2)	O(2)–Ta–N(3)	93.7(2)
O(1)–Ta–N(3)	96.3(2)	O(2)–Ta–N(4)	89.4(2)
O(1)–Ta–N(4)	87.5(2)	N(3)–Ta–N(4)	175.2(2)
O(2)–Ta–Cl(2)	174.1(1)	O(1)–Ta–Cl(2)	90.6(1)
N(3)–Ta–Cl(2)	92.1(2)	N(4)–Ta–Cl(2)	84.9(2)
O(2)–Ta–Cl(1)	91.5(1)	O(1)–Ta–Cl(1)	173.2(1)
N(3)–Ta–Cl(1)	90.5(2)	N(4)–Ta–Cl(1)	85.8(2)
Cl(2)–Ta–Cl(1)	89.77(6)	C(11)–O(1)–Ta	127.7(4)
C(21)–O(2)–Ta	135.6(4)		

Table 6 Selected bond distances (Å) and angles (°) for [Ta(O₂C₂₀H₁₀{SiPh₃}₂-3,3')-(NHMe₂)(NMe₂)Cl₂] (*S*)-**12**

Ta–O(2)	1.956(5)	Ta–O(1)	1.911(4)
Ta–N(31)	1.998(6)	Ta–N(41)	2.326(7)
Ta–Cl(1)	2.3584(2)	Ta–Cl(2)	2.385(2)
O(1)–Ta–O(2)	86.22(2)	O(2)–Ta–N(31)	102.8(4)
O(1)–Ta–N(31)	92.9(2)	O(2)–Ta–N(41)	83.61(2)
O(1)–Ta–N(41)	88.83(2)	O(2)–Ta–Cl(1)	88.40(1)
O(1)–Ta–Cl(1)	172.71(1)	O(2)–Ta–Cl(2)	165.8(2)
O(1)–Ta–Cl(2)	92.82(1)	N(31)–Ta–N(41)	173.4(4)
O(2)–Ta–Cl(2)	170.88(6)	N(31)–Ta–Cl(1)	93.08(2)
N(41)–Ta–Cl(2)	82.20(2)	N(31)–Ta–Cl(2)	91.4(3)
C(321)–N(31)–Ta	123.1(7)	C(11)–O(1)–Ta	141.0(4)
C(21)–O(2)–Ta	122.0(4)	C(322)–N(31)–Ta	124.5(5)

Table 7 Selected bond distances (Å) and angles (°) for [Ta(O₂C₂₀H₁₀{SiMe₃}₂-3,3')Cl₄][(NH₂Me₂)] (*S*)-**15**

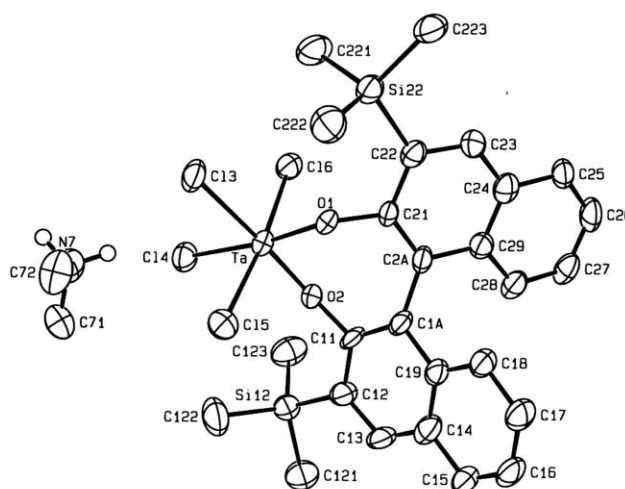
Ta–O(1)	1.889(6)	Ta–Cl(4)	2.431(3)
Ta–O(2)	1.893(7)	Ta–Cl(5)	2.362(2)
Ta–Cl(3)	2.420(3)	Ta–Cl(6)	2.379(2)
Ta–O(1)–C(21)	135.7(6)	O(2)–Ta–Cl(5)	89.5(2)
Ta–O(2)–C(11)	134.7(6)	O(2)–Ta–Cl(6)	93.0(2)
O(1)–Ta–O(2)	89.8(3)	Cl(3)–Ta–Cl(4)	87.6(1)
O(1)–Ta–Cl(3)	89.8(2)	Cl(3)–Ta–Cl(5)	86.9(1)
O(1)–Ta–Cl(4)	173.4(2)	Cl(3)–Ta–Cl(6)	90.7(1)
O(1)–Ta–Cl(5)	96.0(2)	Cl(4)–Ta–Cl(5)	89.9(1)
O(1)–Ta–Cl(6)	90.0(2)	Cl(4)–Ta–Cl(6)	84.0(1)
O(2)–Ta–Cl(3)	176.3(2)	Cl(5)–Ta–Cl(6)	173.5(1)
O(2)–Ta–Cl(4)	93.2(2)		

Ta–HNMe₂ distances are shorter, 2.318(7), 2.246(5) and 2.326(7) Å respectively, presumably due to the increased electron deficiency of the metal center.

