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Studies of six-coordinate adducts all-*trans*-$[M(OAr)_2(X)_2(L)_2]$ ($M = Nb$, Ta; $X = Cl$, Br; $L =$ tertiary phosphine, pyridine)

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Abstract

An extensive series of d^1-derivatives of niobium and tantalum $[M(OAr)_2(X)_2(L)_2]$ ($M = Nb$, Ta; $X = Cl$, Br; $L =$ tertiary phosphine, pyridine) have been isolated by reduction of the corresponding adducts $[M(OAr)_2(X)_3(L)]$ in the presence of excess L. Crystallographic studies show an all-*trans*, octahedral arrangement of ligands about the metal center. The effect of the halide, donor ligand and aryloxide substituents upon the structural parameters is discussed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Niobium complexes; Tantalum complexes; Aryloxide complexes

1. Introduction

The organometallic chemistry of niobium and tantalum supported by aryloxide ligation continues to be an active field of research. Two broad areas of investigation involve the stoichiometric and catalytic reactivity of d^0-alkyl and hydrido aryloxides [1,2], and the activation of unsaturated organic substrates by highly reducing, low valent aryloxides of niobium and tantalum [3,4]. During the exploration of the utility of the mixed halo aryloxides $[M(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3]_2$ ($M = Nb$, **1**; Ta, **2**), $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Br_3]_n$ (**3**) and $[Ta(OC_6H_2Pr^i_2\text{-}2,6\text{-}Br\text{-}4)_2Cl_3]_n$ (**4**) as precursors for the formation of metal-hydride derivatives as well as low-valent aryloxides, we have isolated a series of six coordinate d^1-metal complexes $[M(OAr)_2(X)_2(L)_2]$ ($M = Nb$, Ta; $X = Cl$, Br; $L =$ py, various tertiary phosphines). We wish to report here on the solid state structures of these d^1-molecules and compare their structural parameters with various other aryloxide derivatives of niobium and tantalum as well as the distorted six-coordinate d^0-adducts $[M(OAr)_x(Cl)_{5-x}(L)]$ ($M = Nb$, Ta; $x = 2, 3$).

2. Results and discussion

2.1. Synthesis and spectroscopic characterization of compounds

The chloro-bridged, edge-shared bis-octahedral dimers $[M(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3]_2$ ($M = Nb$, **1**; Ta, **2**) have been previously isolated and fully characterized. The new, mixed halo, aryloxides $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Br_3]_n$ (**3**) and $[Ta(OC_6H_2Pr^i_2\text{-}2,6\text{-}Br\text{-}4)_2Cl_3]_n$ (**4**) have also been obtained directly from the metal halide and 2 equiv. of the corresponding phenol. The exact molecularity of these new derivatives has not been determined. Compounds **1** and **2** have been shown to form an extensive series of adducts $[M(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3(L)]$ with a variety of O[1] [5], N[2], and P donor ligands [6]. These

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[1] A series of diethyl–ether complexes of tantalum have been reported by Wigley et al., see Refs. [2a,c], e.g. *cis,mer*-$[TaCl_3(OAr)_2(OEt_2)]$ and *trans,mer*-$[TaCl_2(OAr)_3(OEt_2)]$ ($OAr = 2$, 6-dimethyl and 2,6-diisopropylphenoxide); a number of tetrahydrofuran complexes of mixed chloro aryloxides of niobium have been structurally characterized by Nakamura et al. [5].

[2] A series of quinoline (quin) complexes. *cis,mer*-$[TaCl_3(OC_6H_3Pr^i_2\text{-}2,6)_2(quin)]$ and *trans,mer*-$[TaCl_2(OC_6H_3Pr^i_2\text{-}2,6)_3(quin)]$ have been reported by Wigley et al., see Refs. [3d–f].

