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Synthesis and structure of some new mixed amido, aryloxide compounds of Group 4, 5 and 6 metals containing the 2,4-di-tert-butyl-6-phenylphenoxide ligand

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Abstract

The reaction of 2,4-di-tert-butyl-6-phenylphenol with dimethylamido compounds of the metals Ti, Nb and W has been investigated. The three new mixed amido, aryloxide complexes [Ti(OC$_6$H$_2$-2,4-Bu$^t_2$-6-Ph)$_2$(NMe$_2$)$_2$] (**1**), [Nb(OC$_6$H$_2$-2,4-Bu$^t_2$-6-Ph)$_2$(NMe$_2$)$_3$] (**2**) and [W$_2$(OC$_6$H$_2$-2,4-Bu$^t_2$-6-Ph)$_2$(NMe$_2$)$_4$] (**3**) have been isolated and structurally characterized. Extended heating of these compounds does not lead to cyclometallation of either the aryl or tert-butyl group of the aryloxide ligand. Crystallographic parameters are as follows. [Ti(OC$_6$H$_2$-2,4-Bu$^t_2$-6-Ph)$_2$(NMe$_2$)$_2$] (**1**): space group $P2_1/c$ (No. 14), $a=11.868(2)$, $b=24.340(5)$, $c=14.328(2)$ Å, $\beta=96.65(1)°$, $V=4111(2)$ Å^3 and $Z=4$ (20 °C). [Nb(OC$_6$H$_2$-2,4-Bu$^t_2$-6-Ph)$_2$(NMe$_2$)$_3$] (**2**): space group $P2_1/c$ (No. 14), $a=20.172(1)$, $b=12.094(2)$, $c=18.620(2)$ Å, $\beta=105.413(7)°$, $V=4379(2)$ Å^3 and $Z=4$ (20 °C). [W$_2$(OC$_6$H$_2$-2,4-Bu$^t_2$-6-Ph)$_2$(NMe$_2$)$_4$] (**3**): space group $P2_1/c$ (No. 14), $a=11.751(3)$, $b=29.29(1)$, $c=15.220(5)$ Å, $\beta=100.24(3)°$, $V=4915(5)$ Å^3 and $Z=4$ (20 °C).

Introduction

One of the important characteristics of sterically crowded aryloxide ligands is their ability to undergo intramolecular carbon–hydrogen bond activation at a range of metal centers [1]. The cyclometallation of 2,6-di-tert-butyl- and 2,6-di-phenylphenoxide at high valent, early d-block and metal centers has been extensively studied [1]. This reactivity typically involves the use of alkyl leaving groups attached to the metal center, although CH bond activation by functional groups such as metal–alkylidene [2] and metal–imido linkages has been demonstrated [3]. More recently the cyclometallation of aryl substituted alkoxide and aryloxide ligands at Sn(IV) metal centers has been shown to be facile in the presence of di-alkylamido leaving groups [4]. The use of alkyl leaving groups for metallation was found to be ineffective with this particular p-block metal. The metallation of 2,6-di-phenylphenoxide has also been achieved using the molybdenum compound [Mo(NMe$_2$)$_4$] [1d]. However, in this case the formal d^2-configuration for the Mo(IV) metal center makes available possible oxidative-addition/reductive-elimination pathways for CH bond activation.

In this paper we report the synthesis and study of a series of new mixed amido, aryloxide compounds of the metals Ti, Nb and W. The aryloxide chosen for study was that derived from 2,4-tert-butyl-6-phenylphenol. This ligand offers the possibility of intramolecular activation of either aliphatic or aromatic CH bonds to generate six-membered metallacyles.

Experimental

Synthesis

All the manipulations 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 nitrogen. ^{1}H NMR spectra were obtained on a Varian Associates Gemini 200 and a General Electric QE-300 spectrometer. Microanalyses were obtained 'in-home' at Purdue University. 2,4-Di-tert-butyl-6-phenylphenol was prepared by a published method [5].

Preparation of [Ti(OC$_6$H$_2$-2,4-Bu$^t_2$-6-Ph)$_2$(NMe$_2$)$_2$] (1)

A solution of Ti(MNe$_2$)$_4$ (0.5 g, 2.2 mmol), which was synthesized by literature methods [6], in benzene (10 ml) was slowly added to 2,4-di-tert-butyl-6-phenyl-

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phenol (1.25 g, 4.4 mmol). The resulting yellow–brown solution was stirred for 24 h at room temperature before the solvent was removed *in vacuo*. Extraction of the resulting solid with hexane followed by warming to 115 °C yielded yellow crystals. Yield 80%. *Anal.* Calc. for $TiO_2N_2C_{44}H_{62}$: C, 75.61; H, 8.94; N, 4.00. Found: C, 75.24; H, 9.88; N, 3.80%. ^1H NMR (C_6D_6, 30 °C): δ 1.32 and 1.63 (s, Bu^t of phenoxide), 2.7 (s, $-NMe_2$); 7–7.6 (m, other aromatics).

Preparation of [Nb(OC_6H_2-2,4-Bu^t_2-6-Ph)$_2$(NMe_2)$_3$] (2)

A solution of $Nb(NMe_2)_5$ (0.31 g, 1 mmol), which was synthesized by literature methods [7], in benzene (20 ml) was slowly added to 2,4-di-tert-butyl-6-phenylphenol (0.56 g, 2 mmol). The resulting orange–brown solution was stirred for 48 h at room temperature before the solvent was removed. The crude product was purified by recrystallization from hexane as red crystals. Yield 80%. ^1H NMR (C_6D_6, 30 °C): δ 1.29 and 1.7 (s, Bu^t of phenoxide); 2.77 (s, $-NMe_2$); 7–7.7 (m, other aromatics).

