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Syntheses and structural characterization of 2,2′-methylene-bis(6-*t*-butyl-4-methyl-phenoxide) complexes of titanium, zirconium and tantalum

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Abstract—The reactions of M(NMe$_2$)$_n$ (M = Ti, Zr, $n = 4$; Ta, $n = 5$) with 2,2′-methylene-bis(6-*t*-butyl-4-methylphenol), HO—CH$_2$—OH, in toluene produce Ti(O—CH$_2$—O)$_2$ (**1**), Zr$_2$(η^2-O—CH$_2$—O)$_2$(μ,η^1-O—CH$_2$—O)$_2$ (**2**) and Ta(O—CH$_2$—O)(NMe$_2$)$_3$ (**3**). Compounds **1** and **2** can also be obtained *via* metathesis of MCl$_4$ with Li$_2$(O—CH$_2$—O). Reducing (O—CH$_2$—O)TiCl$_2$ with 2 equiv. of Na/Hg also generates **1** by ligand redistribution. Reaction of Zr(NMe$_2$)$_4$ with 1 equiv. of HO—CH$_2$—OH yields (O—CH$_2$—O)Zr(NMe$_2$)$_2$ (**4**). Metathesis of TaCl$_5$ with 1 equiv. of Li$_2$(O—CH$_2$—O) produces (O—CH$_2$—O)TaCl$_3$ (**5**). (O—CH$_2$—O)Ta(NMe$_2$)$_2$Cl (**6**) is formed from the reaction of **3** with 1 equiv. of trimethylsilylchloride in toluene. The dimethylamide groups of compounds **3** and **4** reveal dynamic behavior on the NMR time-scale. The compounds **1**, **2** and **3** have been characterized by single-crystal X-ray crystallography. © 1997 Elsevier Science Ltd

Keywords: chelating diphenoxides; titanium; zirconium; tantalum.

Alkoxide ligands have been known to stabilize early and middle transition metal elements in high oxidation states for many years [1]. Early examples include Cr(OBu^t)$_4$ [2] and Mo(OMe)$_6$ [3]. Metal alkoxide complexes have also been used in catalysis, such as Ti(OR)$_4$ for intramolecular nucleophilic acyl substitution [4] and Picet–Spengler reactions [5]. Also Rothwell [6], Wolczanski [7] and Wigley [8] have used bulky aryloxides or trialkylsiloxides of the group 4 and 5 transition elements to develop an extensive organometallic chemistry. Typically in the chemistry developed by these groups there have been two attendant ancillary RO$^-$ ligands. Examples of the latter include (i) the use of the [(Ar′O)$_2$Ti] template for catalytic C—C coupling reactions [9], (ii) the (Ar′O)$_2$Nb(CH$_2$R)$_3$ complexes as catalyst precursors for the all-*cis* hydrogenation of aromatic and polyaromatic hydrocarbons [10] and (iii) the most remarkable series of reactions involving [(silox)$_2$Ta(H)$_2$]$_2$ and carbon monoxide [11]. In some ways bulky RO or Ar′O ligands may be viewed as Cp′ analogs being capable of acting as six-electron donors ($\sigma^2+\pi^4$) and having a predetermined steric pressure at a metal center based on their substituents [7]. Given the now extensive chemistry of the bent [Cp′$_2$M] template it is well recognized that the chemistry within "the wedge" can be controlled by both electronic and steric factors. The linking of the two Cp units influences the energetics of the frontier orbitals [12]. Bearing this in mind we are attracted to the development of diolate chemistry of the early transition metals where the O—M—O angle can be constrained. In this paper we report some work with the chelating phenol, 2,2′-methylene-bis(6-*t*-butyl-4-methylphenol), hereafter referred to as HO—CH$_2$—OH, shown in **A** below. This is an abundantly available, inexpensive ligand which finds industrial use as an antioxidant [13]. Clearly the O—M—O angle has to be constrained to be *cis* in derivatives of this chelating phenol and this has been seen in some preliminary studies by Floriani [14] who reported the synthesis and structures of (O—CH$_2$—O)MX$_2$, where X = BH$_4$ and M = Ti and Zr, and Zubieta [15] who reported the synthesis and structure of V(O)Cl(O—CH$_2$—O). The diolate derived from **A** has also been shown to be capable

