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FULL PAPER

The isolation and chemistry of niobium and tantalum dimethylamides containing mono- and di-aryloxide ancillary ligands

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The salt complex $[Me_2NH_2][Ta(NMe_2)_2Cl_4]$ **4** has been isolated from the reaction of $[Ta_2Cl_{10}]$ with Me_2NH and the anion shown to contain mutually *cis*-dimethylamido ligands. **4** reacts with Me_2NH and pyridine to produce the neutral adducts *mer*,*cis*-$[Ta(NMe_2)_2Cl_3(HNMe_2)]$ **1** (known compound) and $[Ta(NMe_2)_2Cl_3(py)]$ **5**. The solid state structure of $[Ta(NMe_2)_2Cl_3(py\text{-}4Ph)]$ **7** shows a *mer*,*cis* arrangement of Cl and NMe_2 groups. The addition of 2,3,5,6-tetraphenyl- or 2,6-di-isopropyl-phenol (2 equiv) to solutions of **1** in benzene was found to produce a mixture of two isomers each containing a residual Ta–NMe_2 and Ta–$NHMe_2$ group. These were formulated as $[Ta(OAr)_2Cl_2(NMe_2)(NHMe_2)]$ with the coordinated amine *trans* to the Ta–NMe_2 group and aryloxide ligands either mutually *cis* or *trans*. The *cis* isomer was found to thermally convert to the *trans* form. The *trans* isomers $[M(OAr)_2Cl_2(NMe_2)(NHMe_2)]$ (M = Ta, OAr = 2,3,5,6-tetraphenyl- or 2,6-di-isopropyl-phenoxide; M = Nb, OAr = 2,3,5,6-tetraphenylphenoxide) are obtained in high yield by treatment of the corresponding tri(chlorides) $[M(OAr)_2Cl_3]$ with excess Me_2NH. The isomorphous/isostructural compounds $[M(OC_6HPh_4\text{-}2,3,5,6)_2Cl_2(NMe_2)(py)]$ (M = Nb, Ta) were structurally characterized and shown to contain the pyridine ligand *trans* to the Ta–NMe_2 group with mutually *trans* aryloxides. Addition of 2,2′-methylenebis(6-phenylphenol) $\{(HOC_6H_3Ph)_2CH_2\}$ to **1** resulted in formation of the compound $[Ta\{(OC_6H_3Ph)_2CH_2\}Cl_2(NMe_2)(HNMe_2)]$ **15**. The solid state structure of **15** shows the nitrogen atoms to be mutually *trans* with *cis* aryloxide oxygen atoms. The eight-membered dioxametallacycle ring is puckered with the methylene bridge folded up towards the Ta–NMe_2 group. The reaction pathways leading to these products are discussed.

Introduction

The inorganic and organometallic chemistry associated with niobium and tantalum chloro(aryloxide) compounds continues to be an area of research interest.[1–5] These compounds are typically synthesized by reaction of the metal chloride with either the parent phenol, the lithium aryloxide or the trimethylsilyl ether. An initial exploration of the reaction of niobium or tantalum halides with either parent 3,3′-disubstituted-1,1′-bi-2-naphthol or its di-lithium derivative failed to provide tractable products. We have therefore begun to explore the reactivity of mixed chloro(dialkylamido) compounds with phenolic reagents as an alternative strategy for the synthesis of chloro(aryloxides) of niobium and tantalum. In this paper we report an investigation of the reaction chemistry of the compound *mer*,*cis*-$[Ta(NMe_2)_2Cl_3(HNMe_2)]$ **1** (first reported by Carnell and Fowles[6] and later characterized by Chisholm and Tan[7]) with mono- and di-phenols.[8]

Results and discussion

Synthesis of chloro(dimethylamido) compounds

The reaction of $[Ta_2Cl_{10}]$ with dimethylamine in hydrocarbon solvents was shown previously to produce a variety of products including **1**,[6,7] $[Ta(NMe_2)_3Cl_2(HNMe_2)]$ **2** and the oxo impurity $[\{Ta(NMe_2)_2Cl_2(HNMe_2)\}_2(\mu\text{-}O)]$ **3** (Scheme 1). Adduct **1** was found to undergo sublimation with no loss of coordinated dimethylamine. While attempting the synthesis of **1** by condensation of Me_2NH (5 equiv per Ta) to a frozen toluene solution of $[Ta_2Cl_{10}]$ we isolated the salt complex $[Me_2NH_2][Ta(NMe_2)_2Cl_4]$ **4** in moderate yield as a crystalline sample from benzene–hexane mixtures. Compound **4** is formally the result of the reaction of $[Ta_2Cl_{10}]$ with only 4 equivalents of Me_2NH and analysis of the supernatant showed the presence of both **1** and **2**. The isolation of **4** further highlights the complexity of the reaction of $[Ta_2Cl_{10}]$ with dimethylamine in hydrocarbon solvents observed by Chisholm and Tan.[7] It is possible that variations from experiment to experiment are caused by the rate of warming of the frozen toluene solution that has the condensed dimethylamine "frost" on the surface. We found that compound **1** could be isolated reproducibly in high yield by carrying out the reaction in a toluene–diethyl ether solvent mixture.

Table 1 Selected bond distances (Å) and angles (°) for $[Me_2NH_2][Ta(NMe_2)_2Cl_4]$ **4**

Ta–N(1)	1.954(5)	Ta–Cl(2)	2.510(1)
Ta–N(2)	1.945(5)	Ta–Cl(3)	2.404(1)
Ta–Cl(1)	2.483(1)	Ta–Cl(4)	2.400(1)
N(1)–Ta–N(2)	95.3(2)	N(2)–Ta–Cl(4)	91.2(2)
N(1)–Ta–Cl(1)	171.6(2)	Cl(1)–Ta–Cl(2)	83.99(5)
N(1)–Ta–Cl(2)	89.0(1)	Cl(1)–Ta–Cl(3)	85.76(6)
N(1)–Ta–Cl(3)	89.2(2)	Cl(1)–Ta–Cl(4)	87.84(5)
N(1)–Ta–Cl(4)	96.2(2)	Cl(2)–Ta–Cl(3)	87.00(5)
N(2)–Ta–Cl(1)	92.0(2)	Cl(2)–Ta–Cl(4)	85.35(5)
N(2)–Ta–Cl(2)	174.7(2)	Cl(3)–Ta–Cl(4)	170.50(5)
N(2)–Ta–Cl(3)	96.1(2)		