Preparation of [W_2(OC_6H_2-2,4-Bu^t_2-6-Ph)$_2$(NMe_2)$_4$] (3)

A solution of $W_2(NMe_2)_6$ (0.15 g, 0.25 mmol), synthesized by literature methods [8], in benzene (20 ml) was slowly added to 2,4-di-tert-butyl-6-phenylphenol (0.14 g, 0.5 mmol). The resulting yellow–brown solution was stirred for 24 h at ambient temperature. The solvent was removed to give a yellow–green solid. Recrystallization from hexane at room temperature yielded the product as yellow crystals. Yield 70%. ^1H NMR (C_6D_6, 30 °C); δ 1.42 and 1.80 (s, Bu^t of phenoxide), 2.20, 2.29, 3.40, 3.45, 3.92, 3.95 (s, N*Me*); 7.8 (m, other aromatics).

X-ray structural determinations

The three X-ray diffraction studies were completed 'in house' at Purdue University. The crystals were examined under deoxygenated Nujol and mounted in an appropriate size glass capillary surrounded by epoxy resin. They were aligned and indexed and data were collected on an Enraf-Nonius CAD-4 diffractometer. A summary of the crystal and collection data for compounds **1**, **2** and **3** is given in Table 1.

The structures were solved using the Patterson heavy-atom method and subsequent difference Fourier maps. Hydrogen atoms were calculated by assuming idealized geometry and a C–H bond distance of 0.95 Å. For the methyl groups, one hydrogen was found from the difference Fourier map and its position was idealized by assuming it was in the plane defined by R–C–H, made a 109.5° bond angle and had a bond length of 0.95 Å. The positions of the two remaining hydrogens were calculated but their positions were not refined. The final position and equivalent isotropic thermal parameters of all non-hydrogen atoms are given in Tables 2, 3 and 4.

Results and discussion

The reaction of protic reagents with early transition metal di-alkylamido compounds has been shown to be an excellent route for the synthesis of a variety of alkoxide, siloxide and related derivatives of these metals [10]. Recently the ammonolysis of di-alkylamido compounds was shown to be a method for the production of metal nitride thin films [11]. We have investigated the reaction of 2,4-di-tert-butyl-6-phenylphenol with the homoleptic dimethylamido compounds [$Ti(NMe_2)_4$] [6], [$Nb(NMe_2)_5$] [7] and [$W_2(NMe_2)_6$] [8]. In each case substitution of only two amido ligands was found possible (Scheme 1). The three products of each of these reactions are discussed individually below.

[Ti(OC_6H_2-2,4-Bu^t_2-6-Ph)$_2$(NMe_2)$_2$] (1)

The interaction of $Ti(NMe_2)_4$ with 2,4-di-tert-butyl-6-phenylphenol in hydrocarbon solvents resulted in rapid elimination of dimethylamine and gave high yields of the mixed bis(aryloxide) derivative [Ti(OC_6H_2-2,4-Bu^t_2-6-Ph)$_2$(NMe_2)$_2$] (**1**). All attempts to induce further substitution failed. This observation is consistent with the result obtained by the reaction of 2,6-di-tert-butylphenol or 2,4,6-tri-tert-butylphenol with $Ti(NMe_2)_4$ [12, 13]. The ^1H NMR spectrum of **1** shows a singlet at δ 2.70 ppm corresponding to equivalent dimethylamido groups and one set of aryloxide ligand resonances. An ORTEP diagram of **1** is shown in Fig. 1, while selected bond distances and angles are collected in Table 5. The solid-state structure of **1** shows the geometry around the titanium to be a distorted tetrahedron, with the N(30)–Ti–N(40) angle of 103.8(3)° being slightly smaller than the O(10)–Ti–O(20) angle of 118.5(2)°. The Ti–O distances of 1.862(5) and 1.844(6) Å are shorter than the values expected only on the basis of purely σ-bonding, indicating significant oxygen-p to metal-d π-bonding, a characteristic of high valent early transition metal–aryloxide compounds that has been discussed extensively. The Ti–O–Ar angles of

$$Ti(NMe_2)_4 + 2HOAr \longrightarrow \underset{\mathbf{1}}{Ti(OAr)_2(NMe_2)_2} + 2HNMe_2$$

$$Nb(NMe_2)_5 + 2HOAr \longrightarrow \underset{\mathbf{2}}{Nb(OAr)_2(NMe_2)_3} + 2HNMe_2$$

$$W_2(NMe_2)_6 + 2HOAr \longrightarrow \underset{\mathbf{3}}{W_2(OAr)_2(NMe_2)_4} + 2HNMe_2$$

HOAr: 2,4-di-tert-butyl-6-phenylphenol

Scheme 1.