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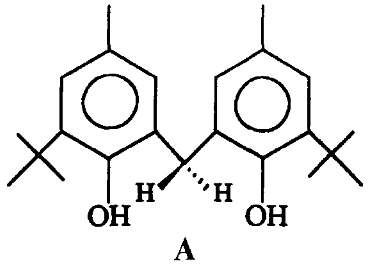


A

of bridging two metal atoms and undergoing C—H oxidative addition to a $(W{\equiv}W)^{6+}$ center [16]. We describe here some syntheses and characterizations of derivatives of **A** with the elements titanium, zirconium and tantalum.

RESULTS AND DISCUSSION

Syntheses

Ti(O—CH$_2$—O)$_2$. Addition of 2 equiv. of HO—CH$_2$—OH to a hydrocarbon solution of Ti(NMe$_2$)$_4$ yields Ti(O—CH$_2$—O)$_2$ (**1**), along with the liberation of HNMe$_2$. Similarly compound **1** is formed in a metathesis reaction involving TiCl$_4$ and 2 equiv. of LiO—CH$_2$—OLi. Attempts to reduce (O—CH$_2$—O)TiCl$_2$ with Na/Hg in THF failed and **1** was again formed and isolated in low yield. Compound **1** can be recrystallized from warm hexanes as a yellow crystalline solid, which is stable to air for short periods.

A compound formulated as (O—CH$_2$—O) Ti(NMe$_2$)$_2$ by NMR spectroscopy can be prepared from the reaction between Ti(NMe$_2$)$_4$ and 1 equiv. of HO—CH$_2$—OH in toluene. The same compound is formed (as evidenced by NMR spectroscopy) upon heating a 1 : 1 mixture of Ti(NMe$_2$)$_4$ and compound **1** in benzene-d_6 at 60°C for 24 h in a J. Young® NMR tube.

The reaction between Zr(NMe$_2$)$_4$ and 2 equiv. of HO—CH$_2$—OH in hydrocarbon solutions yields [Zr(O—CH$_2$—O)$_2$]$_2$ (**2**), which can also be made by a metathesis reaction involving ZrCl$_4$ and LiO—CH$_2$—OLi in toluene upon removal of LiCl. When only 1 equiv. of HO—CH$_2$—OH is allowed to react with Zr(NMe$_2$)$_4$, then the compound Zr(O—CH$_2$—O) (NMe$_2$)$_2$ (**4**), is obtained. Compounds **2** and **4** are white crystalline solids and were purified by crystallization from a toluene solution.

The reaction between Ta(NMe$_2$)$_5$ and HO—CH$_2$—OH in hydrocarbon solvents yielded only partial replacement of NMe$_2$ ligands with the formation of Ta(O—CH$_2$—O)(NMe$_2$)$_3$ (**3**). Treatment of **3** with Me$_3$SiCl in hydrocarbon solvents yielded one NMe$_2$ for Cl group exchange and the formation of Ta(O—CH$_2$—O)(NMe$_2$)$_2$Cl (**6**). The reaction between TaCl$_5$ and LiO—CH$_2$—OLi in toluene yielded Ta(O—CH$_2$—O)Cl$_3$ (**5**). Evidently for tantalum the replacement of Ta—NMe$_2$ or Ta—Cl bonds by reaction with either the diphenol or its lithio salt is more difficult than for related Zr and Ti amide or chloride groups. The compounds **3**, **5** and **6** are white crystalline solids, moderately air-sensitive in the solid-state, but more hydrolytically sensitive in solution.

Solid-state and molecular structures

A summary of the crystal data for the compounds examined in this study is given in Table 1.