Compound **4** was structurally characterized (Fig. 1, Table 1) and shown to contain a distorted octahedral metal center with the dimethylamido ligands mutually *cis*. The distortion from

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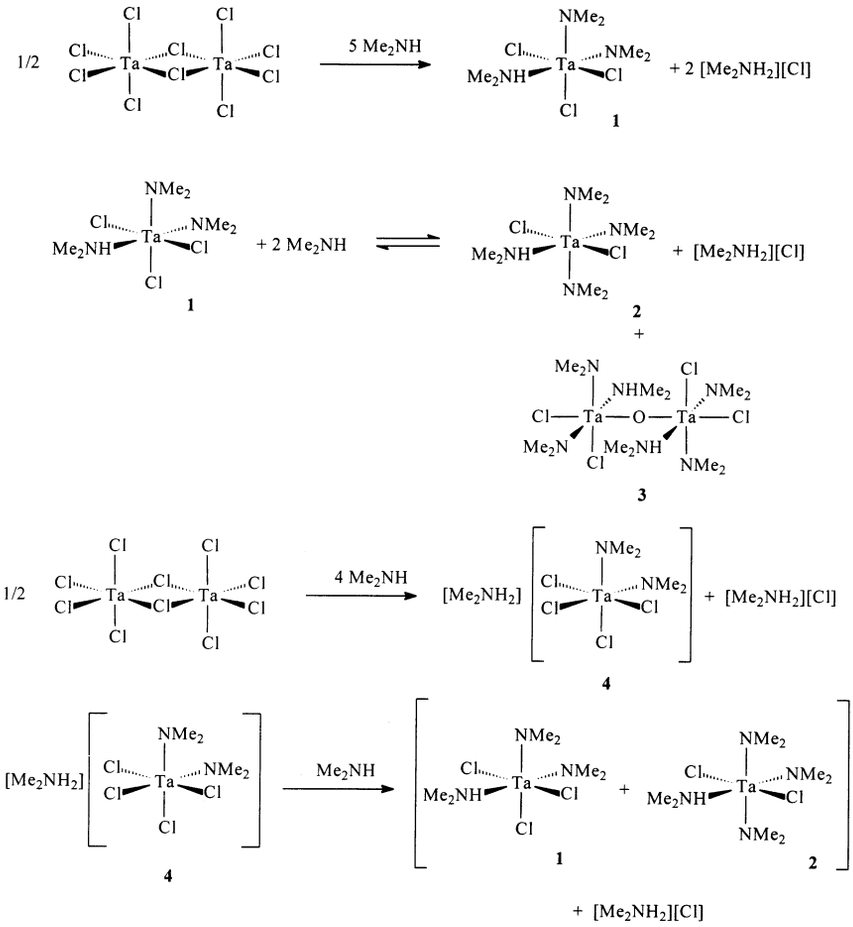

Scheme 1

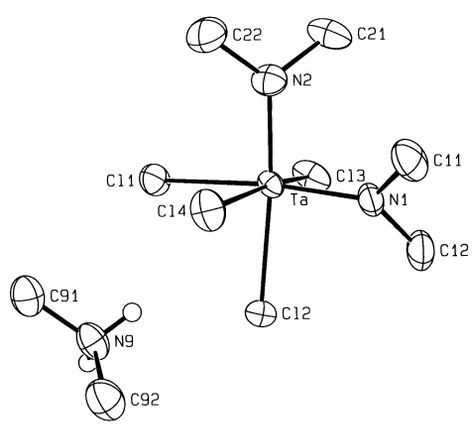

Fig. 1 Molecular structure of $[Me_2NH_2][Ta(NMe_2)_2Cl_4]$ **4**.

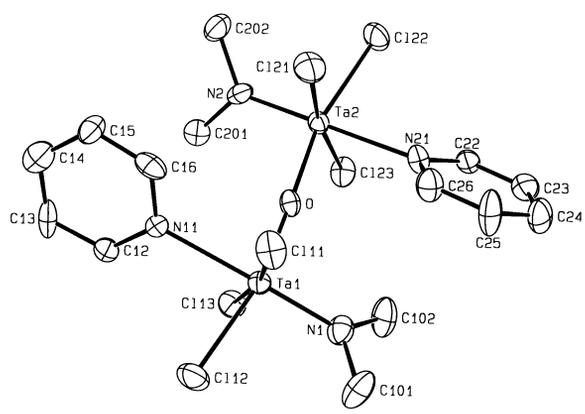

Fig. 2 Molecular structure of $[\{Ta(NMe_2)(py)Cl_3\}_2(\mu\text{-}O)]$ **6**.

octahedral geometry involves an opening up of the N–Ta–N angle to 95.3(2)° while the four chloride ligands are slightly compressed. The *cis*-geometry is expected given the strong π-donor properties of the dimethylamido ligands.

The addition of Me_2NH to a C_6D_6 solution of **4** was found to produce a mixture of **1** and **2** (^{1}H NMR) and a precipitate taken to be $[Me_2NH_2][Cl]$ (Scheme 1).

Addition of pyridine (py) to **4** was found to produce the neutral pyridine adduct $[Ta(NMe_2)_2Cl_3(py)]$ **5** along with a precipitate of $[Me_2NH_2][Cl]$ (Scheme 2). During the recrystallization of **5**, a few crystals of the sparingly soluble μ-oxo compound $[\{Ta(NMe_2)Cl_3(py)\}_2(\mu\text{-}O)]$ **6** were also isolated and structurally characterized (Fig. 2, Table 2). Compound **5** is the direct pyridine analogue of the dimethylamine compound **1**. Compound **6** is structurally related to **3** but has a different ratio of amide to chloride ligands. As stated for the formation of **3**, the origins of **6** "could conceivably arise from an oxide impurity in the commercially available $TaCl_5$ or by trace hydrolysis during the course of these reactions or crystallizations". The formation of an unbridged, linear M–O–M (M = Nb, Ta) core is not an unusual occurrence for these metals in their highest oxidation state.[9] The linearity at oxygen can be readily accounted for by the presence of oxygen-p to metal-d π-bonding to both metals. What is unusual about the structure of **6** is the slight asymmetry in the oxide bridge. The Ta(1)–O distance of 1.877(9) Å is significantly shorter than the Ta(2)–O distance of 1.929(9) Å and the Ta–O distances of 1.917(6) and 1.928(6) Å reported for **3**. We have no ready explanation for this anomaly as all the other types of ligands have essentially identical distances to each tantalum metal center. Although crystals of the pyridine adduct **5** suitable for X-ray diffraction could not be isolated, use of 4-phenylpyridine led to crystals of