TABLE 1. Crystal data and data collection parameters

Formula	$TiO_2N_2C_{44}H_{62}$	$NbO_2N_3C_{46}H_{68}$	$W_2O_2N_4C_{48}H_{74}$
Formula weight	698.90	787.98	1106.85
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	11.868(2)	20.172(1)	11.751(3)
b (Å)	24.340(5)	12.094(2)	29.29(1)
c (Å)	14.328(2)	18.620(2)	15.220(5)
β (Å^3)	96.65(1)	105.413(7)	100.24(3)
V (Å^3)	4111(2)	4379(2)	4915(5)
Z	4	4	4
D_{calc} (g cm^{-3})	1.129	1.195	1.495
Crystal dimensions (mm)	0.52×0.25×0.20	0.43×0.32×0.30	0.22×0.15×0.13
Temperature (°C)	20.	20.	20.
Radiation (wavelength)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
Monochromator	graphite	graphite	graphite
Linear absorption coefficient (cm^{-1})	2.39	2.98	48.15
Absorption correction applied	none	empirical[a]	empirical[a]
Transmission factors: min., max.		0.68, 1.00	0.59, 1.00
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Scan method	ω–2θ	ω–2θ	ω
h, k, l Limits	−12 to 12, 0 to 26, 0 to 15	0 to 21, −13 to 0, −20 to 19	−12 to 11, 0 to 31, 0 to 16
2θ Range (°)	4.00−45.00	4.00−45.00	4.00−45.00
Scan width (°)	0.46+0.35 tan(θ)	0.55+0.35 tan (θ)	0.78+0.35 tan(θ)
Take-off angle (°)	3.15	3.15	2.95
Programs used	Enraf-Nonius SDP	Enraf-Nonius SDP	Enraf-Nonius SDP
F(000)	1512.0	1688.0	2216.0
p Factor used in weighting	0.040	0.040	0.040
Data collected	5584	6029	6534
Unique data	5584	6029	6534
Data with $I > 3.0\sigma(I)$	1953	4202	2115
No. variables	317	469	265
Largest shift/e.s.d. in final cycle	0.00	0.31	0.12
R	0.064	0.035	0.059
R_w	0.076	0.044	0.062
Goodness of fit	1.542	1.200	1.112

[a] Ref. 9.

143.0(5) and 153.6(5)° are well within those usually observed for d^0 metal aryloxide compounds [14].

The Ti–N(amido) distances of 1.854(7) and 1.886(7) Å are similar to those reported by Jones *et al.* for the compound $[Ti(OC_6H_2Bu^t_3\text{-}2,4,6)_2(NMe_2)_2]$ [13] and by us for $[Ti(OC_6H_3Bu^t_2\text{-}2,6)_2(NMe_2)_2]$ [12].

$[Nb(OC_6H_2\text{-}2,4\text{-}Bu^t_2\text{-}6\text{-}Ph)_2(NMe_2)_3]$ (*2*)

Addition of 2,4-di-tert-butyl-6-phenylphenol to the penta(dimethylamido) compound $[Nb(NMe_2)_5]$ afforded the mixed bis(phenoxide), tris(dimethylamido) complex $[Nb(OC_6H_2\text{-}2,4\text{-}Bu^t_2\text{-}6\text{-}Ph)_2(NMe_2)_3]$ (*2*). This reactivity contrasts to the corresponding reaction with 2,6-diphenylphenol which leads to the imido complex $[Nb(NMe)(HNMe_2)(OC_6H_3Ph_2\text{-}2,6)_3]$ [3]. An ORTEP view of the solid state structure of **2** is shown in Fig. 2 while Table 6 contains selected bond distances and angles.

The geometry about the niobium atom in **2** does not fit any idealized geometry but can be described as a severely distorted trigonal bipyramid with mutually *trans* axial dimethylamido ligands, N(30)–Nb–N(40) = 169.1(1)°. The distortion from idealized geometry involves the opening up of the angle between the two formally equatorial aryloxide groups to 144.9(1)°. The opening up of this angle presumably is a reflection of the non-trivial steric nature of these ligands. The extent of this distortion is such that the molecule is beginning to approach a square-pyramidal geometry. It is interesting to note that both the bulky *ortho*-tert-butyl substituents occupy the space opposite the unique dimethylamido group (Fig. 2).

The conformation of the three NMe_2 groups in **2** is of interest. The orientation of the NC_2 'propellers' in early d-block metal di-alkylamido ligands typically attracts attention as they can give considerable information concerning the localized bonding about the metal center. The π-bonding of three NMe_2 groups arranged in a T-shape about a d-block metal center with a d^0-configuration will be maximized with all three NC_2 propellers oriented mutually perpendicular. This would

TABLE 2. Atomic coordinates and equivalent isotropic displacement coefficients for $[\mathrm{Ti(OC_6H_2\text{-}2,4\text{-}Bu^t_2\text{-}6\text{-}Ph)_2(NMe_2)_2}]$ (**1**)