The Ta–O(binaphthoxide) distances in the six-coordinate adducts span the narrow ranges of 2.021(2)–2.075(2) Å in the tris-amides (Tables 1–3) and slightly shorter 1.911(4)–1.956(5) Å in the chlorides (Tables 4–6). The binaphthoxide ligands chelate to the metal with O–Ta–O angles of 84–88° and Ta–O–C angles of 122–141°. The Ta–O–C angles are constrained by the eight-membered ring, and are much lower than typically found for terminal, non-chelated aryloxy ligands.²¹

Reactivity of the Ta–NMe₂ bonds

The Ta–NMe₂ bonds in tris-amido (*S*)-**5** react with SiCl₄ in hydrocarbon solvents to produce the corresponding tris-chloride (Scheme 3). This is a significant result, as it has proved difficult to isolate mixed binaphthoxide, chlorides of tantalum directly from the halide substrate. However, the reaction was found to lead to a mixture of two products, (*S*)-**14** and (*S*)-**15** (Scheme 3). These can be seen to be the adducts of the tri-chloride with Me₂NH and [Me₂NH₂][Cl] respectively. A few quality crystals of (*S*)-**15** were isolated and characterized (Table 7, Fig. 4). A related phosphonium salt containing a 2,2'-methylene-

**Fig. 4** Molecular structure of [Me₂NH₂][Ta(O₂C₂₀H₁₀{SiMe₃}₂-3,3')-Cl₄] (*S*)-**15**.

bis(aryloxy) has been reported.²² The Ta–O distances in the anion of (*S*)-**15**, 1.889(6) and 1.893(7) Å, are slightly shorter than those observed in the neutral amido derivatives above, again reflecting an increase in the *l*-electron deficiency of the metal center upon replacement of dialkylamido ligands by chloride groups.

Treatment of the bis(triphenylsilyl) compound (*S*)-**12** with carbon disulfide was found to generate a reaction mixture from which red crystals of the bis(dithiocarbamate) (*S*)-**16** were isolated and structurally characterized (Scheme 4, Fig. 5 and Table

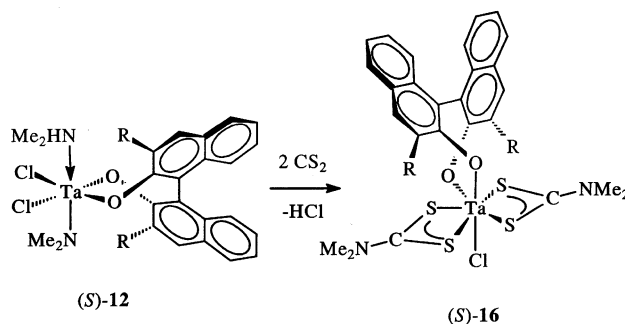
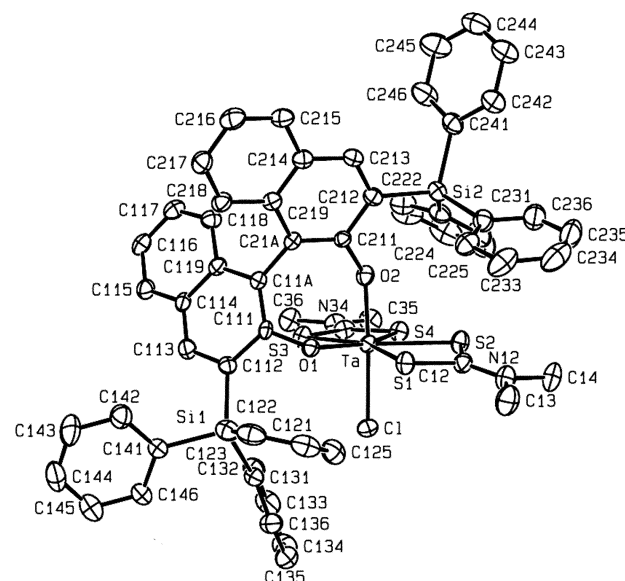
**Scheme 4****Fig. 5** Molecular structure of [Ta(O₂C₂₀H₁₀{SiPh₃}₂-3,3')(CS₂NMe₂)₂-Cl] (*S*)-**16**.

Table 8 Selected bond distances (Å) and angles (°) for [Ta(O₂C₂₀H₁₀{SiPh₃}₂-3,3') (CS₂NMe₂)₂Cl] (*S*)-**16**

Ta–O(2)	1.907(3)	Ta–O(1)	2.014(2)
Ta–S(1)	2.5495(9)	Ta–S(2)	2.552(1)
Ta–S(3)	2.589(1)	Ta–S(4)	2.5385(8)
Ta–Cl	2.3809(9)		
O(1)–Ta–O(2)	86.32(10)	O(2)–Ta–S(1)	95.83(8)
O(1)–Ta–S(1)	73.73(7)	O(2)–Ta–S(2)	91.70(8)
O(1)–Ta–S(2)	140.96(8)	O(2)–Ta–S(3)	88.49(8)
O(1)–Ta–S(3)	82.48(7)	O(2)–Ta–S(4)	89.73(8)
O(1)–Ta–S(4)	149.83(8)	S(4)–Ta–S(1)	136.45(3)
O(2)–Ta–Cl	175.73(8)	S(2)–Ta–Cl	91.26(3)
S(1)–Ta–Cl	88.15(3)	S(3)–Ta–Cl	87.24(3)
S(4)–Ta–S(3)	67.51(3)	S(1)–Ta–S(3)	155.45(3)
S(2)–Ta–S(3)	136.49(3)	C(34)–S(4)–Ta	90.61(12)

8). Compound (*S*)-**16** presumably arises *via* initial reaction of free dimethylamine with CS₂, the resulting dithiocarbamic acid then carries out protonolysis reactions with a Ta–NMe₂ bond to form another equivalent of HNMe₂. The second equivalent of HS₂CNMe₂ generated then leads to displacement of HCl and formation of the final product.