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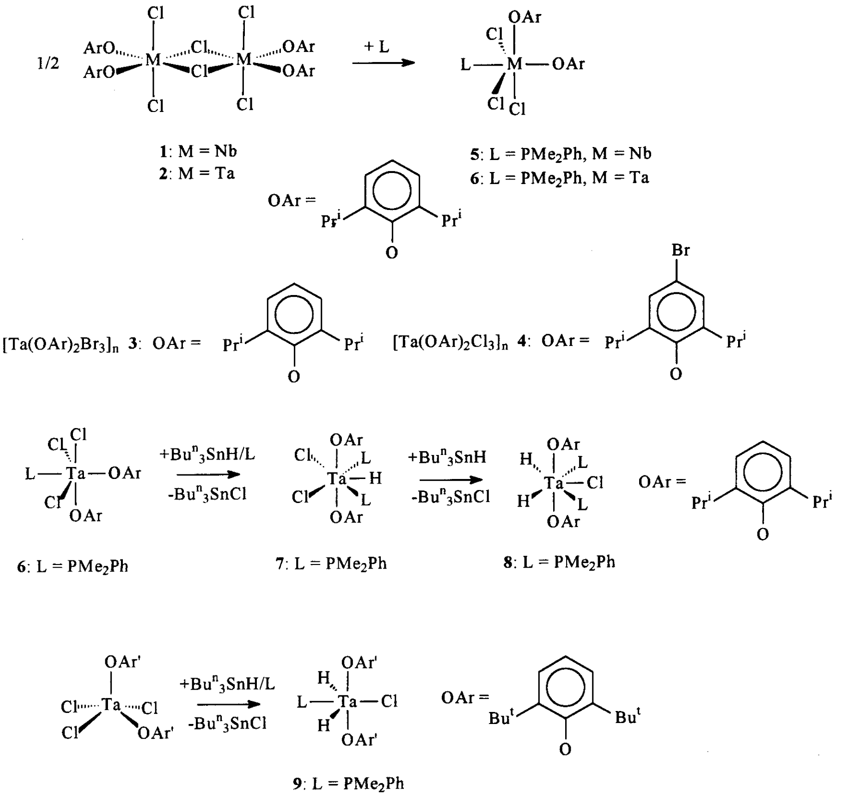
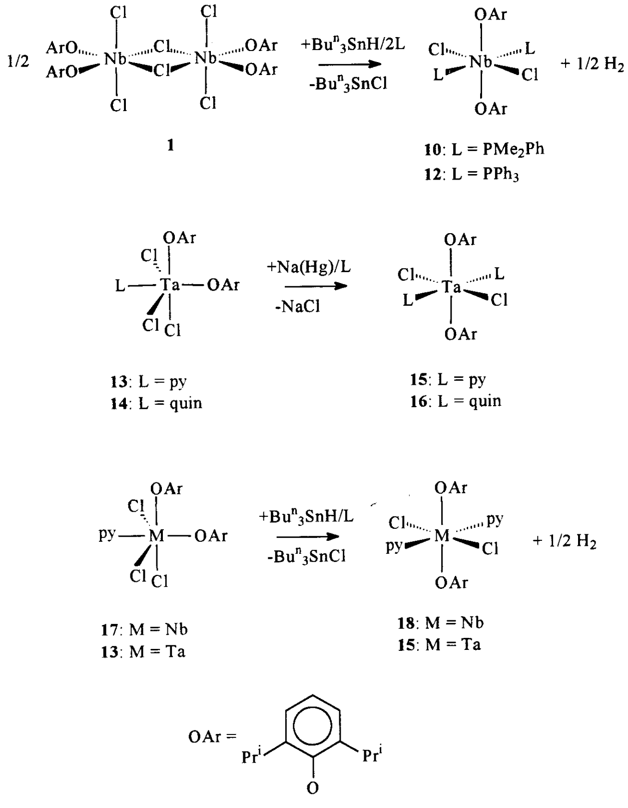


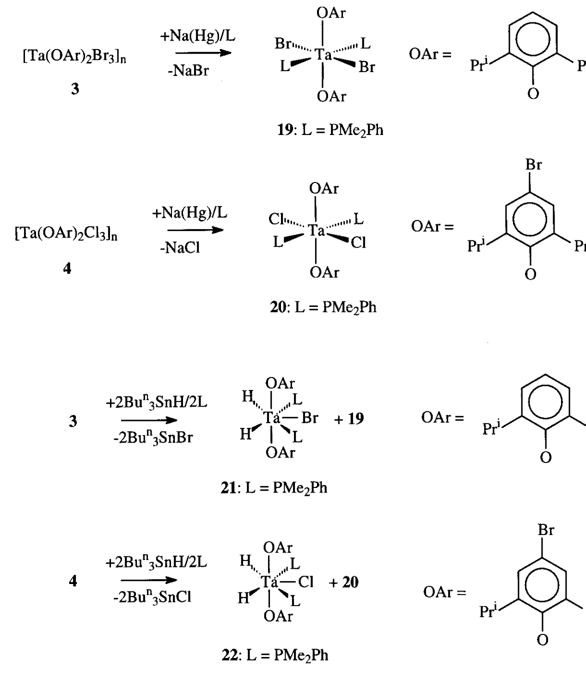
Scheme 1.

adducts contain a distorted octahedral geometry in which the *cis* ligands are bent towards the donor ligand (e.g. PMe_2Ph adducts **5** and **6**, Scheme 1). In the case of the tantalum phosphine adduct $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3(PMe_2Ph)]$ (**4**), reaction with Bu^n_3SnH has been shown to be a good synthetic route to the seven coordinate hydride derivatives $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(Cl)_{3-x}(H)_x(PMe_2Ph)_2]$ ($x = 1$, **7**; $x = 2$, **8**, Scheme 1) [2]. The di-hydride complex **8** has also been obtained by hydrogenolysis of $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(CH_2C_6H_4\text{-}4Me)_2Cl]$ (**7**) in the presence of PMe_2Ph (Scheme 1). The six-coordinate dihydride $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2(Cl)(H)_2(PMe_2Ph)]$ (**9**) containing the bulkier aryloxide was found to be even more distorted than the halide adducts both in solution and in the solid state (Scheme 1) [2,6].