Atom	x	y	z	B (A^2)
Ti	0.0852(1)	0.18277(8)	0.1080(1)	3.14(4)
O(10)	−0.0347(5)	0.1463(3)	0.0389(4)	3.5(2)
O(20)	0.1705(5)	0.1452(3)	0.2031(4)	3.2(2)
N(30)	0.1756(6)	0.2133(3)	0.0244(6)	3.8(2)
N(40)	0.0212(6)	0.2443(3)	0.1623(6)	3.6(2)
C(11)	−0.0751(7)	0.1299(4)	−0.0498(7)	2.9(2)*
C(12)	−0.0087(7)	0.0972(4)	−0.1009(7)	2.9(2)*
C(13)	−0.0484(7)	0.0803(4)	−0.1926(7)	3.3(2)*
C(14)	−0.1571(7)	0.0932(4)	−0.2330(7)	3.3(2)*
C(15)	−0.2227(7)	0.1244(4)	−0.1781(7)	3.1(2)*
C(16)	−0.1879(7)	0.1435(4)	−0.0880(7)	3.2(2)*
C(21)	0.2019(7)	0.1321(4)	0.2942(7)	2.7(2)*
C(22)	0.1245(7)	0.1099(4)	0.3523(7)	3.0(2)*
C(23)	0.1582(7)	0.0958(4)	0.4439(7)	3.0(2)*
C(24)	0.2697(7)	0.1020(4)	0.4858(7)	2.9(2)*
C(25)	0.3435(7)	0.1228(4)	0.4275(7)	3.2(2)*
C(26)	0.3175(7)	0.1392(4)	0.3351(7)	2.7(2)*
C(31)	0.295(1)	0.2132(5)	0.0097(9)	5.8(3)*
C(32)	0.1114(9)	0.2421(5)	−0.0536(9)	5.7(3)
C(41)	0.050(1)	0.3020(4)	0.153(1)	7.5(4)
C(42)	−0.0695(9)	0.2358(4)	0.2179(8)	5.0(3)
C(121)	0.1074(7)	0.0786(4)	−0.0628(7)	3.2(2)*
C(122)	0.1996(8)	0.0902(4)	−0.1103(8)	3.9(2)*
C(123)	0.3062(9)	0.0676(5)	−0.0803(8)	5.1(3)*
C(124)	0.3177(9)	0.0333(5)	−0.0024(9)	5.7(3)*
C(125)	0.2279(9)	0.0205(5)	0.0463(8)	5.2(3)*
C(126)	0.1211(8)	0.0446(4)	0.0148(8)	4.0(2)*
C(141)	−0.2087(8)	0.0718(4)	−0.3273(7)	3.9(3)
C(142)	−0.2867(9)	0.0231(5)	−0.3128(9)	6.0(3)
C(143)	−0.1165(9)	0.0502(4)	−0.3859(7)	4.7(3)
C(144)	−0.274(1)	0.1159(5)	−0.3868(9)	6.4(3)
C(161)	−0.2683(8)	0.1776(4)	−0.0371(7)	4.0(2)
C(162)	−0.2200(9)	0.2375(4)	−0.0218(9)	5.2(3)
C(163)	−0.2855(9)	0.1525(5)	0.0577(8)	5.3(3)
C(164)	−0.3877(8)	0.1832(5)	−0.0918(9)	6.4(3)
C(221)	0.0028(7)	0.0996(4)	0.3150(7)	2.8(2)*
C(222)	−0.0818(8)	0.1173(4)	0.3681(7)	4.1(2)*
C(223)	−0.1950(9)	0.1032(5)	0.3387(8)	5.1(3)*
C(224)	−0.2210(8)	0.0743(4)	0.2597(8)	4.7(3)*
C(225)	−0.1392(8)	0.0559(4)	0.2047(8)	3.9(2)*
C(226)	−0.0257(8)	0.0696(4)	0.2336(8)	3.8(2)*
C(241)	0.3094(8)	0.0830(4)	0.5862(7)	3.5(3)
C(242)	0.3951(9)	0.0360(5)	0.5823(9)	5.8(3)
C(243)	0.367(1)	0.1311(5)	0.6423(9)	5.8(3)
C(244)	0.2117(9)	0.0614(5)	0.6357(8)	5.0(3)
C(261)	0.4089(7)	0.1605(4)	0.2782(8)	3.9(3)
C(262)	0.5254(9)	0.1625(5)	0.3367(9)	6.5(4)
C(263)	0.4203(9)	0.1227(5)	0.1958(8)	5.6(3)
C(264)	0.3807(9)	0.2209(4)	0.2480(9)	5.2(3)

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2\beta(1,1)+b^2\beta(2,2)+c^2\beta(3,3)+ab(\cos\ \gamma)\beta(1,2)+ac(\cos\ \beta)\beta(1,3)+bc(\cos\ \alpha)\beta(2,3)]$.

TABLE 3. Atomic coordinates and equivalent isotropic displacement coefficients for $[\mathrm{Nb(OC_6H_2\text{-}2,4\text{-}Bu^t_2\text{-}6\text{-}Ph)_2(NMe_2)_3}]$ (**2**)