The molecular structure of (*S*)-**16** (Fig. 5) is best described as a pentagonal bipyramidal geometry about the seven-coordinate tantalum metal atom. The four sulfur atoms of the two dithiocarbamate ligands occupy equatorial sites. A chloride and one binaphthoxide oxygen occupy the axial sites. An O–Ta–O angle of 86° exists between the axial and equatorial binaphthoxide oxygen atoms. Although there are no related tantalum compounds, there are a few structurally characterized, pentagonal bipyramidal dithiocarbamates of niobium, which are structurally similar to (*S*)-**16**. The seven-coordinate species [Nb(S₂CNEt₂)Cl₃]²³ and [Nb(S₂CNEt₂)₂(X)(OMe)₂] (X = Cl, Br)²⁴ contain axial chloro or methoxy groups. Also related are the tris(dithiocarbamate) compounds [Nb(S₂CNEt₂)₃(X)] (X = O, S, NAr, ½N₂) in which the axial X group is *trans* to a sulfur atom of a dtc ligand.²⁵

We have also carried out a preliminary study of the reactivity of the mono-amido compound [Ta(O₂C₂₀H₁₀{SiPh₃}₂-3,3') (NHMe₂)(NMe₂)Cl₂] (*S*)-**12** with racemic and chiral forms of the alcohol HOCH(Me)Ph. Unfortunately the reactions did not lead to isolable, pure materials. However, it was possible to spectroscopically identify two *α*-methylbenzyl alkoxide compounds using ¹H NMR spectroscopy. Hence with the racemic alcohol, two well resolved Ta–OCH(Me)Ph quartets were observed at δ 5.51 and 5.77 ppm due to the presence of two diastereoisomers in solution. This was confirmed by use of (*R*)-HOCH(Me)Ph which led to only one signal in this region of the spectrum at δ 5.51 ppm. Further studies of the reaction of these new resolved tantalum compounds with other chiral reagents is underway.

Experimental

General remarks

All manipulations were carried out using standard syringe, Schlenk line, and glovebox techniques.²⁶ Benzene, toluene, ether, THF, and n-hexane were dried over sodium benzophenone ketyl and were freshly distilled before use. Pentane was dried over sodium ribbon. The substrates [Ta(NMe₂)₅] and *mer,cis*-[Ta(NMe₂)₂Cl₃(HNMe₂)]¹³ were obtained by literature procedures. CAUTION! Explosions have been associated with the synthesis of [Ta(NMe₂)₅].^{6,27} The 3,3'-disubstituted-2,2'-dihydroxy-1,1'-binaphthyl ligands [H₂O₂C₂₀H₁₀(R)₂-3,3'] (R = SiMe₃, **1**; SiMe₂Ph, **2**; SiMePh₂, **3**; SiPh₃, **4**) were prepared according to literature procedures or slight variations thereof.^{28,29} ¹H NMR spectra were recorded on a Varian INOVA-300 NMR spectrometer or a Bruker DRX-500 NMR spectrometer and were referenced to residual protio solvent. ¹³C

NMR spectra were recorded on a Bruker DRX-500 NMR spectrometer at 125.7 MHz and were internally referenced to the solvent signal.

Synthesis

[Ta(O₂C₂₀H₁₀{SiMe₃}₂-3,3') (NHMe₂)(NMe₂)₃] (*S*)-**5**. A 50 mL round bottom flask was charged with [Ta(NMe₂)₅] (500 mg, 1.25 mmol), a stir bar and benzene (3 mL). This solution was stirred as (*S*)-3,3'-bis(trimethylsilyl)-2,2'-dihydroxy-1,1'-dinaphthyl **1** (536 mg, 1.25 mmol) dissolved in benzene was slowly added. This mixture was stirred for 1 hour and evaporated to dryness. The crude solid that resulted was dissolved in a minimal amount of benzene and layered with pentane affording yellow crystals (200 mg, 22%), which were washed with pentane and dried *in vacuo*. Anal. calc. for C₃₄H₅₃N₄O₂Si₂Ta: C, 51.89; H, 6.79; N, 7.12. Found: C, 51.14; H, 6.54; N, 6.30%. ¹H NMR (C₆D₆, 30 °C): δ 8.12 (s), 7.77 (d), 6.82–7.20 (m, aromatics); 3.19 (s, NMe₂); 1.87 (br, NHMe₂); 0.47 (s, SiMe₃). ¹³C NMR (C₆D₆, 30 °C): δ 164.9 (Ta–O–C); 46.7 (NMe₂); 40.5 (NHMe₂); –0.1 (SiMe₃).

[Ta(O₂C₂₀H₁₀{SiMe₂Ph}₂-3,3') (NHMe₂)(NMe₂)₃] (*R*)-**6**. To a 5 mm NMR tube was added solid [Ta(NMe₂)₅] and benzene-d₆ (~1 mL). This solution was slowly titrated with (*R*)-3,3'-bis(dimethylphenylsilyl)-2,2'-dihydroxy-1,1'-dinaphthyl **2** until reaction was complete as monitored by NMR. The compound was only characterized spectroscopically. ¹H NMR (C₆D₆, 30 °C): δ 8.09 (s), 7.63–7.76 (m), 6.86–7.25 (m, aromatics); 3.14 (s, NMe₂); 1.98 (s, NHMe₂); 0.70 (s), 0.69 (s, SiMe₂Ph). ¹³C NMR (C₆D₆, 30 °C): δ 165.0 (Ta–O–C); 47.1 (NMe₂); 39.6 (NHMe₂); –0.8, –1.4 (SiMe₂Ph).