In contrast, addition of Bu^n_3SnH to hydrocarbon solutions of the niobium adduct $[Nb(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3(PMe_2Ph)]$ (**3**) was found to lead to the evolution of H_2 gas and formation of the pale yellow, sparingly soluble derivative $[Nb(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2(PMe_2Ph)_2]$ (**10**) in high yield (Scheme 2). Large, well formed crystals of **8** were also obtained by hydrogenolysis of the bis(4-methylbenzyl) complex $[Nb(OC_6H_3Pr^i_2\text{-}2,6)_2(CH_2C_6H_4\text{-}4Me)_2Cl]$ (**11**) in the presence of PMe_2Ph (Scheme 2). This product presumably arises via a ligand redistribution reaction in solution. During an attempt to carry out the catalytic hydrogenation of triphenylphosphine by a mixture of



Scheme 2.



Scheme 3.

$[Nb(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3]_2$ (**1**) and Bu$^n_3$SnH, dark orange crystals of the sparingly soluble complex $[Nb(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2(PPh_3)_2]$ (**12**) were also obtained (Scheme 2). ^{31}P NMR detected no hydrogenation of phenyl-phosphine groups within the reaction mixture.

Previously it has been shown by Wigley et al. that reduction of the adducts $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3(py)]$ (**13**) and $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3(quin)]$ (**14**) by sodium amalgam (1 Na per Ta) in the presence of pyridine (py) or quinoline (quin) led to the corresponding d^1-derivatives $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2(py)_2]$ (**15**) and $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2(quin)_2]$ (**16**) respectively (Scheme 2) [3f]. We find that treatment of a benzene solution of the adduct $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3(py)]$ (**13**) with Bu$^n_3$SnH in the presence of excess py leads to a mixture of unreacted **13** (detected by ^{1}H NMR) along with a small amount of **15** (crystallographically characterized). This reaction mixture yielded both dark red crystals of **13** along with purple crystals of **15** when diluted with hexane. The reaction of a benzene solution of $[Nb(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3(py)]$ (**17**) with Bu$^n_3$SnH results in the rapid evolution of H_2 and formation of a reaction mixture from which d^1-$[Nb(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2(py)_2]$ (**18**) can be isolated upon dilution with hexane (Scheme 2).

The sodium amalgam (1 Na per Ta) reduction of **3** or **4** in the presence of excess PMe_2Ph led to the formation of the corresponding derivatives $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Br_2(PMe_2Ph)_2]$ (**19**) and $[Ta(OC_6H_2Pr^i_2\text{-}2,6\text{-}Br\text{-}4)_2Cl_2(PMe_2Ph)]$ (**20**) (Scheme 3). The reaction of **3** or **4** with Bu$^n_3$SnH (excess) in the presence of PMe_2Ph proved to be more complex. The d^1-complexes **19** and **20** were detected in the reaction mixture by EPR. However, the majority of the product was determined to be the dihydride derivatives $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(H)_2Br(PMe_2Ph)_2]$ (**21**) and $[Ta(OC_6H_2Pr^i_2\text{-}2,6\text{-}Br\text{-}4)_2(H)_2Cl(PMe_2Ph)]$ (**22**) respectively (Scheme 3). One crystal obtained directly from the reaction mixture and analyzed by X-ray diffraction was solved as a solid solution of 7% of **19** with 93% **21**. In the ^{1}H NMR spectrum of bromide, dihydride **21** the Ta-*H* resonance appears at δ 15.92 ppm, upfield of the value of δ 16.55 ppm found for the corresponding chloride $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(H)_2Cl(PMe_2Ph)_2]$ [2c]. However, the *p*-bromo substituent in **22** has a minimal impact, causing the hydride signal to shift upfield only slightly to δ 16.45 ppm.

2.2. Structural studies

The compounds **10**, **12**, **19**, **20** (including the benzene solvate) and isomorphous **15** and **18** have been subjected to X-ray diffraction analysis. Table 1 collects some important structural parameters, while Tables 2 and 3 contain crystallographic data. The molecular structures of **10**, **15** and **20** (benzene solvate) are shown in Figs. 1–3 respectively. All of the compounds can be seen to adopt an all-*trans* arrangement of the halide, aryloxide and donor ligands. The bond angles around the metal centers are very close to those expected for an octahedral geometry. This is in sharp contrast to the situation found for the parent d^0-adducts *cis*-*mer*-

Table 1
Selected bond distances (Å) and angles (°) for all-*trans*-$[M(OAr)_2X_2L_2]$