Ti(O—CH$_2$—O)$_2$ (**1**). An ORTEP drawing of the structure of **1** is shown in Fig. 1 and selected bond distances and angles are given in Table 2. Although the molecule has a pseudotetrahedral TiO$_4$ core with all the O—Ti—O angles close to 107.9° the presence of the two chelate rings reduces the virtual symmetry to C_2. The tetrahedral sp^3 methylene carbons make each chelate ring roof-shaped. Thus, while all four *t*-butyl groups and all four methyl groups are crystallographically independent, the virtual symmetry of C_2 relates each set, Bu^t and Me, in a pair-wise manner. The Ti—O—C bond angles span the range 135–151°. There is no significant correlation of Ti—O distances with Ti—O—C angles.

[Zr(η^2—O—CH$_2$—O)(μ,η^1,η^1-O—CH$_2$—O)]$_2$·4C$_6$H$_5$Me. Crystals of **2** were obtained from a toluene solution as a solvate though the toluene showed no significant interaction with the Zr atoms. An ORTEP drawing of **2** is shown in Fig. 2 and a listing of selected bond distances and bond angles is given in Table 3.

The two zirconium atoms in **2** are five-coordinate and the dimeric structure contains a crystallographic center of symmetry that resides at the mid-point between the two metal atoms. Each zirconium is bonded solely to one chelating O—CH$_2$—O ligand, while it shares the other chelate in a μ,η^1,η^1 manner. As expected the Zr—μ—O distances are notably longer than the Zr—O terminal ones but are similar in other respects to dimeric zirconium alkoxides. The O—Zr—O angle of the η^2-chelate is 94°, while that of the μ,η^1,η^1 group is 112°, again revealing a relatively small deviation from the tetrahedral angle. An inspection of the angles subtended at Zr reveals that the ZrO$_5$ moiety deviates significantly from both an idealized square-based pyramid and trigonal bipyramidal geometry.

Ta(O—CH$_2$—O)(NMe$_2$)$_3$ (**3**). An ORTEP drawing of **3** is given in Fig. 3 and selected bond distances and bond angles are given in Table 4. This compound has a pseudo trigonal bipyramidal TaO$_2$N$_3$ core wherein the chelating O—CH$_2$—O ligand occupies an axial and equatorial position. The O—Ta—O angle of 85°, less than 90°, is unusual for M(OAr′)$_2$X$_3$ compounds, where Ar′ represents a bulky aryl oxide. This is seen in the structural data presented in Table 3. An inspection of the Ta—O and Ta—N distances for **3** reveals that the axial bonds are slightly longer than those of their equatorial counterparts. Note the sum of the equatorial angles [O(25)—Ta—N(8), N(8)—Ta

Table 1. Summary of crystal data

	1	**2**	**3**
Color of crystal	Yellow	Colorless	Colorless
Space group	$P\bar{1}$	$P\bar{1}$	$P21/n$
Cell dimensions (mm)	0.28 × 0.25 × 0.30	0.08 × 0.36 × 0.56	0.25 × 0.30 × 0.30
Temperature (°C)	−171	−173	−169
a (Å)	13.313(2)	14.111(3)	9.187(2)
b (Å)	16.405(2)	15.236(3)	18.283(3)
c (Å)	11.657(1)	13.583(3)	18.126(3)
α (°)	106.87(1)	103.24(1)	
β (°)	101.09(1)	100.05(1)	98.92(1)
γ (°)	106.28(1)	110.72(1)	
Z (molecules/cells)	2	1	4
Volume (Å^3)	2232.30	2552.05	3007.76
Calculated density (g cm^{-3})	1.143	1.240	1.439
Wavelength (Å)	0.71069	0.71069	0.71069
Molecular weight	767.97	1904.97	651.67
Linear absorption coefficient (cm^{-1})	2.272	2.614	36.771
Detector to sample distance (cm)	22.5	22.5	22.5
Sample to source distance (cm)	23.5	23.5	23.5
Scan speed (min^{-1})	8.0	6.0	8.0
Scan width (° + dispersion)	2.0	2.0	2.1
Individual Background (s)	4	4	4
Two-theta scan	6–45	6–45	6–50
Total number of reflections collected	6076	9604	9220
Number of unique intensities	5843	6686	5322
Number with $F > 0.00$	5405	6347	5056
Number with $F > 3.0\sigma(F)$	4398	5733	4789
$R(F)$	0.0377	0.0564	0.0281
$Rw(F)$	0.0362	0.0561	0.0269
Goodness of fit for last cycle	1.303	1.430	1.199
Maximum γ/σ for last cycle	0.03	0.0012	0.12