[Ta(O₂C₂₀H₁₀{SiMePh₂}₂-3,3') (NHMe₂)(NMe₂)₃] (*R*)-**7**. To a 5 mm NMR tube was added solid [Ta(NMe₂)₅] and benzene-d₆ (~1 mL). This solution was slowly titrated with (*R*)-3,3'-bis(methylphenylsilyl)-2,2'-dihydroxy-1,1'-dinaphthyl **3** until reaction was complete as monitored by NMR. Upon standing yellow crystals of **7** (benzene solvate) formed which were washed with pentane and dried *in vacuo*. Anal. calc. for C₅₄H₆₁N₄O₂Si₂Ta: C, 62.65; H, 5.94; N, 5.41. Anal. calc. for C₇₂H₇₉N₄O₂Si₂Ta (+ 3C₆H₆): C, 68.12; H, 6.27; N, 4.41. Found: C, 67.81; H, 6.21; N, 4.99%. ¹H NMR (C₆D₆, 30 °C): δ 7.88 (s), 7.72 (m), 7.40 (d), 6.81–7.30 (m, aromatics); 2.89 (s, NMe₂); 1.81 (s, NHMe₂); 1.00 (s, SiMePh₂). ¹³C NMR (C₆D₆, 30 °C): δ 165.8 (Ta–O–C); 46.9 (NMe₂); 40.9 (NHMe₂); –2.1 (SiMePh₂).

[Ta(O₂C₂₀H₁₀{SiPh₃}₂-3,3') (NHMe₂)(NMe₂)₃] (*R,S*)-**8**. To a 5 mm NMR tube was added solid [Ta(NMe₂)₅] and benzene-d₆ (~1 mL). This solution was slowly titrated with racemic-3,3'-bis(triphenylsilyl)-2,2'-dihydroxy-1,1'-dinaphthyl **4** until reaction was complete as monitored by NMR. Upon standing yellow crystals of **8** (benzene solvate) formed which were washed with pentane and dried *in vacuo*. Anal. calc. for C₆₄H₆₅N₄O₂Si₂Ta: C, 66.30; H, 5.65; N, 4.83. Anal. calc. for C₇₀H₇₁N₄O₂Si₂Ta (+ C₆H₆): C, 67.94; H, 5.78; N, 4.52. Found: C, 66.81; H, 5.49; N, 4.74%. ¹H NMR (C₆D₆, 30 °C): δ 8.12 (s), 7.85–8.12 (m), 7.44 (d), 7.29 (d), 7.10–7.16 (m), 6.86–6.97 (m, aromatics); 2.70 (s, NMe₂); 1.79 (s, NHMe₂). ¹³C NMR (C₆D₆, 30 °C): δ 165.7 (Ta–O–C); 46.1 (NMe₂); 40.0 (NHMe₂).

[Ta(O₂C₂₀H₁₀{SiMe₃}₂-3,3') (NHMe₂)(NMe₂)Cl₂] (*S*)-**9**. To a 50 mL solvent seal round bottom flask was added [TaCl₃(NMe₂)₂(NHMe₂)] (230 mg, 0.55 mmol) and benzene (15 mL). One equivalent of **1** (240 mg, 0.55 mmol) dissolved in 10 mL of benzene was slowly added with stirring. This mixture was stirred for 1 hour and then evaporated to dryness. The crude solid was dissolved in a small amount of benzene and filtered through Celite to remove salts. The yellow–orange supernatant

was reduced in volume to 5 mL and carefully layered with pentane–hexane to afford yellow–orange crystals. Yield: 0.39 g (79%). Anal. calc. for $C_{30}H_{41}O_2Cl_2Si_2N_2Ta$: C, 46.81; H, 5.40; N, 3.64; Cl, 9.22. Found: C, 46.60; H, 5.09; N, 3.62; Cl, 9.25%. 1H NMR (C_6D_6 , 25 °C): δ 8.17 (s, 1H, *meta* H); 8.13 (s, 1H, *meta* H); 6.76–7.72 (aromatics); 3.70 (s, 6H, *NMe_2*); 2.36(d, 3H, *HNMe*); 1.95 (septet, 1H, *HNMe_2*); 1.75 (d, 3H, *HNMe*); 0.61 (s, 9H, *SiMe_3*); 0.59 (s, 9H, *SiMe_3*). ^{13}C NMR (C_6D_6 , 25 °C): δ 163.7, 160.43 (Ta–O–C); 48.40 (*NMe_2*); 42.14 (*HNMe*); 40.90 (*HNMe*); 0.21 (*SiMe_3*); –0.12 (*SiMe_3*).

[Ta(O₂C₂₀H₁₀{SiMe₂Ph}₂-3,3')(NHMe₂)(NMe₂)Cl₂] (S)-10.

An identical procedure was used as for **9** above. Yield: 1.93 g (81%) based on 1.11 g of [TaCl₃(NMe₂)₂(NHMe₂)]. Anal. calc. for $C_{40}H_{45}O_2Cl_2Si_2N_2Ta$: C, 53.75; H, 5.07; N, 3.13; Cl, 7.93. Found: C, 53.71; H, 5.24; N, 3.10; Cl, 7.96%. 1H NMR (C_6D_6 , 25 °C): δ 8.24 (s, 1H, *meta* H); 8.09 (s, 1H, *meta* H); 6.79–7.77 (aromatics); 3.57 (s, 6H, *NMe_2*); 2.41 (br, 1H, *HNMe_2*); 1.97 (d, 3H, *HNMe*); 1.57 (d, 3H, *HNMe*); 1.02 (s, 3H, *SiMePh*); 0.92 (s, 6H, *SiMe_2Ph*); 0.67 (s, 3H, *SiMePh*). ^{13}C NMR (C_6D_6 , 25 °C): δ 164.26, 160.27 (Ta–O–C); 48.89 (*NMe_2*); 42.74 (*HNMe*); 40.44 (*HNMe*); 0.69 (*SiMePh*); –0.83 (*SiMePh*); –1.60 (*SiMePh*); –3.21 (*SiMePh*).

[Ta(O₂C₂₀H₁₀{SiMePh}₂-3,3')(NHMe₂)(NMe₂)Cl₂] (S)-11.