Compound	M	OAr	X	L	M–OAr [M–O–C]	M–X	M–L
10	Nb	$OC_6H_3Pr^i_2$-2,6	Cl	PMe_2Ph	1.901(2) [177]	2.4552(9)	2.6647(8)
12	Nb	$OC_6H_3Pr^i_2$-2,6	Cl	PPh_3	1.892(7) [174]	2.456(3)	2.782(4)
19	Ta	$OC_6H_3Pr^i_2$-2,6	Br	PMe_2Ph	1.904(2) [175]	2.6004(6)	2.659(1)
20	Ta	$OC_6H_2Pr^i_2$-2,6-Br-4	Cl	PMe_2Ph	1.909(3) [175]	2.450(1)	2.646(1)
20·C_6H_6	Ta	$OC_6H_2Pr^i_2$-2,6-Br-4	Cl	PMe_2Ph	1.893(4) [179]	2.448(1)	2.655(1)
18	Nb	$OC_6H_3Pr^i_2$-2,6	Cl	py	1.903(2) [164]; 1.889(2) [164]	2.4413(8); 2.4464(8)	2.256(2); 2.253(2)
15	Ta	$OC_6H_3Pr^i_2$-2,6	Cl	py	1.906(3) [164]; 1.896(3) [164]	2.429(1); 2.450(1)	2.231(3); 2.231(3)

Table 2
Crystal data and data collection parameters for **10**, **12**, **15** and **18**

	10	**12**	**15**	**18**
Formula	$C_{40}H_{56}Cl_2O_2P_2Nb$	$C_{60}H_{64}Cl_2O_2P_2Nb$	$C_{34}H_{44}Cl_2O_2N_2Ta$	$C_{34}H_{44}Cl_2O_2N_2Nb$
Formula weight	794.65	1042.94	764.60	676.55
Space group	$P2_1/c$	*Pbca* (no. 61)	*P*1 (no. 2)	*P*1 (no. 2)
Unit cell parameters				
a (Å)	9.4842(7)	13.342(1)	11.603(3)	11.649(1)
b (Å)	10.8233(9)	18.842(2)	13.318(3)	13.283(1)
c (Å)	20.307(2)	20.823(2)	13.598(3)	13.616(1)
α (°)	90	90	69.16(2)	69.328(7)
β (°)	97.393(7)	90	86.49(2)	86.592(9)
γ (°)	90	90	64.86(2)	64.887(9)
V (Å)	2067.2(6)	5234(1)	1767.8(8)	1774.7(4)
Z	2	4	2	2
ρ_{calc} (g cm^{-3})	1.277	1.323	1.436	1.266
Temperature (K)	293	293	293	293
Radiation (wavelength, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
R	0.037	0.047	0.029	0.033
R_W	0.052	0.052	0.033	0.042

Table 3
Crystal data and data collection parameters for **19**, **20** and **21**

	19	**20**	**20**·C_6H_6	0.93**21**+0.07**19**
Formula	$C_{40}H_{56}Br_2O_2P_2Ta$	$C_{40}H_{54}Br_2Cl_2O_2P_2Ta$	$C_{46}H_{60}Br_2Cl_2O_2P_2Ta$	$C_{40}H_{57.87}Br_{1.07}O_2P_2Ta$
Formula weight	971.61	1040.50	1118.61	898.78
Space group	$P2_1/c$ (no. 14)	*P*1 (no. 2)	*C*2/*c* (no. 15)	$P2_1/n$ (no. 14)
Unit cell parameters				
a (Å)	9.3486(7)	9.3866(2)	29.3085(10)	9.7230(3)
b (Å)	10.9854(3)	11.0972(4)	10.7106(4)	24.3048(8)
c (Å)	20.1368(9)	11.1275(4)	17.7393(4)	17.6904(5)
α (°)	90	77.0487(13)	90	90
β (°)	97.2516(19)	77.570(2)	120.215(2)	90.7760(18)
γ (°)	90	81.546(2)	90	90
V (Å)	2051.5(2)	1097.17(8)	4812.0(6)	4180.1(4)
Z	2	1	4	4
ρ_{calc} (g cm^{-3})	1.573	1.575	1.544	1.428
Temperature (K)	173	203	173	173
Radiation (wavelength, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
R	0.043	0.035	0.054	0.039
R_W	0.106	0.084	0.136	0.083