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$[Ta(NMe_2)_2Cl_3(py\text{-}4Ph)]$ **7** (Scheme 2) whose underlying molecular structure was successfully elucidated by X-ray diffraction (Fig. 3, Table 3). The Ta–N(py-4Ph) distance of 2.371(4) Å in **7** is identical to the Ta–N($HNMe_2$) distance reported for **1**, and much longer than the Ta–NMe_2 bond distances. There are definite distortions away from octahedral geometry involving a bending of chloride ligands towards the pyridine ligand, away from the strongly π-bonding dimethylamido ligands. The influence of these ligands is also seen in the Ta–Cl(2) distance of 2.442(2) Å which is longer than the corresponding distances of 2.377(1) and 2.404(1) Å for the mutually *trans* chloride ligands.

Table 2 Selected bond distances (Å) and angles (°) for $[\{Ta(NMe_2)(py)Cl_3\}_2(\mu\text{-}O)]$ **6**

Ta(1)–O	1.877(9)	Ta(2)–O	1.929(9)
Ta(1)–Cl(11)	2.370(3)	Ta(2)–Cl(21)	2.358(3)
Ta(1)–Cl(12)	2.383(3)	Ta(2)–Cl(22)	2.382(3)
Ta(1)–Cl(13)	2.399(3)	Ta(2)–Cl(23)	2.382(3)
Ta(1)–N(1)	1.92(1)	Ta(2)–N(2)	1.92(1)
Ta(1)–N(11)	2.389(9)	Ta(2)–N(21)	2.36(1)
Ta(1)–O–Ta(2)	176.0(5)	O–Ta(2)–Cl(21)	93.3(3)
O–Ta(1)–Cl(11)	91.8(3)	O–Ta(2)–Cl(22)	165.5(2)
O–Ta(1)–Cl(12)	166.4(2)	O–Ta(2)–Cl(23)	88.1(3)
O–Ta(1)–Cl(13)	88.4(3)	O–Ta(2)–N(2)	97.5(4)
O–Ta(1)–N(1)	97.6(4)	O–Ta(2)–N(21)	82.2(3)
O–Ta(1)–N(11)	83.5(3)	Cl(21)–Ta(2)–Cl(22)	87.3(1)
Cl(11)–Ta(1)–Cl(12)	88.1(1)	Cl(21)–Ta(2)–Cl(23)	170.5(1)
Cl(11)–Ta(1)–Cl(13)	170.2(1)	Cl(21)–Ta(2)–N(2)	93.9(3)
Cl(11)–Ta(1)–N(1)	95.8(3)	Cl(21)–Ta(2)–N(21)	84.9(3)
Cl(11)–Ta(1)–N(11)	85.3(3)	Cl(22)–Ta(2)–Cl(23)	88.9(1)
Cl(12)–Ta(1)–Cl(13)	89.4(1)	Cl(22)–Ta(2)–N(2)	96.9(3)
Cl(12)–Ta(1)–N(1)	96.0(3)	Cl(22)–Ta(2)–N(21)	83.4(3)
Cl(12)–Ta(1)–N(11)	82.9(3)	Cl(23)–Ta(2)–N(2)	95.2(3)
Cl(13)–Ta(1)–N(1)	94.0(3)	Cl(23)–Ta(2)–N(21)	86.0(3)
Cl(13)–Ta(1)–N(11)	85.0(3)	N(2)–Ta(2)–N(21)	178.7(4)
N(1)–Ta(1)–N(11)	178.5(4)		

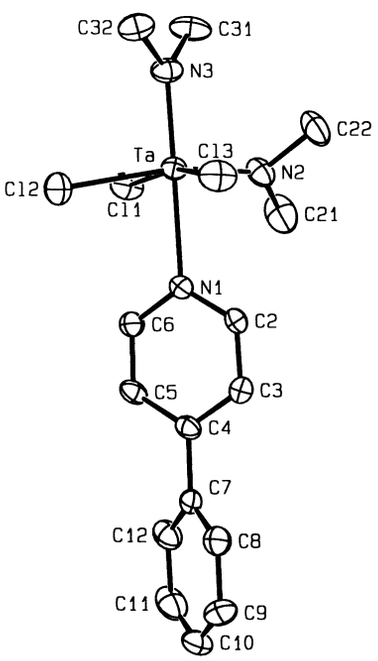


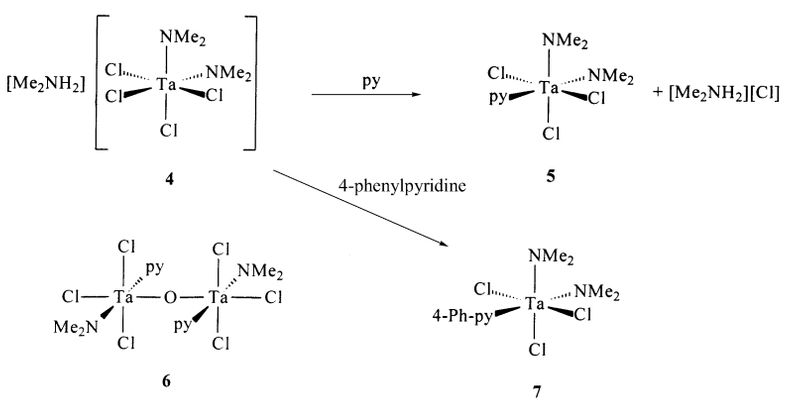
Fig. 3 Molecular structure of $[Ta(NMe_2)_2(NC_6H_4Ph\text{-}4)Cl_3]$ **7**.