An identical procedure was used as for **9** above. Yield: 1.54 g (89%) based on 0.71 g [TaCl₃(NMe₂)₂(NHMe₂)]. Anal. calc. for $C_{50}H_{49}O_2Cl_2Si_2N_2Ta$: C, 58.99; H, 4.85; N, 2.75; Cl 6.97. Found: C, 58.75; H, 4.85; N, 2.70; Cl, 7.03%. 1H NMR (C_6D_6 , 25 °C): δ 8.22 (s, 1H, *meta* H); 8.15 (s, 1H, *meta* H); 6.81–7.88 (aromatics); 3.44 (s, 6H, *NMe_2*); 2.03 (br, 1H, *HNMe_2*); 1.84 (d, 3H, *HNMe*); 1.50 (d, 3H, *HNMe*); 1.35 (s, 6H, *SiMePh_2*); 1.33 (s, 6H, *SiMePh_2*). ^{13}C NMR (C_6D_6 , 25 °C): δ 164.17, 160.14 (Ta–O–C); (115.37–140.87 (aromatics); 48.49 (*NMe_2*); 42.62 (*HNMe*); 39.91 (*HNMe*); –3.42 (*SiMePh_2*); –3.99 (*SiMePh_2*).

[Ta(O₂C₂₀H₁₀{SiPh}₂-3,3')(NHMe₂)(NMe₂)Cl₂] (S)-12.

An identical procedure was used as for **9** above. Yield: 0.35 g (57%) based on 0.22 g of [TaCl₃(NMe₂)₂(NHMe₂)]. Anal. calc. for $C_{60}H_{53}O_2Cl_2Si_2N_2Ta$: C, 63.10; H, 4.68; N, 2.45; Cl, 6.21. Found: C, 63.50; H, 4.99; N, 2.07; Cl, 6.45%. 1H NMR (C_6D_6): δ 8.34 (s, 1H, *meta* H); 8.24 (s, 1H, *meta* H); 6.80–7.91 (aromatics); 3.57 (s, 6H, *NMe_2*); 1.15 (br, 1H, *NHMe_2*); 1.28 (d, 3H, *NHMe*); 1.76 (d, 3H, *NHMe*). ^{13}C NMR (C_6D_6 , 25 °C): 164.79, 160.11 (Ta–O–C); 49.61 (*NMe_2*); 43.40 (*NHMe_2*); 40.08 (*NHMe_2*).

[Ta(O₂C₂₀H₁₀{SiMe₃}₂-3,3')(NMe₂)₃] (S)-13. A flask was charged with [Ta(NMe₂)₅] (1.0 g, 2.5 mmol) and benzene (20 mL). This solution was stirred as (S)-3,3'-bis(trimethylsilyl)-2,2'-dihydroxy-1,1'-dinaphthyl **1** (1.1 g, 2.6 mmol) dissolved in benzene was slowly added. The mixture was stirred for 20 minutes and evacuated to dryness. The resulting solid was heated at 100 °C under vacuum for several minutes affording 1.7 g of **8** (92%). 1H NMR (C_6D_6 , 30 °C): δ 8.14 (s), 7.78 (d), 7.28 (d), 7.08 (t), 6.89 (t, aromatics); 3.07 (s, *NMe_2*); 0.48 (s, *SiMe_3*). ^{13}C NMR (C_6D_6 , 30 °C): δ 164.9 (Ta–O–C); 45.6 (*NMe_2*); –0.1 (*SiMe_3*).

[Ta(O₂C₂₀H₁₀{SiMe₃}₂-3,3')(NHMe₂)Cl₂] (S)-14 and [Me₂NH₂][Ta(O₂C₂₀H₁₀{SiMe₃}₂-3,3')Cl₂] (S)-15. A flask was charged with [Ta(NMe₂)₅] (1.0 g, 2.5 mmol) and benzene (50 mL). This mixture was stirred as (S)-3,3'-bis(trimethylsilyl)-2,2'-dihydroxy-1,1'-dinaphthyl **1** (1.1 g, 2.6 mmol) dissolved in benzene was slowly added. The reaction was stirred for 30 minutes and [SiCl₄] (1.4 mL, 12.2 mmol) added under a nitrogen flush. The resulting red solution was stirred for 30 minutes and evacuated to dryness affording a red solid which was washed with CHCl₃ and pentane successively and dried *in vacuo* (1.8 g, 95%). Microanalysis data leads to the conclusion that a mixture