$[M(OAr)_2(Cl)_3(L)]$ (M = Nb, Ta) [6]. In these compounds there is a distinct distortion away from octahedral geometry with the *cis*-chloride ligands being bent towards the single donor ligand. This distortion has been rationalized in terms of allowing an increase in the π-bonding between the aryloxide trans- to the L group and the metal center. The all-*trans* geometry in the d^1-compounds means that there is nothing to be gained by any distortion away from a regular octahedral geometry. The geometry of six-coordinate adducts of the tetrahalides $[MX_4L_2]$ has been the focus of many studies dating back to the work of McCarlet et al. [7] and Walton et al. [8]. Both *cis* and *trans* isomers have been isolated and structurally characterized, e.g. *cis*-$[NbCl_4(NCMe)_2]$ [9], *cis*-$[TaBr_4(PMe_2Ph)_2]$ [10], *trans*-$[TaCl_4(py)_2]$ [11], *trans*-$[NbCl_4(PEt_3)_2]$ and *trans*-$[NbCl_4(PEtPh_2)_2]$ [12]. Interestingly in the *cis*-isomers there is a distinct bending of the halides towards the donor ligands. Seven-coordinate tris(phosphine) adducts and fused, square-antiprismatic dinuclear derivatives of the metal(IV) halides have also been isolated [13].

Of most interest to this study are the interatomic distances around the central coordination sphere of the metal center. The metal–oxygen distances for all compounds span the very narrow range of 1.889(2)–1.909(3) Å. These distances are indistinguishable within experimental error. Previous studies have shown that

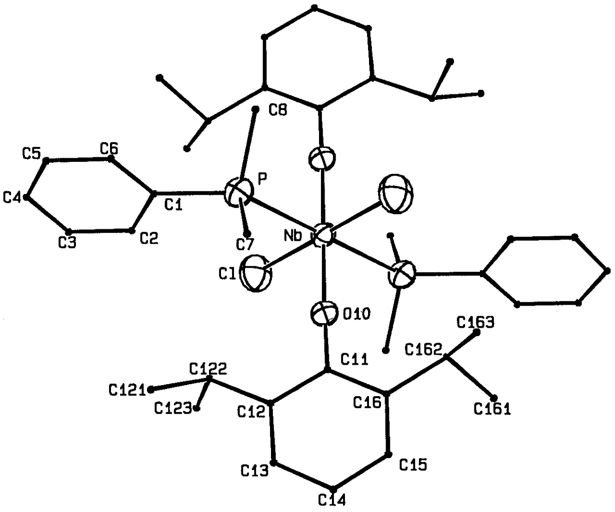


Fig. 1. Molecular structure of **10** showing the atomic numbering scheme.

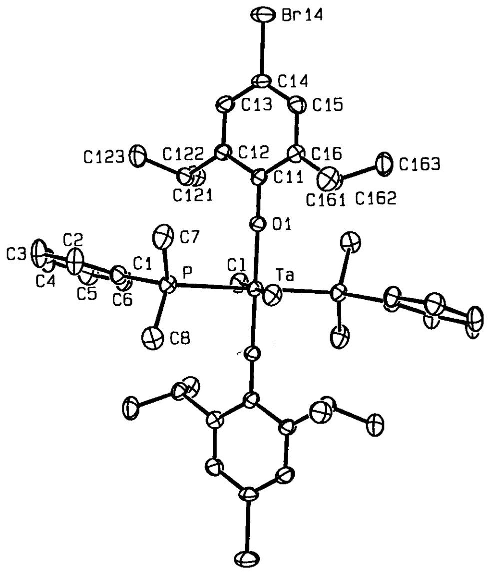


Fig. 3. Molecular structure of **20** (benzene solvate) showing the atomic numbering scheme.

the metal–ligand distances for isomorphous niobium and tantalum compounds are essentially the same. Hence we can say that the replacement of chloride ligands in niobium compound **10** by bromide in tantalum compound **19** has minimal effect on the metal aryloxide bond length. Also the introduction of a *p*-bromo-substituent onto the phenoxide nucleus has no effect upon this parameter. The M–O–Ar angles are all large, as typically found for early d-block metal aryloxides [14]. The metal–chloride distances are also identical for all new compounds, varying from 2.429(1)–2.456(3) Å. The metal–aryloxide and metal–chloride distances in these d^1-derivatives are, however, slightly longer than those found in the parent d^0-adducts. For example the compound *cis*-*mer*-$[Nb(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3(PMe_2Ph)]$ has Nb–O and Nb–Cl distances of 1.82(2), 1.83(2) and 2.366(8)–2.425(7) Å respectively. The isomorphous pyridine adducts *cis*-*mer*-$[M(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3(py)]$ have corresponding distances of 1.832(3)–1.852(3) and 2.366(2)–2.403(1) Å [6]. There appears to be slightly less oxygen (or chlorine) to metal π-bonding in the d^1-compounds, consistent with other studies which have shown the dramatic sensitivity of the metal–aryloxide bond to the electrophilicity of the metal center [4b].