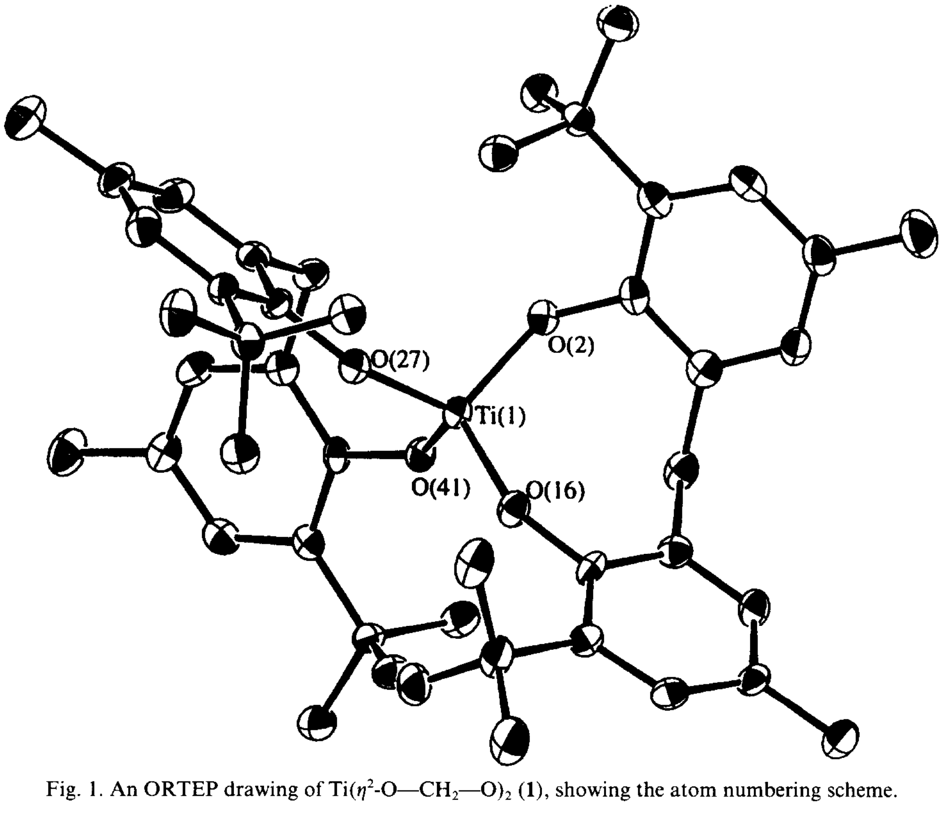


Fig. 1. An ORTEP drawing of Ti(η^2-O—CH$_2$—O)$_2$ (**1**), showing the atom numbering scheme.

Table 2. Selected bond distances (Å) and angles (°) for $(O—CH_2—O)_2Ti \cdot 1/2C_6H_{14}$ (**1**)

Ti(1)—O(2)	1.800(1)
Ti(1)—O(16)	1.797(1)
Ti(1)—O(27)	1.797(2)
Ti(1)—O(41)	1.816(1)
O(2)—Ti(1)—O(16)	106.24(7)
O(2)—Ti(1)—O(27)	111.46(7)
O(2)—Ti(1)—O(41)	108.22(6)
O(16)—Ti(1)—O(27)	111.26(6)
O(16)—Ti(1)—O(41)	112.40(5)
O(27)—Ti(1)—O(41)	107.28(8)
Ti(1)—O(2)—C(3)	140.05(5)
Ti(1)—O(16)—C(15)	151.1(1)
Ti(1)—O(27)—C(28)	148.36(8)
Ti(1)—O(41)—C(40)	134.7(2)

—N(2), N(2)—Ta—O(25)] is very close to 360°. The bulky Bu^t group of the axial phenyl is closer to N(8) than the N(2) making the O(11)—Ta—N(8) angle, 97.7°, notably larger than O(11)—Ta—N(2), which remains close to 90°. It is also worthy of note that the Bu^t group of the equatorial phenyl group influences the relative magnitude of the O—Ta—N and N—Ta—N angles within the equatorial plane, i.e. while O(25)—Ta—N(8) is 120°, N(2)—Ta—N(8) = 108° and O(25)—Ta—N(2) = 132°.