Synthesis of aryloxy(dimethylamido) compounds

The addition of 2,3,5,6-tetraphenyl- or 2,6-di-isopropyl-phenol (2 equiv) to solutions of **1** in benzene was found to produce a mixture of two compounds. Spectroscopic data (^1H NMR) was consistent with the presence of two isomers containing a residual Ta–NMe_2 and Ta–$NHMe_2$ group. We formulated these as the *cis*/*trans* isomers **8**–**11** (Scheme 3) based upon other experiments (see below). These isomers contain the amine coordinated *trans* to the amide group. There are four other geometric isomers possible for this particular formulation (Scheme 3). However, we feel there will be a strong electronic driving force (in the absence of overwhelming steric factors) for the amine to coordinate *trans* to the strongest π-donor ligand, which in this case is clearly the dimethylamido group. This hypothesis is not contradicted by any of the structures obtained in this study, where the donor ligand is consistently *trans* to the dimethylamido group. When C_6D_6 solutions of these mixtures were heated at 100 °C for several hours, isomer **8** or **9** were found to isomerize to the alternative isomer **10** or **11** respectively. It was found that isomers **10** and **11** could be formed exclusively by the addition of excess dimethylamine to the chloro(aryloxides) $[Ta(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3]$ or $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3]$ in hydrocarbon solvents. The niobium analogue **12** was also obtained from the corresponding substrate (Scheme 3). Although crystals of **10**–**12** suitable for X-ray diffraction could not be obtained, addition of pyridine to benzene solutions of **10** or **12** led to formation of well formed crystals of the sparingly soluble pyridine adducts **14** and **13** respectively.

Table 3 Selected bond distances (Å) and angles (°) for $[Ta(NMe_2)_2(NC_6H_4Ph\text{-}4)Cl_3]$ **7**

Ta–N(1)	2.371(4)	Ta–Cl(1)	2.404(1)
Ta–N(2)	1.951(5)	Ta–Cl(2)	2.442(2)
Ta–N(3)	1.936(5)	Ta–Cl(3)	2.377(1)
N(1)–Ta–N(2)	85.7(2)	N(2)–Ta–Cl(3)	95.7(2)
N(1)–Ta–N(3)	177.3(2)	N(3)–Ta–Cl(1)	97.8(2)
N(1)–Ta–Cl(1)	84.4(1)	N(3)–Ta–Cl(2)	95.4(2)
N(1)–Ta–Cl(2)	83.2(1)	N(3)–Ta–Cl(3)	94.2(2)
N(1)–Ta–Cl(3)	83.6(1)	Cl(1)–Ta–Cl(2)	85.14(6)
N(2)–Ta–N(3)	96.0(2)	Cl(1)–Ta–Cl(3)	167.11(5)
N(2)–Ta–Cl(1)	87.9(2)	Cl(2)–Ta–Cl(3)	88.87(6)
N(2)–Ta–Cl(2)	167.4(2)		



Scheme 2

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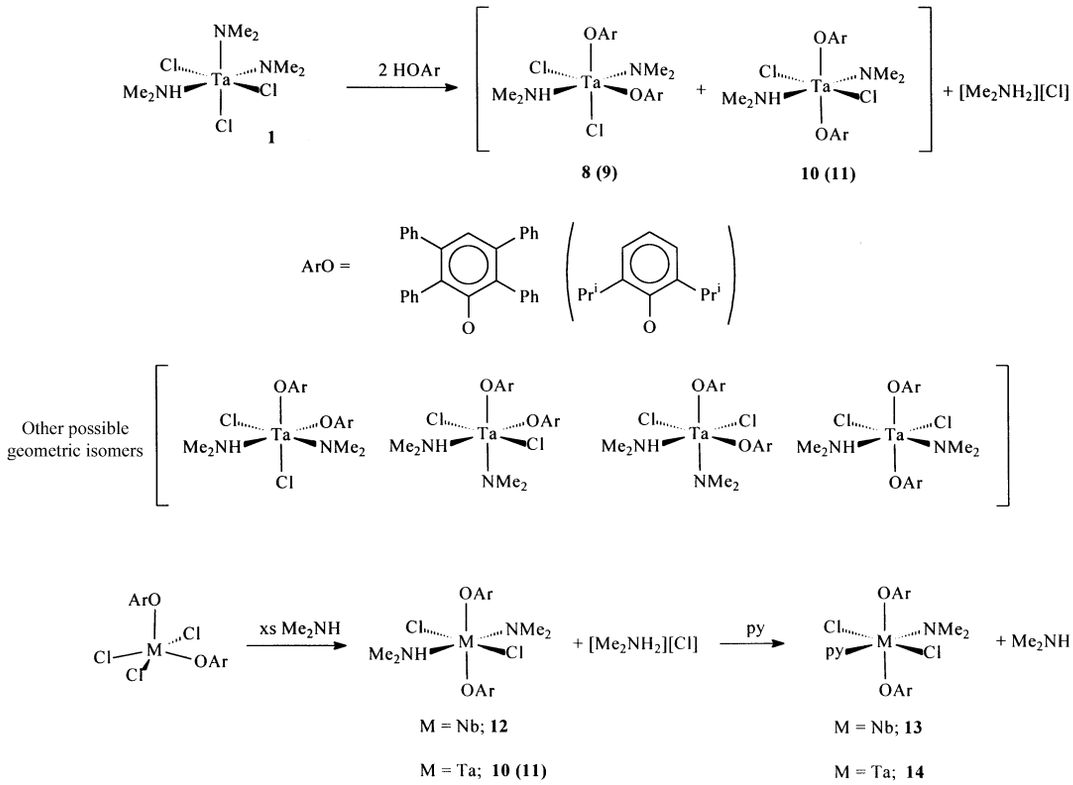

Scheme 3

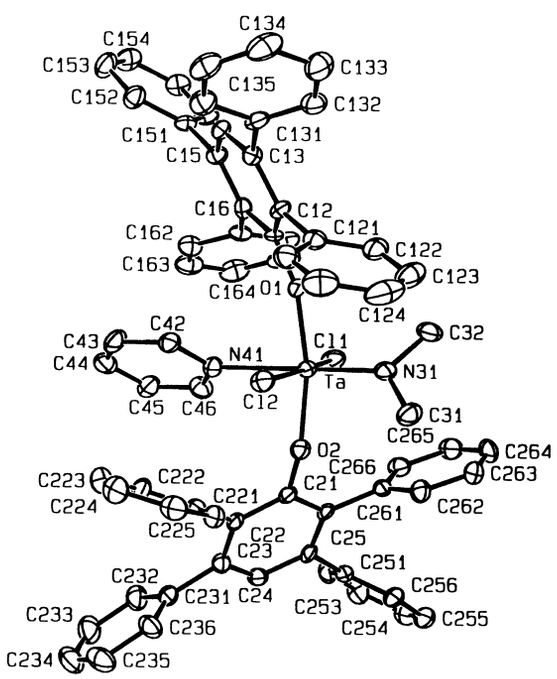

Fig. 4 Molecular structure of $[Ta(OC_6HPh_4\text{-}2,3,5,6)_2Cl_2(NMe_2)(py)]\cdot 5C_6H_6$ **14**. The niobium compound **13** is isomorphous and isostructural.