Table 9 Crystal data and data collection parameters

	(S)-5	(R)-7-3C ₆ H ₆	(R,S)-8-C ₆ H ₆	(S)-9	(S)-10	(S)-12	(S)-15-1/2C ₆ H ₆	(S)-16-3C ₆ H ₆
Formula	C ₃₄ H ₄₃ N ₄ O ₂ Si ₂ Ta	C ₇₃ H ₇₀ N ₄ O ₂ Si ₂ Ta	C ₇₀ H ₇₁ N ₄ O ₂ Si ₂ Ta	C ₃₀ H ₄₁ O ₂ Cl ₂ N ₂ Si ₂ Ta	C ₄₀ H ₄₅ O ₂ Cl ₂ N ₂ Si ₂ Ta	C ₆₀ H ₅₃ Cl ₂ N ₂ O ₂ Si ₂ Ta	C ₃₁ H ₃₉ Cl ₄ NO ₂ Si ₂ Ta	C ₃₀ H ₇₀ ClN ₂ O ₂ S ₂ Si ₂ Ta
Formula weight	786.95	1269.58	1237.49	769.70	893.84	1142.13	836.59	1492.29
Space group	P2 ₁ 2 ₁ 2 ₁ (no. 19)	C22 ₂ (no. 20)	P2 ₁ /c (no. 14)	P2 ₁ (no. 4)	P2 ₁ 2 ₁ 2 ₁ (no. 19)	P2 ₁ (no. 4)	C2 (no. 5)	P2 ₁ (no. 4)
<i>a</i> /Å	11.0515(3)	11.4866(2)	11.6987(2)	9.6800(2)	10.2160(1)	11.1790(2)	27.604(2)	9.99840(10)
<i>b</i> /Å	15.2435(4)	20.5325(4)	18.2575(4)	10.4416(2)	12.5988(1)	20.4517(5)	12.7559(7)	19.1501(3)
<i>c</i> /Å	21.8989(5)	26.7517(5)	28.1025(5)	16.3287(4)	31.0769(4)	13.5288(4)	11.549(1)	18.4535(3)
β /°	90	90	94.759(1)	97.3445(8)	90	109.9264(10)	100.591(3)	94.3520(10)
<i>V</i> /Å ³	3689.2(3)	6309.4(4)	5981.7(4)	1636.9(1)	3999.9(1)	2907.9(2)	3997.4(9)	3523.11(15)
<i>Z</i>	4	4	4	2	4	2	4	2
<i>T</i> /K	193	173	173	150	150	150	173	150
Radiation (wavelength)	Mo-K α (0.71073 Å)	Mo-K α (0.71073 Å)	Mo-K α (0.71073 Å)	Mo-K α (0.71073 Å)	Mo-K α (0.71073 Å)	Mo-K α (0.71073 Å)	Mo-K α (0.71073 Å)	Mo-K α (0.71073 Å)
<i>R</i>	0.045	0.040	0.048	0.046	0.048	0.047	0.054	0.032
<i>R_w</i>	0.088	0.073	0.077	0.101	0.091	0.106	0.130	0.075

of **14** and **15** were formed. A few crystals of **15** (½ benzene solvate per Ta) were isolated from benzene solution. Anal. calc. for **14**, C₂₈H₃₅Cl₃NO₂Si₂Ta: C, 44.19; H, 4.64; N, 1.84; Cl, 13.97. Calc. for **15**, C₂₈H₃₆Cl₄NO₂Si₂Ta: C, 42.17; H, 4.55; N, 1.76; Cl, 17.78. Found: C, 42.87; H, 4.60; N, 1.58; Cl, 15.66%. ¹H NMR (C₆D₆, 30 °C): δ 8.23 (s), 7.65 (d), 6.65–7.16 (m, aromatics); 6.77 (br, NH); 2.07 (br, NMe₂); 0.77 (s, SiMe₃). ¹³C NMR (C₆D₆, 30 °C): δ 163.0 (Ta–O–C); 35.8 (NMe₂); 0.4 (SiMe₃). Attempts at separation/purification have thus far failed.

[Ta(O₂C₂₀H₁₀{SiPh₃}₂-3,3')CS₂NMe₂Cl] (*S*)-**16**. A 50 mL solvent seal round bottom flask was charged with (*S*)-**12** (430 mg, 0.42 mmol) and dissolved in 20 mL of benzene. An excess of CS₂ (0.2 mL, 3.3 mmol) was slowly added to the stirring reaction mixture. This mixture was stirred for 24 h and evaporated to dryness. A pure red solid was obtained from layering a benzene solution with hexane. (Yield = 0.34 g, 67%). Anal. calc. for C₆₂H₅₂O₂ClS₄Si₂N₂Ta: C, 56.66; H, 4.16; N, 2.23; Cl, 2.81. Found: C, 56.46; H, 4.61; N, 2.00; Cl, 2.25%. ¹H NMR(C₆D₆); δ 8.51 (s, 1H, *meta* H); 8.25 (s, 1H, *meta* H); 6.66–8.23 (aromatics); 0.84–2.31 (m, CS₂NMe₂).

X-Ray data collection and reduction

Crystal data and data collection parameters are contained in Table 9. A suitable crystal was mounted on a glass fiber in a random orientation under a cold stream of dry nitrogen. Preliminary examination and final data collection were performed with Mo-Kα radiation (λ = 0.71073 Å) on a Nonius Kappa CCD. Lorentz and polarization corrections were applied to the data.³⁰ An empirical absorption correction using SCALEPACK was applied.³¹ Intensities of equivalent reflections were averaged. The structure was solved using the structure solution program PATTY in DIRDIF92.³² The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least-squares where the function minimized was Σw(|F_o|² - |F_c|²)² and the weight w is defined as w = 1/[σ²(F_o)² + (0.0585P)² + 1.4064P] where P = (F_o)² + 2F_c²/3. Scattering factors were taken from the *International Tables for Crystallography*.³³ Refinement was performed on a AlphaServer 2100 using SHELXS97.³⁴ Crystallographic drawings were done using ORTEP.³⁵

CCDC reference numbers 200553–200559 and 203123.

See <http://www.rsc.org/suppdata/dt/b2/b212910h/> for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the National Science Foundation (Grant CHE-0078405) for financial support of this research.