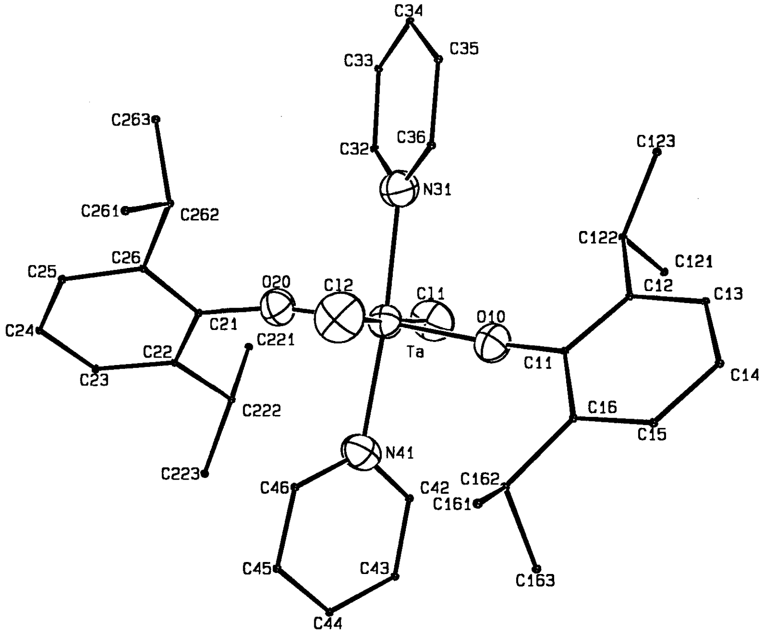


Fig. 2. Molecular structure of **15** showing the atomic numbering scheme.

The metal-donor ligand distances are also worthy of comment. The M–N distances in isomorphous **15** and **18**, 2.231(3)–2.256(2) Å, are shorter than the M–N distances of 2.331(4) and 2.315(6) Å in isomorphous *cis*-*mer*-[M($OC_6H_3Pr^i_2$-2,6)$_2Cl_3$(py)] (M = Nb, Ta) [6]. This possibly reflects the fact that in the d^0-adducts the pyridine ligand is *trans* to an aryloxide (*trans* influence). The Ta–N distance is 2.222(7) Å in *trans*-[$TaCl_4(py)_2$], very similar to that found in **15** (**18**). The Nb–P distance of 2.6647(8) Å in **10** is also shorter than the distance of 2.742(8) Å found in *cis*-*mer*-[Nb($OC_6H_3Pr^i_2$-2,6)$_2Cl_3$(PMe_2Ph)]. As expected, the less basic PPh_3 derivative **12** has a longer Nb–P distance of 2.782(4) Å compared to **10**.

3. Experimental

3.1. General

All operations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. The hydrocarbon solvents were distilled from sodium benzophenone and stored over sodium ribbons under nitrogen until use. Reagents were purchased from Aldrich Chemical Co., Inc. and used without further purification. The ^1H and ^{13}C NMR spectra were recorded on a Varian Associates Gemini-200 spectrometer and referenced to protio impurities of commercial benzene-d_6 or deuterated chloroform as internal standards. Mass spectra, elemental analyses and X-ray diffraction studies were obtained in-house at Purdue University. General operating procedures have been reviewed elsewhere.

3.2. Synthesis of compounds

3.2.1. [Ta($OC_6H_3Pr^i_2$-2,6)$_2Br_3$] (**3**)

To a stirred solution of [$TaBr_5$] (13.47 g, 23.0 mmol) in toluene (250 ml), was slowly added 2,6-diisopropylphenol (9.49 ml, 51.0 mmol) via syringe. The solution became dark orange and was stirred for 24 h. Removal of solvent and generated HBr under vacuum yielded the crude product as a brown solid. Layering a saturated benzene solution of the crude material with hexane yielded the pure product as a yellow crystalline solid, which was washed with hexane and dried. Yield 10.75 g (59.8%). ^1H NMR (C_6D_6, 30°C): δ 6.8–7.2 (m, 6H, aromatics); 3.7 (m, 2H, C*H*Me$_2$); 1.22 (d, 9H, CH*Me*$_2$). *Anal.* Calc. for $C_{24}H_{34}Br_3O_2Ta$: C, 37.19; H, 4.42; Br, 30.92. Found: C, 37.96; H, 4.11; Br, 30.11%.

3.2.2. [Ta($OC_6H_2Pr^i_2$-2,6-Br-4)$_2Cl_3$] (**4**)

To a suspension of [$TaCl_5$] (39.9 g, 0.11 mol) in benzene (500 ml) was added $HOC_6H_2Pr^i_2$-2,6-Br-4 (61.0 g, 0.237 mol) via syringe resulting in gas evolution (HCl) and a change in color from yellow to deep red. This solution was stirred for 40 min and the solvent removed in vacuo to yield the product as a yellow powder which was washed with hexane and dried. Yield 88.8g (almost quantitative). ^1H NMR (C_6D_6, 30°C): δ 7.17–7.36 (m, 4H, aromatics); 3.75 (m, 2H, C*H*Me$_2$); 0.967 (d, 9H, CH*Me*$_2$). *Anal.* Calc. for $TaO_2Cl_3Br_2C_{24}H_{32}$: C, 36.05; H, 4.03. Found C, 35.94; H, 4.07%.