Table 4 Selected bond distances (Å) and angles (°) for $[M(OC_6HPh_4\text{-}2,3,5,6)_2Cl_2(NMe_2)(py)]$ (M = Nb, **13**; Ta, **14**)

	13	**14**
M–O(1)	1.926(3)	1.927(3)
M–O(2)	1.913(3)	1.932(4)
M–Cl(1)	2.397(1)	2.370(1)
M–Cl(2)	2.391(1)	2.386(1)
M–N(31)	1.935(4)	1.929(5)
M–N(41)	2.395(4)	2.400(5)
O(1)–M–O(2)	168.7(1)	167.3(2)
O(1)–M–N(31)	95.9(2)	96.6(2)
O(2)–M–N(31)	95.4(2)	96.1(2)
O(1)–M–N(41)	84.0(1)	83.5(2)
O(2)–M–N(41)	84.7(1)	83.8(2)
O(1)–M–Cl(1)	90.0(9)	90.1(1)
O(1)–M–Cl(2)	90.2(9)	90.1(1)
O(2)–M–Cl(1)	88.9(1)	88.9(1)
O(2)–M–Cl(2)	89.2(1)	88.9(1)
N(31)–M–N(41)	179.3(2)	179.8(2)
N(31)–M–Cl(1)	93.4(1)	94.5(2)
N(31)–M–Cl(2)	95.4(1)	94.8(2)
N(41)–M–Cl(1)	86.0(1)	85.7(1)
N(41)–M–Cl(2)	85.3(1)	85.1(1)
Cl(1)–M–Cl(2)	171.2(5)	170.7(5)

Crystallographic studies showed **13** and **14** to be isomorphous, with five molecules of benzene per Nb/Ta in the unit cell. The molecular structure of these isomorphous/isostructural compounds (Fig. 4, Table 4) shows the pyridine to be bound *trans* to the dimethylamido group and the aryloxide ligands to be mutually *trans*. It can be seen (Table 4) that the chloride and aryloxide ligands are bent slightly away from the p-donating dimethylamido group towards the neutral donor amine ligand.

Addition of 2,2′-methylenebis(6-phenylphenol) $\{(HOC_6H_3Ph)_2CH_2\}$ to benzene solutions of **1** resulted in formation of the compound $[Ta\{(OC_6H_3Ph)_2CH_2\}Cl_2(NMe_2)(HNMe_2)]$ **15** (Scheme 4). The solid-state structure of **15** (Fig. 5, Table 5) shows the nitrogen atoms to be mutually *trans* with *cis* aryloxide oxygen atoms. The eight-membered ring formed by this bis(aryloxide) has been shown to typically adopt a puckered conformation in which the methylene linker is folded above the chelate ring.[10] Inversion of this ring is typically slow on the NMR timescale resulting in a distinctive AB(AX) pattern for the non-equivalent methylene protons. In the case of **15** the solid-state structure shows that the methylene group is folded towards the Ta–NMe_2 group. It is possible that the molecule could exist as two isomers in solution with the chelate ring folded either towards the amide group (as in the solid state)

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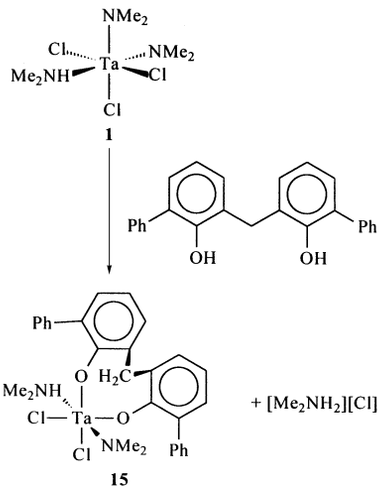
Table 5 Selected bond distances (Å) and angles (°) for [Ta{$(OC_6H_3Ph)_2CH_2$}$Cl_2(NMe_2)(HNMe_2)$] **15**

Ta–O(2)	1.887(2)	Ta–O(1)	1.896(2)
Ta–N(4)	1.961(2)	Ta–N(3)	2.372(7)
Ta–Cl(1)	2.4105(8)	Ta–Cl(2)	2.4180(7)
O(2)–Ta–O(1)	92.15(9)	O(2)–Ta–N(4)	96.08(9)
O(1)–Ta–N(4)	98.2(1)	O(2)–Ta–N(3)	90.8(2)
O(1)–Ta–N(3)	78.5(2)	N(4)–Ta–N(3)	172.5(2)
O(2)–Ta–Cl(1)	89.77(7)	O(1)–Ta–Cl(1)	167.93(6)
N(4)–Ta–Cl(1)	93.44(8)	N(3)–Ta–Cl(1)	89.6(2)
O(2)–Ta–Cl(2)	170.88(6)	O(1)–Ta–Cl(2)	88.67(7)
N(4)–Ta–Cl(2)	92.80(7)	N(3)–Ta–Cl(2)	80.4(2)
Cl(1)–Ta–Cl(2)	87.58(3)	C(11)–O(1)–Ta	154.5(2)
C(21)–O(2)–Ta	155.2(2)		



Scheme 4

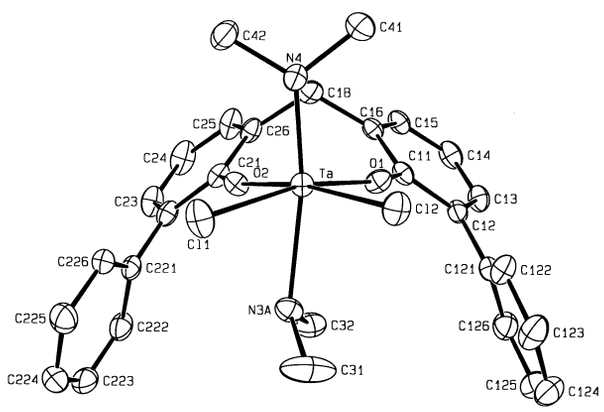


Fig. 5 Molecular structure of [Ta{$(OC_6H_3Ph)_2CH_2$}$Cl_2(NMe_2)$-$(HNMe_2)$] **15**.

or towards the amine donor ligand. However, in solution only one sharp AB pattern is observed at δ 4.76 and 3.24. A possible reason for the observed folding of the chelate lies in the distortion from octahedral geometry imposed by the dimethylamido ligand. It can be seen (Table 5) that the N(amide)–Ta–O angles are opened up to 96 and 98°. It seems reasonable, therefore, that the chelate would fold towards the amide instead of towards the amine towards which the bis(aryloxide) is being "pushed".