References

- 1 D. C. Bradley, R. C. Mehrotra, I. P. Rothwell and A. Singh, *Alkoxo and Aryloxo Derivatives of Metals*, Academic Press, London, 2001.
- 2 (a) M. A. Bruck, A. S. Copenhaver and D. E. Wigley, *J. Am. Chem. Soc.*, 1987, **109**, 6525; (b) J. R. Strickler, M. A. Bruck, P. A. Wexler and D. E. Wigley, *Organometallics*, 1990, **9**, 266; (c) D. J. Arney, P. A. Wexler and D. E. Wigley, *Organometallics*, 1990, **9**, 1282; (d) S. D. Gray, D. P. Smith, M. A. Bruck and D. E. Wigley, *J. Am. Chem. Soc.*, 1992, **114**, 5462; (e) S. D. Gray, P. A. Fox, R. P. Kingsborough, M. A. Bruck and D. E. Wigley, *ACS Prepr. Div. Petrol. Chem.*, 1993, **39**, 706; (f) K. D. Allen, M. A. Bruck, S. D. Gray, R. P. Kingsborough, D. P. Smith, K. J. Weller and D. E. Wigley, *Polyhedron*, 1995, **14**, 3315; (g) P. A. Fox, M. A. Bruck, S. D. Gray, N. E. Gruhn, C. Grittini and D. E. Wigley, *Organometallics*, 1998, **17**, 2720; (h) K. J. Weller, I. Filippov, P. M. Briggs and D. E. Wigley, *Organometallics*, 1998, **17**, 322; (i) D. S. J. Arney, P. A. Fox, M. A. Bruck and D. E. Wigley, *Organometallics*, 1997, **16**, 3421; (j) S. D. Gray, K. J. Weller, M. A. Bruck, P. M. Briggs and D. E. Wigley, *J. Am. Chem. Soc.*, 1995, **117**, 10678.

- 3 (a) V. M. Visciglio, J. R. Clark, M. T. Nguyen, D. R. Mulford, P. E. Fanwick and I. P. Rothwell, *J. Am. Chem. Soc.*, 1997, **119**, 3490; (b) T. W. Coffindaffer, B. D. Steffy, I. P. Rothwell, K. Folting, J. C. Huffman and W. E. Streib, *J. Am. Chem. Soc.*, 1989, **111**, 4742.
- 4 (a) I. P. Rothwell, *Acc. Chem. Res.*, 1988, **21**, 153; (b) L. R. Chamberlain, J. L. Keddington and I. P. Rothwell, *Organometallics*, 1992, **1**, 1098; (c) L. R. Chamberlain, I. P. Rothwell and J. C. Huffman, *Inorg. Chem.*, 1984, **23**, 2575; (d) L. R. Chamberlain, I. P. Rothwell and J. C. Huffman, *J. Am. Chem. Soc.*, 1986, **108**, 1502; (e) L. R. Chamberlain, I. P. Rothwell, K. Folting and J. C. Huffman, *J. Chem. Soc., Dalton Trans.*, 1987, 155; (f) L. R. Chamberlain and I. P. Rothwell, *J. Chem. Soc., Dalton Trans.*, 1987, 163; (g) R. W. Chesnut, L. D. Durfee, P. E. Fanwick and I. P. Rothwell, *Polyhedron*, 1987, **6**, 2019; (h) L. R. Chamberlain, J. L. Kerscher, A. P. Rothwell, I. P. Rothwell and J. C. Huffman, *J. Am. Chem. Soc.*, 1987, **109**, 6471; (i) L. R. Chamberlain, B. D. Steffy and I. P. Rothwell, *Polyhedron*, 1989, **8**, 341; (j) B. D. Steffy, R. W. Chesnut, J. L. Kerschner, P. J. Pellechia, P. E. Fanwick and I. P. Rothwell, *J. Am. Chem. Soc.*, 1989, **111**, 378; (k) B. D. Steffy, L. R. Chamberlain, R. W. Chesnut, D. E. Chebi, P. E. Fanwick and I. P. Rothwell, *Organometallics*, 1989, **8**, 1419; (l) R. W. Chesnut, J. S. Yu, P. E. Fanwick and I. P. Rothwell, *Polyhedron*, 1990, **8**, 1051; (m) B. D. Steffy, P. E. Fanwick and I. P. Rothwell, *Polyhedron*, 1990, **9**, 963; (n) J. S. Yu, P. E. Fanwick and I. P. Rothwell, *J. Am. Chem. Soc.*, 1990, **112**, 8171; (o) R. W. Chesnut, G. G. Jacob, J. S. Yu, P. E. Fanwick and I. P. Rothwell, *Organometallics*, 1991, **10**, 321; (p) J. S. Vilaro, M. A. Lockwood, L. G. Hanson, J. R. Clark, B. C. Parkin, P. E. Fanwick and I. P. Rothwell, *J. Chem. Soc., Dalton Trans.*, 1997, 3353; (q) P. N. Riley, M. G. Thorn, J. S. Vilaro, M. A. Lockwood, P. E. Fanwick and I. P. Rothwell, *Organometallics*, 1999, **18**, 3016; (r) M. G. Thorn, P. E. Fanwick and I. P. Rothwell, *Organometallics*, 1999, **18**, 4442; (s) M. G. Thorn, P. E. Fanwick, R. W. Chesnut and I. P. Rothwell, *J. Chem. Soc., Chem. Comm.*, 1999, 2543.
- 5 (a) I. P. Rothwell, *Chem. Commun.*, 1997, 1331 (Feature Article); (b) J. R. Clark, P. E. Fanwick and I. P. Rothwell, *J. Chem. Soc., Chem. Commun.*, 1995, 553; (c) B. C. Parkin, J. C. Clark, V. M. Visciglio, P. E. Fanwick and I. P. Rothwell, *Organometallics*, 1995, **14**, 3002.
- 6 P. N. Riley, J. R. Parker, P. E. Fanwick and I. P. Rothwell, *Organometallics*, 1999, **18**, 3579.
- 7 P. J. H. Carnell and G. W. Fowles, *J. Chem. Soc.*, 1959, 4113.
- 8 M. H. Chisholm, J. C. Huffman and L. S. Tan, *Inorg. Chem.*, 1981, **20**, 1859.
- 9 M. G. Thorn, J. E. Moses, P. E. Fanwick and I. P. Rothwell, *J. Chem. Soc., Dalton Trans.*, 2000, 2659.
- 10 For some related halo(dialkylamido)compounds of Nb and Ta see (a) P. A. Fox, S. D. Gray, M. A. Bruck and D. E. Wigley, *Inorg. Chem.*, 1996, **35**, 6027; (b) Zhongzhi Wu, J. B. Diminnie and Ziling Xue, *J. Am. Chem. Soc.*, 1999, **121**, 4300; (c) D. M. Hoffman and S. P. Rangarajan, *Acta Crystallogr., Sect. C*, 1996, **52**, 1616; (d) P. Berno and S. Gambarotta, *Organometallics*, 1995, **14**, 2159; (e) L. Scoles, K. B. P. Ruppia and S. Gambarotta, *J. Am. Chem. Soc.*, 1996, **118**, 2529; (f) J. C. Fuggle, D. W. A. Sharp and J. M. Winfield, *J. Chem. Soc., Dalton Trans.*, 1972, 1766.
- 11 Y. W. Chao, P. A. Wexler and D. E. Wigley, *Inorg. Chem.*, 1989, **28**, 3860.
- 12 C. S. Weinert, P. E. Fanwick and I. P. Rothwell, *J. Chem. Soc., Dalton Trans.*, 2002, 2948.
- 13 S. W. Schweiger, D. L. Tillison, M. G. Thorn, P. E. Fanwick and I. P. Rothwell, *J. Chem. Soc., Dalton Trans.*, 2001, 2401.
- 14 Including *mer,cis*-[Ta(NMe₂)₂Cl₃(HNMe₂)] itself.
- 15 P. N. Riley, P. E. Fanwick and I. P. Rothwell, *J. Chem. Soc., Dalton Trans.*, 2001, 181 and references therein.
- 16 J. A. M. Canich and F. A. Cotton, *Inorg. Chem.*, 1987, **26**, 4236.
- 17 (a) M. H. P. Rietveld, W. Teunissen, H. Hagen, L. van de Water, D. M. Grove, P. A. van der Schaaf, A. Muhlebach, H. Kooijman, W. J. J. Smeets, N. Veldman, A. L. Spek and G. van Koten, *Organometallics*, 1997, **16**, 1674; (b) M. H. P. Rietveld, H. Hagen, L. van de Water, D. M. Grove, H. Kooijman, N. Veldman, A. L. Spek and G. van Koten, *Organometallics*, 1997, **16**, 168; (c) H. C. L. Abbenhuis, R. van Belzen, D. M. Grove, A. J. A. Klomp, G. P. M. van Mier, A. L. Spek and G. van Koten, *Organometallics*, 1993, **12**, 210.
- 18 (a) V. Christou and J. Arnold, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1450; (b) J. A. R. Schmidt, S. A. Chmura and J. Arnold, *Organometallics*, 2001, **20**, 1062.
- 19 M. M. Banaszak Holl, P. T. Wolczanski and G. D. Van Duyne, *J. Am. Chem. Soc.*, 1990, **112**, 7989.
- 20 K. S. Heinselman, V. M. Miskowski, S. J. Geib, L. C. Wang and M. D. Hopkins, *Inorg. Chem.*, 1997, **36**, 5530.