Atom	x	y	z	B (A^2)
Nb	0.25450(2)	0.06847(3)	0.00893(2)	2.716(6)
O10	0.3025(1)	0.0126(2)	−0.0600(1)	3.52(5)
O20	0.1866(1)	0.0354(2)	0.0613(1)	3.02(5)
N30	0.1755(2)	0.1155(3)	−0.0784(2)	3.94(7)
N40	0.3261(2)	−0.0080(3)	0.0919(2)	3.96(7)
N50	0.2877(2)	0.2174(3)	0.0362(2)	4.21(7)
C11	0.3350(2)	−0.0140(3)	−0.1132(2)	3.08(8)
C12	0.3816(2)	0.0616(3)	−0.1289(2)	3.15(8)
C13	0.4124(2)	0.0398(3)	−0.1857(2)	3.56(8)
C14	0.3990(2)	−0.0557(3)	−0.2279(2)	3.27(8)
C15	0.3541(2)	−0.1307(3)	−0.2091(2)	3.56(8)
C16	0.3216(2)	−0.1145(3)	−0.1528(2)	3.42(8)
C21	0.1479(2)	0.0195(3)	0.1098(2)	2.85(7)
C22	0.1387(2)	0.1075(3)	0.1544(2)	3.07(8)
C23	0.1059(2)	0.0900(3)	0.2102(2)	3.61(8)
C24	0.0814(2)	−0.0127(3)	0.2235(2)	3.42(8)
C25	0.0868(2)	−0.0968(3)	0.1747(2)	3.36(8)
C26	0.1185(2)	−0.0842(3)	0.1170(2)	2.99(7)
C31	0.1048(2)	0.1383(5)	−0.0775(3)	5.9(1)
C32	0.1835(3)	0.1410(5)	−0.1519(2)	6.4(1)
C41	0.3927(2)	−0.0492(5)	0.0878(3)	6.2(1)
C42	0.3213(2)	−0.0224(5)	0.1678(2)	6.2(1)
C51	0.3488(3)	0.2442(5)	0.0966(3)	6.4(1)
C52	0.2566(3)	0.3189(4)	−0.0010(3)	6.4(1)
C121	0.4027(2)	0.1667(4)	−0.0873(2)	4.97(9)
C122	0.3750(3)	0.2648(5)	−0.1157(3)	8.4(2)
C123	0.4006(4)	0.3647(6)	−0.0818(4)	15.2(2)
C124	0.4514(4)	0.3632(6)	−0.0218(4)	17.2(2)
C125	0.4834(3)	0.2660(7)	0.0112(4)	13.9(2)
C126	0.4574(3)	0.1660(6)	−0.0233(3)	8.9(2)
C141	0.4312(2)	−0.0822(3)	−0.2916(2)	3.78(8)
C142	0.3748(3)	−0.1026(5)	−0.3637(2)	5.8(1)
C143	0.4763(2)	−0.1847(4)	−0.2719(3)	5.7(1)
C144	0.4760(2)	0.0128(4)	−0.3062(2)	4.9(1)
C161	0.2743(2)	−0.2043(4)	−0.1362(2)	4.42(9)
C162	0.3002(3)	−0.2419(4)	−0.0551(3)	6.2(1)
C163	0.2732(3)	−0.3086(4)	−0.1836(3)	7.1(1)
C164	0.2005(2)	−0.1611(5)	−0.1524(3)	6.5(1)
C221	0.1591(2)	0.2241(3)	0.1446(2)	3.56(8)
C222	0.1142(2)	0.2929(4)	0.0970(3)	5.2(1)
C223	0.1279(3)	0.4058(4)	0.0950(3)	6.9(1)
C224	0.1863(3)	0.4482(4)	0.1403(3)	6.7(1)
C225	0.2321(3)	0.3817(4)	0.1866(3)	6.4(1)
C226	0.2188(2)	0.2681(4)	0.1892(2)	5.0(1)
C241	0.0482(2)	−0.0279(3)	0.2879(2)	4.34(9)
C242	0.0217(2)	−0.1453(4)	0.2918(2)	5.1(1)
C243	0.1022(3)	−0.0054(6)	0.3620(2)	7.6(2)
C244	−0.0117(3)	0.0524(4)	0.2787(3)	7.8(1)
C261	0.1186(2)	−0.1808(3)	0.0633(2)	3.68(8)
C262	0.1920(2)	−0.2241(4)	0.0731(3)	5.4(1)
C263	0.0869(3)	−0.1434(4)	−0.0172(2)	5.5(1)
C264	0.0755(2)	−0.2784(4)	0.0771(2)	5.3(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2\beta(1,1)+b^2\beta(2,2)+c^2\beta(3,3)+ab(\cos\ \gamma)\beta(1,2)+ac(\cos\ \beta)\beta(1,3)+bc(\cos\ \alpha)\beta(2,3)]$.

allow each nitrogen atom to π-donate into individual, empty d-orbitals. However, in compound **2** the two mutually *trans* $\mathrm{NMe_2}$ groups are oriented co-planar with each other. The resulting π-competition results in Nb–N(30) and Nb–N(40) distances of 2.032(3) and 2.036(3) Å, being significantly larger than the distance of 1.94(3) Å to N(50).The co-planarity of these groups is probably due to a compromise given the presence of the aryloxide ligands which are themselves able to π-donate to the metal through oxygen p-orbital of the correct symmetry.

TABLE 4. Atomic coordinates and equivalent isotropic displacement coefficients for $[W_2(OC_6H_2\text{-}2,4\text{-}Bu^t_2\text{-}6\text{-}Ph)_2(NMe_2)_4]$ (3)