Mechanistic discussion

The addition of either the mono- or bis-(phenol) reagents to [$TaCl_3(NMe_2)_2(HNMe_2)$] **1** does not lead to displacement of both amido ligands. This observation can be rationalized by considering the probable intermediates in the reaction. In order for protonolysis of the first Ta–NMe_2 function to occur, the phenolic reagent must coordinate to a vacant metal site, *i.e.* displacement of the amine ligand. This can readily lead to an intermediate mono(aryloxide), mono(amido) compound as shown (Scheme 5). However, the protonolysis of the last remaining amido group is problematic in this system as the incoming phenol will coordinate *trans* to the Ta–NMe_2 bond. Hence, elimination of HCl (trapped by $HNMe_2$) will occur to produce the *cis*/*trans* isomers observed (Scheme 5). In the case of the bis(phenol), only the *cis* isomer can be formed.

Experimental

All operations were carried out under a dry nitrogen atmosphere or *in vacuo* either in a Vacuum Atmosphere Dri-Lab or by standard Schlenk techniques. Hydrocarbon solvents were dried by distillation from sodium–benzophenone and stored under dry nitrogen. All reagents were dried over 3 Å molecular sieves prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Associates Gemini 200 and an Inova 300 spectrometer and were referenced using protio impurities of commercial benzene-d_6 as an internal standard. Microanalytical data were obtained in-house; however in some cases accurate microanalytical data were difficult to obtain due to partial loss of hydrocarbon solvate during analysis. This is compounded by the fact that poly(phenylated)phenoxide ligands tend to generate low carbon analyses due to incomplete combustion. The X-ray diffraction studies were completed in-house at Purdue University.

[Me_2NH_2][$Ta(NMe_2)_2Cl_4$] (4)

A 1 L round-bottomed flask was charged with $TaCl_5$ (13 g, 0.04 mol) and toluene (300 mL) forming a yellow suspension. This suspension was frozen at −178 °C and Me_2NH (0.185 mol) added *via* a calibrated glass manifold. The mixture was slowly warmed to room temperature, stirred overnight, and the solvent evaporated. The mixture was then extracted with benzene, filtered and evacuated to dryness affording an orange solid that could be recrystallized from benzene–hexane. Yield: 10.7 g (63%). Anal. Calc. for $C_6H_{20}Cl_4N_3Ta$: C, 15.77; H, 4.41; N, 9.19; Cl, 31.03. Found: C, 15.97; H, 4.45; N, 9.07; Cl, 30.95%. ^{1}H NMR (C_6D_6, 30 °C): δ 7.87 (br, NH_2); 4.10 (s, H_2NMe_2); 2.39 (s, Ta–NMe_2).

Alternative synthesis of [$TaCl_3(NMe_2)_2(HNMe_2)$] (1)

$TaCl_5$ (43.55 g, 0.12 mol) was suspended in a 50 : 50 (v/v) solution of toluene–ether (100 mL/100 mL). The yellow suspension was frozen in a liquid nitrogen bath (−178 °C). $HNMe_2$ (11.74 mL, 0.48 mol) was condensed in *via* a calibrated glass manifold. The suspension was allowed to warm to room temperature and stirred overnight. The red solution was dried under vacuum, suspended in benzene and filtered to remove salts. The red supernatant was collected and dried to yield the product as a fine red powder. Yield: 48.03 g (94.0%). ^{1}H NMR (C_6D_6, 25 °C): δ 4.04 (s, NMe_2); 3.60 (s, NMe_2); 2.49 (m, HNMe_2); 2.24 (s, HNMe); 2.20 (s, HNMe).

[$Ta(NMe_2)_2Cl_3(py)$] (5) and [{$TaCl_3(NMe_2)(py)$}$_2$(μ-O)] (6)

A round-bottomed flask was charged with **4** (1.6 g, 3.5 mmol) and benzene (20 mL). This red solution was stirred as pyridine (0.3 mL, 4.2 mmol) was slowly added. Stirring was continued for 30 minutes whereupon the solution was filtered and the filtrate evacuated to dryness affording a red solid that could be recrystallized from benzene–hexane. Yield: 1.4 g (88%). Anal. Calc. for $C_9H_{17}Cl_3N_3Ta$, **5**: C, 23.78; H, 3.77; N, 9.24. Found: C, 23.88; H, 3.66; N, 8.53%. ^{1}H NMR (C_6D_6, 30 °C): δ 8.95 (d, *ortho*-py$H$); 6.46–6.80 (*meta* and *para*-py$H$); 4.11 (s, NMe_2), 3.61 (s, NMe_2). ^{13}C NMR (C_6D_6, 30 °C): δ 151.8, 138.6, 124.1 (*py*); 48.9, 48.0 (NMe_2). A minor amount of oxo-bridged **6** formed during either the reaction or workup and was identified by X-ray analysis.

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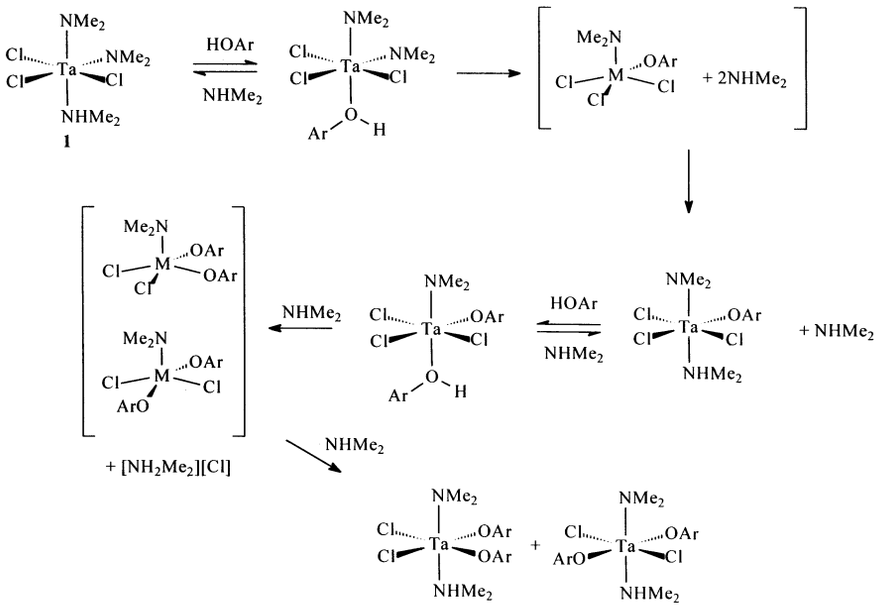