-
- 21 B. D. Steffey, P. E. Fanwick and I. P. Rothwell, *Polyhedron*, 1990, **9**, 963.
- 22 D. R. Mulford, P. E. Fanwick and I. P. Rothwell, *Polyhedron*, 2000, **19**, 35.
- 23 (a) J. A. M. Canich and F. A. Cotton, *Inorg. Chim. Acta*, 1989, **159**, 163; (b) R. A. Henderson, D. L. Hughes and A. N. Stephens, *J. Chem. Soc., Dalton Trans.*, 1990, 1097.
- 24 J. W. Moncrief, D. C. Pantaleo and N. E. Smith, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 255.
- 25 (a) L. S. Tan, G. V. Goeden and B. L. Haymore, *Inorg. Chem.*, 1983, **22**, 1744; (b) M. G. B. Drew, D. A. Rice and D. M. Williams, *J. Chem. Soc., Dalton Trans.*, 1985, 1821; (c) J. C. Dewan, D. L. Kepert, C. L. Raston, D. Taylor, A. H. White and E. N. Maslen, *J. Chem. Soc., Dalton Trans.*, 1973, 2082; (d) Youngkyu Do and R. R. Holm, *Inorg. Chim. Acta*, 1985, **104**, 33; (e) P. F. Gilletti, D. A. Femec, F. I. Keen and T. M. Brown, *Inorg. Chem.*, 1992, **31**, 4008; (f) E. J. Peterson, R. B. Von Dreele and T. M. Brown, *Inorg. Chem.*, 1978, **17**, 1410; (g) 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.
- 26 D. F. Shriver and M. A. Drezdson, *The Manipulation of Air Sensitive Compounds*, 2nd edn., John Wiley & Sons, New York, 1986.
- 27 D. C. Bradley and M. Thomas, *Can. J. Chem.*, 1962, **40**, 1355.
- 28 G. J. H. Buisman, L. A. van der Veen, A. Klootwijk, W. G. J. de Lange, P. C. J. Kamer, P. W. N. M. Van Leeuwen and D. Vogt, *Organometallics*, 1997, **16**, 2929.
- 29 P. J. Cox, W. Wang and V. Snieckus, *Tetrahedron Lett.*, 1992, **33**, 2253.
- 30 P. C. McArdle, *J. Appl. Crystallogr.*, 1996, **239**, 306.
- 31 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1996, 276.
- 32 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The DIRDIF92 Program System, Technical Report, Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.
- 33 *International Tables for Crystallography*, vol. C, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992, Tables 4.2.6.8 and 6.1.1.4.
- 34 G. M. Sheldrick, SHELXS97, A Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- 35 C. K. Johnson, ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA, 1976.