Atom	x	y	z	B (A^2)
W(1)	0.0677(1)	0.15835(4)	0.34801(9)	3.22(3)
W(2)	0.1255(1)	0.16677(4)	0.21786(9)	3.52(3)
O(1)	0.073(2)	0.0970(6)	0.389(1)	3.2(5)
O(2)	0.269(1)	0.1268(6)	0.243(1)	2.9(5)
N(10)	−0.087(2)	0.1884(9)	0.305(2)	4.9(8)
N(11)	0.183(2)	0.1951(7)	0.439(2)	3.0(6)
N(20)	−0.008(2)	0.1454(8)	0.116(2)	4.1(7)
N(21)	0.140(2)	0.2311(7)	0.214(2)	4.5(7)
C(11)	0.089(3)	0.051(1)	0.388(2)	3.6(7)*
C(12)	0.199(3)	0.031(1)	0.440(2)	4.0(8)*
C(13)	0.220(2)	−0.0160(9)	0.431(2)	3.3(7)*
C(14)	0.134(3)	−0.044(1)	0.369(2)	4.7(8)*
C(15)	0.024(2)	−0.0254(9)	0.326(2)	3.3(7)*
C(16)	−0.004(3)	0.022(1)	0.330(2)	5.3(9)*
C(21)	0.313(3)	0.123(1)	0.167(2)	3.9(7)*
C(22)	0.284(3)	0.086(1)	0.109(2)	3.6(7)*
C(23)	0.318(3)	0.086(1)	0.030(2)	4.1(8)*
C(24)	0.371(3)	0.124(1)	0.006(2)	3.9(7)*
C(25)	0.414(3)	0.158(1)	0.067(2)	4.5(7)*
C(26)	0.0386(3)	0.159(1)	0.154(2)	5.6(9)*
C(101)	−0.158(3)	0.216(1)	0.229(3)	6(1)*
C(102)	−0.147(3)	0.189(1)	0.376(3)	6(1)*
C(111)	0.166(3)	0.203(1)	0.532(3)	7(1)*
C(112)	0.302(3)	0.216(1)	0.444(2)	6(1)*
C(121)	0.299(3)	0.056(1)	0.515(2)	5.0(9)*
C(122)	0.401(3)	0.027(1)	0.587(2)	5.4(9)*
C(123)	0.363(3)	0.091(1)	0.474(2)	4.9(9)*
C(124)	0.251(3)	0.082(1)	0.584(3)	7(1)*
C(141)	0.158(3)	−0.096(1)	0.354(2)	5.3(9)
C(142)	0.069(4)	−0.122(1)	0.386(3)	9(1)*
C(143)	0.278(4)	−0.110(2)	0.419(3)	11(2)*
C(144)	0.136(4)	−0.103(2)	0.255(3)	9(1)*
C(161)	−0.134(3)	0.0383(9)	0.285(2)	3.3(7)*
C(162)	−0.197(3)	0.027(1)	0.196(2)	4.8(8)*
C(163)	−0.322(3)	0.041(1)	0.151(3)	6(1)*
C(164)	−0.366(3)	0.067(1)	0.203(2)	4.9(8)*
C(165)	−0.304(3)	0.081(1)	0.289(3)	6.1*
C(166)	−0.181(3)	0.066(1)	0.336(2)	4.7(8)*
C(201)	−0.004(3)	0.151(1)	0.020(3)	7(1)*
C(202)	−0.131(3)	0.127(1)	0.102(2)	5.3(9)*
C(211)	0.117(3)	0.273(1)	0.263(2)	4.7(8)*
C(212)	0.165(3)	0.251(1)	0.131(3)	6(1)*
C(221)	0.234(3)	0.040(1)	0.133(2)	3.9(7)*
C(222)	0.318(3)	0.027(1)	0.229(3)	7(1)*
C(223)	0.243(3)	−0.002(1)	0.072(3)	7(1)*
C(224)	0.109(3)	0.041(1)	0.142(3)	7(1)*
C(241)	0.399(3)	0.124(1)	−0.090(2)	5.6(9)*
C(242)	0.466(5)	0.164(2)	−0.098(4)	16(2)*
C(243)	0.279(5)	0.125(2)	−0.164(4)	13(2)*
C(244)	0.460(4)	0.083(2)	−0.101(3)	9(1)*
C(261)	0.448(2)	0.1922(9)	0.227(2)	3.1(7)*
C(262)	0.491(3)	0.180(1)	0.321(2)	4.2(8)*
C(263)	0.561(3)	0.212(1)	0.388(2)	5.3(9)*
C(264)	0.583(3)	0.252(1)	0.365(3)	7(1)*
C(265)	0.533(3)	0.267(1)	0.272(2)	5.5(9)*
C(266)	0.473(3)	0.237(1)	0.202(2)	4.6(8)*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2\beta(1,1)+b^2\beta(2,2)+c^2\beta(3,3)+ab(\cos\gamma)\beta(1,2)+ac(\cos\beta)\beta(1,3)+bc(\cos\alpha)\beta(2,3)]$.

$[W_2(OC_6H_2\text{-}2,4\text{-}Bu^t_2\text{-}6\text{-}Ph)_2(NMe_2)_4]$ (3)

Reaction of the di-tungsten hexa(dimethylamido) compound $[W_2(NMe_2)_6]$ with 2,4-di-tert-butyl-6-phenylphenol in hydrocarbon solvents leads to the di-substituted compound 1,2-$[W_2(OC_6H_2\text{-}2,4\text{-}Bu^t_2\text{-}6\text{-}Ph)_2(NMe_2)_4]$ (**3**). Further substitution of dimethylamido ligands by the bulky phenol failed. This result is consistent with previous work and has shown that the degree of substitution by phenoxide ligands about the M_2^{6+} core in $[M_2(NMe_2)_6]$ substrates is highly dependent on the size of the parent phenol [15]. Complete substitutions of all six dimethylamido ligands occurs with small phenols leading either to confacial bi-octahedral anions such as $[Mo_2(OC_6H_4\text{-}4Me)_7(HNMe_2)_2]^-$ or hexa-aryloxides such as $[Mo_2(OC_6H_3Me_2\text{-}2,6)_6]$ [16]. With bulkier ligands only partial substitution occurs, leading to molecules such as 1,1,2-$[Mo_2(OC_6H_3Ph_2\text{-}2,6)_3(NMe_2)_3]$ [17] and 1,2-$[M_2(OC_6H_3Bu^t\text{-}2\text{-}Me\text{-}6)_2(NMe_2)_4]$ (M = Mo, W) [15a] even under forcing conditions.