Variable-temperature ^1H *NMR studies*

A characteristic feature of the ^1H NMR spectrum of **1** in toluene-d_8 is the presence of two Bu^t and two Me signals (each of equal intensity) and an AX pattern for the methylene protons. As noted in the description of the solid-state structure the molecule has virtual C_2 symmetry and evidently this is maintained in solution. This clearly rules out any rapid and reversible M—O bond cleavage involving a trigonal intermediate and also the "inversion" through a planar $Ti—O_4$ moiety. It further emphasizes that the eight-membered rings of each chelate do not invert on the NMR time-scale. Similarly in the ^1H NMR spectra of $M(O—CH_2—O)(NMe_2)_2$ compounds, M = Ti, Zr, there are two NMe_2 groups in the integral ratio 1 : 1.

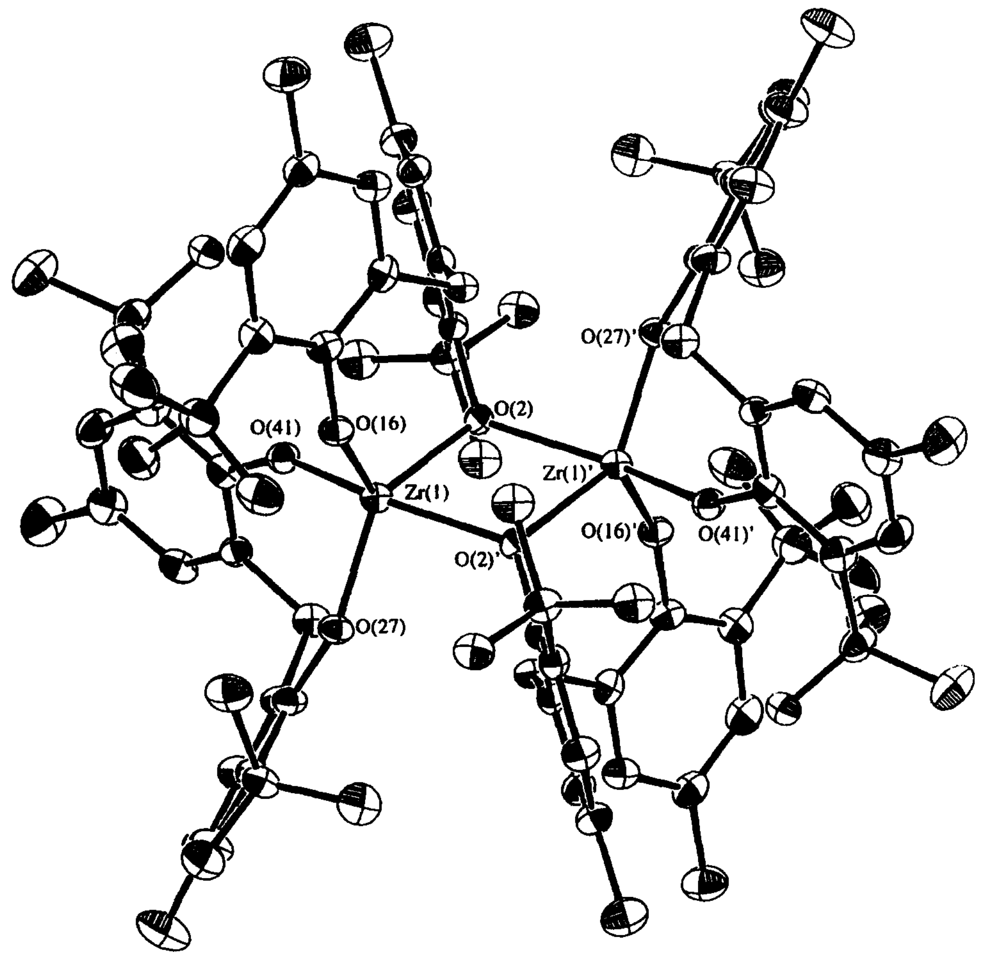


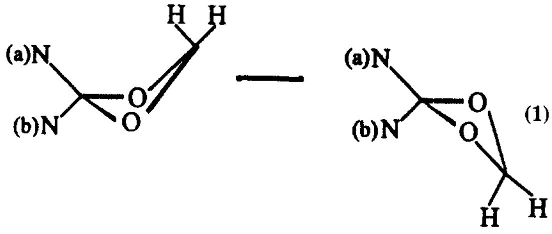
Fig. 2. An ORTEP drawing of $[Zr(\eta^2\text{-}O—CH_2—O)(\mu,\eta^1,\eta^1\text{-}O—CH_2—O)]_2$, showing the atom numbering scheme.

Table 3. Selected bond distances (Å) and angles (°) for $Zr_2(\eta^2$-$O—CH_2—O)$-$(\mu,\eta^1,\eta^1$-$O—CH_2—O)\cdot 4C_6H_5CH_5$ (**2**)

Zr(1)—Zr(1)′	3.649(1)
Zr(1)—O(2)	2.182(3)
Zr(1)—O(2)′	2.251(3)
Zr(1)—O(16)	1.959(3)
Zr(1)—O(27)	1.973(3)
Zr(1)—O(41)	1.944(3)

O(2)—Zr(1)—O(2)′	69.2(1)
O(2)—Zr(1)—O(16)	112.4(1)
O(2)′—Zr(1)—O(16)	99.9(1)
O(2)—Zr(1)—O(27)	135.2(1)
O(2)′—Zr(1)—O(27)	90.5(1)
O(2)—Zr(1)—O(41)	91.4(1)
O(2)′—Zr(1)—O(41)	155.9(1)