Scheme 5

$[TaCl_3(NMe_2)_2(py\text{-}4Ph)]$ (7)

A round-bottomed flask was charged with **4** (1.0 g, 2.2 mmol) and benzene (20 mL). This red solution was stirred as 4-phenylpyridine (370 mg, 2.4 mmol) was slowly added as a solid. Stirring was continued for 30 minutes whereupon the solution was filtered and the filtrate evacuated to dryness affording a red solid that could be recrystallized from benzene–hexane. Yield: 1.1 g (92%). Anal. Calc. for $C_{15}H_{21}Cl_3N_3Ta$: C, 33.95; H, 3.99; N, 7.92. Found: C, 34.23; H, 3.96; N, 7.77%. ^{1}H NMR (C_6D_6, 30 °C): δ 9.05 (d, *ortho*-py*H*); 6.70–7.40 (*meta* and *para*-py*H*); 4.18 (s, NMe_2), 3.70 (s, NMe_2).

Reaction of 1 with 2,3,5,6-tetraphenylphenol

To a solution of **1** (1.0 g, 2.4 mmol) in benzene (25 mL) was added 2,3,5,6-tetraphenylphenol (1.89 g, 4.8 mmol). The red reaction mixture was stirred overnight. The reaction was filtered to remove salts and the yellow supernatant was collected and dried under vacuum to yield a yellow powder as a 60–40 mixture of **8** and **10** (NMR data identical with following experiment). Yield: 2.69 g (83.3%). ^{1}H NMR (C_6D_6, 25 °C) of **8**: δ 6.9–7.5 (m, aromatics); 3.79 (s, NMe_2); 2.08 (d, HNMe_2); 0.70 (m, *H*NMe_2).

$[Ta(OC_6HPh_4\text{-}2,3,5,6)_2Cl_2(NMe_2)(HNMe_2)]$ (10)

In a round-bottomed flask, $[Ta(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3]$ (1.00 g, 0.8525 mmol) was dissolved in benzene (25 mL). The flask was exposed to one atmosphere of dimethylamine using a calibrated gas manifold. The reaction flask became warm and the solution turned pale yellow. A precipitate formed on the side of the flask. Benzene and any left over dimethylamine was removed by vacuum after two hours. The resulting yellow powder was dissolved in benzene (25 mL) and filtered using Celite as a filter aid. The benzene was again removed by vacuum to yield a yellow powder. Yield: 0.65 g (71%). The ^{1}H NMR spectrum clearly showed the presence of benzene solvate trapped within the solid. This is consistent with the microanalytical data. Anal. Calc. for $C_{64}H_{55}Cl_2N_2O_2Ta$: C, 67.67; H, 4.88; N, 2.47; Cl, 6.24. For $C_{64}H_{55}Cl_2N_2O_2Ta\cdot 2C_6H_6$: C, 70.64; H, 5.22; N, 2.17; Cl, 5.48. Found: C, 69.89; H, 5.10; N, 1.78; Cl, 5.08%. ^{1}H NMR (C_6D_6, 25 °C): δ 6.9–7.5 (m, aromatics); 3.43 (s, NMe_2); 1.76 (d, HNMe_2); 0.37 (m, *H*NMe_2).

Reaction of 1 with 2,6-di-isopropylphenol

To a solution of **1** (1.0 g, 2.4 mmol) in benzene (25 mL) was added 2,6-di-isopropylphenol (0.84 g, 4.8 mmol). The reaction mixture turned yellow almost instantly. It was stirred for 1 hour, filtered and the yellow supernatant collected. The supernatant was dried under vacuum to yield a yellow powder as a mixture of **9** and **11** (NMR data identical with following experiment). Yield: 1.51 g (92%). ^{1}H NMR (C_6D_6, 25 °C) of **9**: δ 6.9–7.3 (m, aromatics); 4.37 (septet, C*H*Me_2); 4.14 (s, NMe_2); 2.41 (d, HNMe_2); 1.24 (d, CHMe_2); 0.90 (m, *H*NMe_2).

$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2(NMe_2)(HNMe_2)]$ (11)

In a round-bottomed flask, $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3]$ (1.0 g, 1.56 mmol) was dissolved in benzene (25 mL). The flask was exposed to one atmosphere of dimethylamine using a calibrated gas manifold. The reaction flask became warm and the solution turned pale yellow. A precipitate formed on the side of the flask. Benzene and any left over dimethylamine was removed by vacuum after two hours. The resulting yellow powder was dissolved in benzene (25 mL) and filtered using Celite as a filter aid. The benzene was again removed by vacuum to yield a yellow powder. Yield: 0.81 g (73%). Anal. Calc. for $TaC_{28}H_{47}Cl_2N_2O_2$: C, 48.35; H, 6.81; N, 4.02; Cl, 10.19. Found: C, 48.09; H, 6.64; N, 4.00; Cl, 10.26%. ^{1}H NMR (C_6D_6, 25 °C): δ 7.15 (d, m-*H*); 6.96 (t, m-*H*); 4.33 (septet, C*H*Me_2), 3.90 (s, NMe_2); 2.73 (m, *H*NMe_2); 2.08 (d, HNMe_2); 1.35 (d, CHMe_2). ^{13}C NMR (C_6D_6, 25 °C): δ 154.7 (*C*-O); 141.5–124.0 (aromatics), 49.9 (s, NMe_2), 40.3 (s, HNMe_2), 26.6 (s, CHMe_2), 25.3 (s, CHMe_2).