Considerable difficulties were encountered in trying to obtain crystals of **3** suitable for X-ray diffraction studies. Eventually a weak data set was collected and refined. Although the errors in both distances and angles are significant, the molecular structure obtained (Fig. 3) is clearly correct. The molecule can be seen to adopt a gauche conformation for the central $W_2O_2N_4$ core (Fig. 4). Both anti and gauche conformations for 1,2$[M_2X_2Y_4]$ (M = Mo, W) molecules have been characterized [18]. In solution both the anti and gauche forms of **3** are present as evidenced from the complexity of the ^{1}H NMR spectrum. At 20 °C, not only are non-equivalent dimethylamido and aryloxide ligand resonances present, but also sets of proximal and distal methyl groups of the N*Me*$_2$ groups are also observed. Hence at room temperature, rotation about the W–NMe$_2$ bond as well as the W≡W bond is slow on the NMR time scale. The W–W, W–O and W–N distances (Table 7) are typical for molecules of this type [19]. However, the W–O(20)–C(21) angle of 114(2)° is unusually small. Typically the M–O–C angle for aryloxide ligands bound to M_2^{6+} (M = Mo, W) varies from 126 to 148°. The small angle observed for the aryloxide ligand bound to O(20) in **3** possibly reflects an attempt to relieve steric congestion about this crowded central part of the molecule.

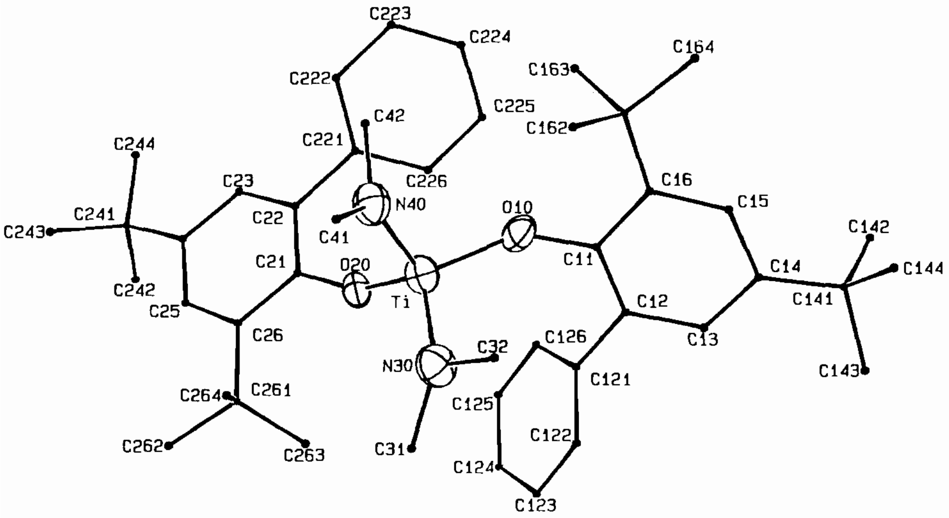

Fig. 1. ORTEP view of [Ti(OC_6H_2-2,4-Bu^t_2-6-Ph)$_2$(NMe_2)$_2$] (**1**) emphasizing the central coordination sphere.

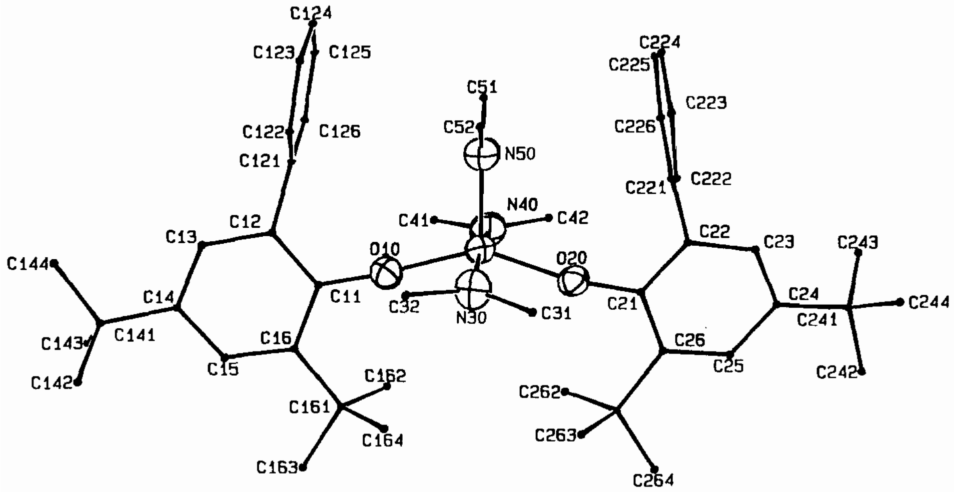

Fig. 2. ORTEP view of [Nb(OC_6H_2-2,4-Bu^t_2-6-Ph)$_2$(NMe_2)$_3$] (**2**) emphasizing the central coordination sphere.

TABLE 5. Selected bond distances (Å) and angles (°) for [Ti(OC_6H_3-2,4-Bu^t_2-6-Ph)$_2$(NMe_2)$_2$] (**1**)

Bond distances			
Ti–O(10)	1.862(5)	Ti–N(30)	1.854(7)
Ti–O(20)	1.844(6)	Ti–N(40)	1.886(7)
O(10)–C(11)	1.365(9)	O(20)–C(21)	1.354(9)
N(30)–C(31)	1.46(1)	N(40)–C(41)	1.46(1)
N(30)–C(32)	1.46(1)	N(40)–C(42)	1.43(1)
Bond angles			
O(10)–Ti–O(20)	118.5(2)	O(20)–Ti–N(40)	107.6(3)
O(10)–Ti–N(30)	108.1(3)	N(30)–Ti–N(40)	103.8(3)
O(10)–Ti–N(40)	106.1(3)	Ti–O(10)–C(11)	143.0(5)
O(20)–Ti–N(30)	111.6(3)	Ti–O(20)–C(21)	153.6(5)