O(16)—Zr(1)—O(27)	110.2(1)
O(16)—Zr(1)—O(41)	100.7(1)
O(27)—Zr(1)—O(41)	94.0(1)
Zr(1)—O(2)—Zr(1)′	110.8(1)
Zr(1)′—O(2)—C(3)	125.3(3)
Zr(1)—O(2)—C(3)	114.6(3)
Zr(1)—O(16)—C(15)	149.0(3)
Zr(1)—O(27)—C(28)	149.4(3)
Zr(1)—O(2)—C(40)	145.5(3)

Upon heating in toluene-d_8 to 125°C these start to coalesce. From this we can deduce that the barrier to inversion of the eight-membered ring is of the order 18–20 kcal mol^{-1}, eq. (1), below.



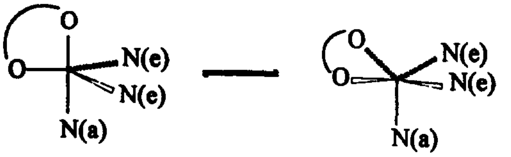
Note the ring flipping process depicted in eq. (1) interconverts the two otherwise inequivalent NMe_2 groups denoted by (a)N and (b)N.

The NMR spectra of $Ta(O—CH_2—O)(NMe_2)_3$ are also interesting, especially when compared with the solid-state structure which has been described in terms of a TBP with axial O—Ta—N bonds and one Ta—O and two Ta—N equatorial bonds. In toluene-d_8, even at −80°C we only observe one type of Bu^t and Me signal, which, excluding accidental degeneracy, indicates that the molecule is still stereochemically labile. Two NMe_2 signals are seen in the ratio 2 : 1 and these persist at room temperature. Only heating to above 100°C causes these to coalesce to a singlet. These observations lead us to propose that $Ta(O—CH_2—O)(NMe_2)_3$ undergoes a rapid TBP to SBP interconversion of the type shown in eq. (2). This leads to a rapid site exchange of the otherwise inequivalent equatorial NMe_2 ligands and the axial and equatorial phenyl groups.