$[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_2(NMe_2)(HNMe_2)]$ (12)

In a round-bottomed flask, $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3]$ (1.00 g, 1.01 mmol) was dissolved in benzene (25 mL). The flask was exposed to one atmosphere of dimethylamine using a calibrated gas manifold. The reaction flask became warm and the solution turned pale yellow. A precipitate formed on the side of the flask. Benzene and any left over dimethylamine was removed by vacuum after two hours. The resulting yellow powder was dissolved in benzene (25 mL) and filtered using Celite as a filter aid. The benzene was again removed by vacuum to yield a dark red powder, 0.81g (77.14%). ^{1}H NMR (C_6D_6, 25 °C): δ 6.8–7.3 (m, aromatics); 3.11 (s, NMe_2); 1.71 (d, HNMe_2); 0.32 (m, 1H, *H*NMe_2).

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Table 6 Crystallographic data for complexes **4**, **6**, **7** and **13**–**15**

	4	**6**	**7**	**13**	**14**	**15**
Formula	$C_6H_{20}Cl_4N_3Ta$	$C_{14}H_{22}Cl_6N_4OTa_2$	$C_{15}H_{21}Cl_3N_3Ta$	$C_{67}H_{53}Cl_2N_2O_2Nb\cdot 5C_6H_6$	$C_{67}H_{53}Cl_2N_2O_2Ta\cdot 5C_6H_6$	$C_{29}H_{31}Cl_2N_2O_2Ta\cdot C_6H_6$
Formula weight	457.01	836.97	530.66	1472.57	1560.61	769.55
Space group	$P2_1/n$ (no. 14)	$P2_12_12_1$ (no. 19)	$P2_1/c$ (no. 14)	$Pna2_1$ (no. 33)	$Pna2_1$ (no. 33)	$P\bar{1}$ (no. 2)
a/Å	8.6567(3)	11.9310(6)	19.1788(7)	30.4539(2)	30.47090(10)	10.0975(2)
b/Å	17.9638(7)	14.3050(4)	7.2144(4)	22.0854(4)	22.0751(2)	11.1400(2)
c/Å	10.2052(3)	14.3949(7)	14.3129(6)	11.4593(9)	11.4756(4)	15.5664(3)
α/°	90	90	90	90	90	80.5543(8)
β/°	107.121(2)	90	104.191(3)	90	90	84.6022(8)
γ/°	90	90	90	90	90	67.3869(7)
V/Å^3	1516.7(2)	2456.8(3)	1919.3(3)	7707.4(5)	7719.0(2)	1593.55(8)
Z	4	4	4	4	4	2
ρ_{calc}/g cm^{-3}	2.001	2.263	1.836	1.27	1.343	1.604
T/K	173	173	173	150	150	150
R, R_w	0.041, 0.107	0.045, 0.107	0.037, 0.085	0.058, 0.095	0.046, 0.085	0.027, 0.058

$[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_2(NMe_2)(py)]$ (13)

A sample of **12** (0.62 g, 0.591 mmol) was dissolved in benzene. To this, an excess (100 μL) of pyridine was added. The mixture was then layered with pentane and left overnight. Red crystals of product were formed within a 24 hour period. The benzene–pentane solution was decanted away and the crystals (0.38 g, 60.3%) were dried by vacuum. ^{1}H NMR analysis of the crystals was unobtainable due to low solubility. X-Ray analysis showed five benzene molecules in the coordination sphere. Anal. Calc. for $C_{67}H_{53}Cl_2N_2O_2Nb\cdot 5C_6H_6$: C, 79.12; H, 5.68; N, 1.90; Cl, 4.82. Found: C, 79.02; H, 5.47; N, 2.17; Cl, 5.40%.

$[Ta(OC_6HPh_4\text{-}2,3,5,6)_2Cl_2(NMe_2)(py)]$ (14)

In a vial, **10** (0.69 g, 0.607 mmol) was dissolved in benzene. To this, three drops of pyridine were added. The mixture was then layered with pentane and left overnight. Orange crystals of product were formed within a 24 hour period. The benzene–pentane solution was decanted away and the crystals (0.35 g, 49.3%) were dried by vacuum. ^{1}H NMR analysis was again unobtainable due to low solubility of crystals. X-Ray analysis showed five benzene molecules in the coordination sphere. Anal. Calc. for $C_{67}H_{53}Cl_2N_2O_2Ta\cdot 5C_6H_6$: C, 74.66; H, 5.36; N, 1.80; Cl, 4.54. Found: C, 73.90; H, 5.40; N, 1.85; Cl, 4.15%.

$[Ta\{(OC_6H_3Ph)_2CH_2\}Cl_2(NMe_2)(HNMe_2)]$ (15)

To a solution of **1** (1.0 g, 2.4 mmol) in benzene (20 mL) was added a 10 mL benzene solution of 2,2′-methylenebis-(6-phenylphenol) (0.84 g, 2.4 mmol). The solution was stirred for 24 hours, filtered to remove salts and the red supernatant collected. The supernatant was layered with pentane and allowed to stand for 24 hours resulting in an orange crystalline precipitate. Crystallographic studies indicated one benzene molecule of crystallization per Ta. Microanalytical data indicated some loss of these solvate molecules. Anal. Calc. for $TaC_{29}H_{31}Cl_2N_2O_2$: C, 50.38; H, 4.52. For $TaC_{29}H_{31}Cl_2N_2O_2\cdot C_6H_6$: C, 54.63; H, 4.85. Found: C, 53.49; H, 4.86. Repeat: C, 52.76; H, 4.68%. Yield: 1.63 g (98%). ^{1}H NMR (C_6D_6, 25 °C): δ 6.70–7.61 (m, aromatics); 4.76 (d, CH_2); 3.24 (d, CH_2); 3.92 (s, NMe_2); 1.40 (d, HNMe_2).

X-Ray crystallography data

Crystal data and data collection parameters are contained in Table 6. 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 MoKα radiation ($\lambda = 0.71073$ Å) on a Nonius Kappa-CCD. Lorentz and polarization corrections were applied to the data.[11] An empirical absorption correction using SCALEPACK was applied.[12] Intensities of equivalent reflections were averaged and the structures solved using the structure solution program PATTY in DIRDIF92.[13] 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 structures were refined in full-matrix least-squares where the function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$ and the weight w is defined as $w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 1.4064P]$ where $P = (F_o^2 + 2F_c^2)/3$. Scattering factors were taken from the *International Tables for Crystallography*.[14] Refinement was performed on a Alpha-Server 2100 using SHELX-97.[15] Crystallographic drawings were done using the program ORTEPII.[16]

CCDC reference numbers 159025–159030.

See http://www.rsc.org/suppdata/dt/b1/b101723n/ for crystallographic data in CIF or other electronic format.

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