Thermal stability of mixed amido, aryloxide compounds

The three compounds obtained in this study exhibit great thermal stability in hydrocarbon solvents. Heating solutions of **1**, **2** or **3** in C_6D_6 in 5 mm NMR tubes

TABLE 6. Selected bond distances (Å) and angles (°) for [Nb(OC_6H_2-2,4-Bu^t_2-6-Ph)$_2$(NMe_2)$_3$] (**2**)

Bond distances			
Nb–O(10)	1.925(2)	Nb–N(30)	2.032(3)
Nb–O(20)	1.923(2)	Nb–N(40)	2.036(3)
Nb–N(50)	1.941(3)	N(30)–C(31)	1.456(5)
N(40)–C(41)	1.454(5)	N(30)–C(32)	1.454(5)
N(40)–C(42)	1.451(5)	N(50)–C(51)	1.467(6)
O(10)–C(11)	1.363(4)	N(50)–C(52)	1.467(6)
O(20)–C(21)	1.355(4)		
Bond angles			
O(10)–Nb–O(20)	144.9(1)	O(20)–Nb–N(50)	107.6(1)
O(10)–Nb–N(30)	89.5(1)	N(30)–Nb–N(40)	169.1(1)
O(10)–Nb–N(40)	88.0(1)	N(30)–Nb–N(50)	95.3(1)
O(10)–Nb–N(50)	107.5(1)	N(40)–Nb–N(50)	95.6(1)
O(20)–Nb–N(30)	87.2(1)	Nb–O(10)–C(11)	172.6(2)
O(20)–Nb–N(40)	88.7(1)	Nb–O(20)–C(21)	169.0(2)

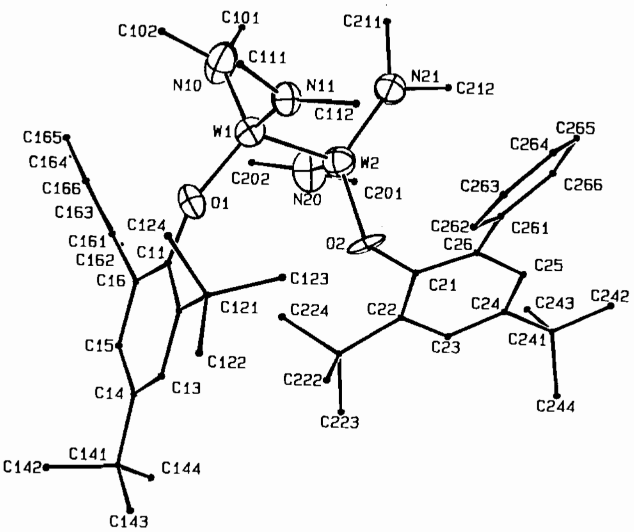

Fig. 3. ORTEP view of $[W_2(OC_6H_2\text{-}2,4\text{-}Bu^t_2\text{-}6\text{-}Ph)_2(NMe_2)_4]$ (**3**) emphasizing the central coordination sphere.

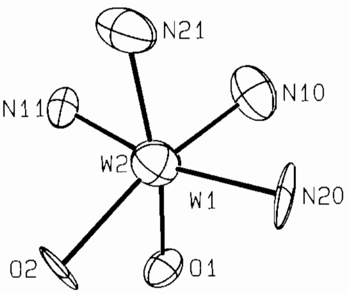

Fig. 4. ORTEP view of the central skeleton of $[W_2(OC_6H_2\text{-}2,4\text{-}Bu^t_2\text{-}6\text{-}Ph)_2(NMe_2)_4]$ (**3**) viewed down the W–W bond.

TABLE 7. Selected bond distances (Å) and angles (°) for $[W_2(OC_6H_2\text{-}2,4\text{-}Bu^t_2\text{-}6\text{-}Ph)_2(NMe_2)_4]$ (**3**)

Bond distances			
W(1)–W(2)	2.319(2)	W(2)–O(2)	1.98(2)
W(1)–O(1)	1.90(2)	W(2)–N(20)	1.89(2)
W(1)–N(10)	1.92(3)	W(2)–N(21)	1.89(2)
W(1)–N(11)	1.90(2)		
Bond angles			
W(2)–W(1)–O(1)	113.3(6)	W(1)–W(2)–N(20)	105.4(8)
W(2)–W(1)–N(10)	100.6(9)	W(1)–W(2)–N(21)	101.0(9)
W(2)–W(1)–N(11)	102.6(7)	O(2)–W(2)–N(20)	112(1)
O(1)–W(1)–N(10)	118(1)	O(2)–W(2)–N(21)	120.9(9)
O(1)–W(1)–N(11)	111.1(9)	N(20)–W(2)–N(21)	111(1)
N(10)–W(1)–N(11)	110(1)	W(1)–O(1)–C(11)	157(2)
W(1)–W(2)–O(2)	104.7(6)	W(2)–O(2)–C(21)	114(2)

showed no evidence for the intramolecular activation of either the aromatic or aliphatic CH bonds of the aryloxide ligand. This reactivity is consistent with that found for related amido derivatives of these metals containing either 2,6-di-tert-butyl- or 2,6-diphenylphenoxide ligation and contrasts markedly with the facile metallation of the aromatic CH bonds of both 2,6-diphenylphenoxide and 2,4-di-tert-butyl-6-phenylphenoxide that can be achieved at Sn(IV) metal centers [4].

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