Table 4. Selected bond distances (Å) and angles (°) for $(O—CH_4—O)Ta(NMe_2)_3$ (**3**)

Ta(1)—O(11)	1.968(3)
Ta(1)—O(25)	1.941(3)
Ta(1)—N(2)	1.955(4)
Ta(1)—N(5)	2.017(4)
Ta(1)—N(8)	1.955(4)

O(11)—Ta(1)—O(25)	84.8(1)
O(11)—Ta(1)—N(2)	88.7(1)
O(11)—Ta(1)—N(5)	167.0(1)
O(11)—Ta(1)—N(8)	97.7(1)
O(25)—Ta(1)—N(2)	131.8(1)
O(25)—Ta(1)—N(5)	85.0(1)
O(25)—Ta(1)—N(8)	119.9(1)
N(2)—Ta(1)—N(5)	92.1(2)
N(2)—Ta(1)—N(8)	108.3(2)
N(5)—Ta(1)—N(8)	94.4(2)



(2)

Note the N(e) groups of a TBP geometry in eq. (2) are inequivalent because of the roofing of the $O—CH_2—O$ ligand. At higher temperatures the reaction causing a time-averaging of all the NMe_2 groups must arise by a second mechanism of higher energy, E_{act} ~ 16 kcal mol^{-1}, wherein N(a) and N(e) site exchange occurs by what is equivalent to a turnstile motion.

Concluding remarks

We have prepared a number of early transition metal complexes incorporating the diphenoxide ligand A and shown that there are some interesting modes of bonding accessible to this ligand. We are particularly attracted to the relatively high barrier to inversion of the eight-membered chelate ring since this could have interesting stereochemical consequences in organometallic chemistry using a $[(O—CH_2—O)M]$ template.

EXPERIMENTAL

All reactions and manipulations were carried out in a glove box or Schlenk line under nitrogen. Solvents were dried by distillation over Na dispersion/benzophenone under nitrogen. $TiCl_4$, $ZrCl_4$ and $TaCl_5$ were used as received. $LiNMe_2$, $Ti(NMe_2)_4$, $Zr(NMe_2)_4$, $Ta(NMe_2)_5$ and $(O—CH_2—O)TiCl_2$ were made following the procedures described in the litera-