3.2.3. [Nb($OC_6H_3Pr^i_2$-2,6)$_2Cl_2$(PMe_2Ph)$_2$] (**10**)

To a suspension of [Nb_2($OC_6H_3Pr^i_2$-2,6)$_4Cl_6$] (**1**) (2.01 g, 1.81 mmol) in benzene (10 ml) was added PMe_2Ph (1.10 g, 7.95 mmol) with stirring. To this stirred reaction mixture was added Bu^n_3SnH (2.0 ml, 7.4 mmol) dropwise over 10 min. The initial orange solution darkened and gas (H_2) was evolved. After complete addition the mixture was allowed to stand for 24 h yielding the product as orange crystals, which were washed with hexane and dried. Yield 2.29 g (79%). *Anal.* Calc. for $NbO_2Cl_2P_2C_{40}H_{56}$: C, 60.46; H, 7.10; Cl, 8.92; P, 7.80. Found C, 60.71; H, 7.41; Cl, 8.65; P, 7.36%. EPR (C_7H_8, 30°C): $g = 1.9346$ ($a_{Nb} = 134$ G).

3.2.4. [Nb($OC_6H_3Pr^i_2$-2,6)$_2Cl_2$(PPh_3)$_2$] (**12**)

A 50 ml round bottomed flask was charged in a Dri-Lab with a mixture of PPh_3 (2.50 g, 9.5 mmol) and [Nb_2($OC_6H_3Pr^i_2$-2,6)$_4Cl_6$] (**1**) (0.25 g, 0.23 mmol) in benzene (20 ml). The mixture was 'activated' with Bu^n_3SnH (0.40 ml, 1.5 mmol) and placed in a Parr model 4561, 300 ml minireactor, pressurized with H_2 (1200 psi) and heated to 60°C for 24 h. After cooling and depressurizing, the flask was removed from the minireactor within the Dri-Lab. A few golden crystals of **12** were observed and isolated from the mother liquor. These were characterized entirely by X-ray crystallography. Analysis of the solution by ^1H and ^{31}P NMR showed no hydrogenation of benzene or PPh_3.

3.2.5. [Ta($OC_6H_3Pr^i_2$-2,6)$_2Cl_2$(py)$_2$] (**15**)

To a suspension of [Ta_2($OC_6H_3Pr^i_2$-2,6)$_4Cl_6$] (**1**) (2.31 g, 1.80 mmol) in benzene (20 ml) was added pyridine (1.0 ml, 12.3 mmol) with stirring. To this stirred reaction mixture was added Bu^n_3SnH (2.0 ml, 7.4 mmol) dropwise over 10 min. The initial yellow solution darkened. After complete addition the mixture was allowed to stand for 24 h before the solvent was removed under vacuum to yield a dark brown tar. Dissolving the crude material in benzene and layering with pentane yielded a mixture of yellow crystals of adduct [Ta($OC_6H_3Pr^i_2$-2,6)$_2Cl_3$(py)] (NMR) and dark red crystals of **15** (identified crystallographically).

3.2.6. [Nb($OC_6H_3Pr^i_2$-2,6)$_2Cl_2$(py)$_2$] (**18**)

To a suspension of [Nb_2($OC_6H_3Pr^i_2$-2,6)$_4Cl_6$] (**1**) (2.00 g, 1.80 mmol) in benzene (20 ml) was added pyridine

(1.0 ml, 12.3 mmol) with stirring. To this stirred reaction mixture was added Bu^n_3SnH (2.0 ml, 7.4 mmol) dropwise over 10 min. The initial orange solution darkened and gas (H_2) was evolved. After complete addition the mixture was allowed to stand for 24 h before the solvent was removed under vacuum to yield a dark tar. Dissolving the crude material in benzene and layering with pentane yielded a few red crystals of adduct $[Nb(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3(py)]$ (NMR) with the majority being dark orange crystals of **18**. *Anal.* Calc. for $NbO_2Cl_2N_2C_{34}H_{44}$: C, 60.36; H, 6.55; Cl, 10.48; N, 4.14. Found C, 60.46; H, 6.44; Cl, 9.99; N, 4.92%.

3.2.7. $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Br_2(PMe_2Ph)_2]$ (**19**)

An orange suspension of $[Ta(OC_6H_3\text{-}2,6\text{-}Pr^i_2)_2Br_3$ (1.0 g, 1.38 mmol) in benzene (25 ml), was added to an Na/Hg amalgam (0.03 g, 1.38 mmol) upon which the solution turned dark red. Upon addition of PMe_2Ph (0.587 ml, 4.12 mmol) via syringe the solution turned dark green. The reaction mixture was stirred overnight, filtered to remove sodium salts and dried in vacuo to give the crude product as a green solid (0.48 g, 32%). Recrystallization from hot benzene afforded a green crystalline sample that was washed with pentane and dried in vacuo. *Anal.* Calc. for $C_{40}H_{56}Br_2O_2P_2Ta$: C, 49.44; H, 5.81. Found: C, 48.94; H, 5.71%.

3.2.8. $[Ta(OC_6H_2Pr^i_2\text{-}2,6\text{-}Br\text{-}4)_2Cl_2(PMe_2Ph)_2]$ (**20**)

An orange suspension of $[Ta(OC_6H_2Pr^i_2\text{-}2,6\text{-}Br\text{-}4)_2Cl_3$ (1.0 g, 1.33 mmol) in benzene (25 ml), was added to an Na/Hg amalgam (0.03 g, 1.33 mmol) upon which the solution turned dark red. Upon addition of PMe_2Ph (0.568 ml, 3.99 mmol) via syringe the solution turned dark green. The reaction mixture was stirred overnight, filtered to remove sodium salts and dried in vacuo to give the crude product as a green solid (0.59 g, 43%). Recrystallization from an ambient benzene solution layered with pentane was found to lead to crystals of **20** containing no solvent of crystallization. However, recrystallization from hot benzene afforded large green crystals of the benzene solvate. *Anal.* Calc. for **20**·C_6H_6, $C_{46}H_{62}Cl_2Br_2O_2P_2Ta$: C, 49.39; H, 5.59. Found: C, 49.33; H, 5.35%.

3.2.9. $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(H)_2Br(PMe_2Ph)_2]$ (**21**)

To a solution of $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Br_3]$ (**3**) (0.51 g, 0.66 mmol) in benzene (5 ml) was added PMe_2Ph (0.27 ml, 1.91 mmol) and Bu^n_3SnH (0.52 ml, 1.91 mmol) with stirring. The mixture was then diluted with hexane (15 ml) and allowed to stand. Almost colorless crystals of product were formed over 24 h. Yield 0.19 g (34%). *Anal.* Calc. for $TaO_2BrP_2C_{40}H_{58}$: C, 53.76; H, 6.54; Br, 8.94; P, 6.93. Found C, 53.46; H, 6.74; Br, 9.18; P, 6.62%. ^1H NMR (C_6D_6, 30°C): δ 15.92 (m, 2H, Ta*H*); 6.9–7.5 (m, 6H, aromatics), 4.25 (septet, 2H, C*H*Me_2), 3.78 (septet, 2H, C*H*Me_2), 0.8–1.8 (series of overlapping doublets, CH*Me*$_2$ and P*Me*$_2$). Analysis of one crystal obtained from this procedure by X-ray crystallography showed a disordered mixture of 7% **19** and 93% **21**.

3.2.10. $[Ta(OC_6H_2Pr^i_2\text{-}2,6\text{-}Br\text{-}4)_2(H)_2Cl(PMe_2Ph)_2]$ (**22**)

To a suspension of $[Ta(OC_6H_2Pr^i_2\text{-}2,6\text{-}Br\text{-}4)_2Cl_3]$ (5.0 g, 6.2 mmol) in benzene (25 ml) was added PMe_2Ph (3.11g, 23 mmol) giving a yellow solution. To this was added Bu^n_3SnH (10.92 g, 36.8 mmol) resulting in a brown solution, which was stirred overnight. Addition of hexane led to a pale precipitate which was dried in vacuo, washed three times with hexane and re-dried to yield 4.3 g (46%) of a yellow solid which is a mixture of **20** and **22**. ^1H NMR (C_6D_6, 30°C): δ 16.45 (m, 2H, Ta*H*); 6.85–7.3 (m, 14H, aromatics); 4.00 (m, 2H, C*H*Me_2); 3.89 (m, 2H, C*H*Me_2); 1.53 (m, 12H, P*Me*$_2$Ph); 1.11 (d, 6H, CH*Me*$_2$); 1.00 (d, 6H, CH*Me*$_2$). ^{31}P NMR (C_6D_6, 30°C): δ −3.0 ppm.

3.2.11. X-ray data collection and reduction

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 ($\lambda = 0.71073$ Å) on a Nonius Kappa CCD. Lorentz and polarization corrections were applied to the data [15]. An empirical absorption correction using SCALEPACK was applied [16]. Intensities of equivalent reflections were averaged. The structure was solved using the structure solution program PATTY in DIRDIF92 [17]. 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 $\Sigma w(|F_o|^2 - |F_c|^2)^2$ 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 [18]. Refinement was performed on a AlphaServer 2100 using SHELX-97 [19]. Crystallographic drawings were done using programs ORTEP [20].

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 144478 (**10**), 144479 (**12**), 144480 (**15**), 144481 (**18**), 144482 (**19**), 144483 (**20**), 144484 (**20**·C_6H_6), and 144485 (mixture of 7% **19** and 93% **21**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-

336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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