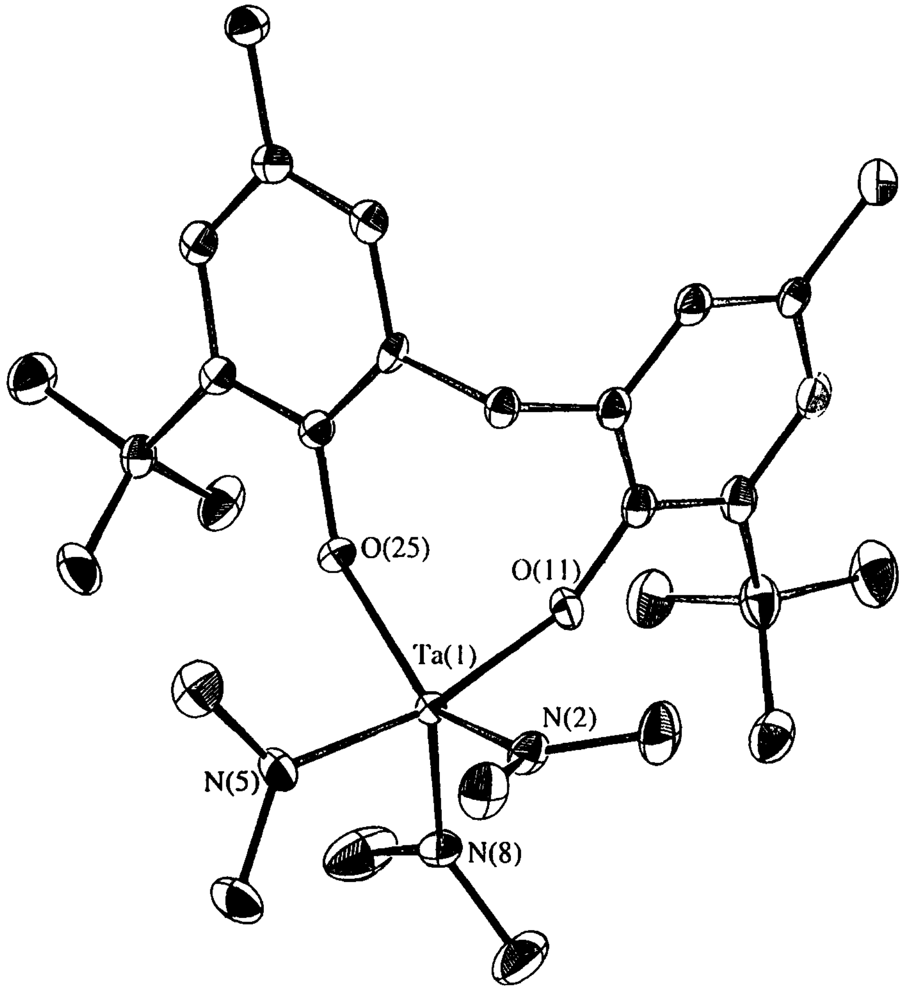


Fig. 3. An ORTEP drawing of the Ta(η^2-O—CH$_2$—O)$_2$(NMe$_2$)$_3$ molecule, showing the atom numbering scheme.

Table 5. The O—Ta—O bond angles of bis-aryloxide tantalum compounds

Compound	Structure	O—Ta—O angle	Ref.
Ta(OC$_6$H$_3$-Bu$^t_2$-2,6)$_2$Cl$_3$	sp	104.2(2)	[5a]
Ta(OC$_6$H$_3$-Bu$^t_2$-2,6)$_2$Me$_3$	tbp	164.1(2)	[5f]
Ta(OC$_6$H$_3$-Bu$^t_2$-2,6-4-OMe)$_2$Me$_3$	tbp	167.2(2)	[5f]
Ta(CCMe$_3$=CHCH—CCCMe$_3$)	tbp	92.5(1)	[6b]
(TpO)$_2$TaNp$_3$	tbp	178.3(8)	[6a]
TpO = 9-oxytriptycene			
Np = neopentyl			
Ta(OC$_6$H$_3$Me$_2$-2,6)$_2$(CH$_2$Ph)$_3$	tbp	165.5(2)	[5g]
Ta(OC$_6$H$_3$Ph$_2$-2,6)$_2$ (CH$_2$C$_6$H$_4$-4-Me)$_3$	tbp	174.77(9)	[5c]

ture [17]. ^{1}H and ^{13}C NMR were recorded on Varian Gemini-300 NMR spectrometer and referenced to the residual protio impurities of duterated solvent. All the spectra were taken at room temperature except when indicated otherwise.

2,2′-Methylene-bis(6-t-butyl-4-methylphenoxylithium)

The 2,2′-methylene-bis(6-*t*-butyl-4-methylphenol) (2.3 g, 6.8 mmol) was suspended in hexane (50 cm^3 hexane) and cooled to 0°C. Bu^{n}Li (5.3 cm^3, 2.5 M, 13.3 mmol) was then added *via* syringe over a 30 min period. During the addition, the solution color changed from pale yellow to pale green and finally became a milky white suspension. The suspension was stirred for another hour and the solid was filtered and dried in vacuum. A pale yellow solid was obtained (100% yield).

Bis[2,2′-*methylene-bis*(6-t-*butyl*-4-*methylphenoxide*)] *titanium* (**1**)

Method a. The 2,2′-methylene-bis(6-*t*-butyl-4-methylphenoxylithium) (0.98 g, 2.8 mmol) was suspended in toluene (20 cm^3) at -40°C and $TiCl_4$ (0.14 cm^3, 1.3 mmol) was added. The solution color changed from orange to red immediately when the $TiCl_4$ was added. The solution was stirred at room temperature for 1 h and filtered through Celite. The filtrate was collected and the solvent removed under vacuum. The residue was recrystallized from hexane to give 0.60 g of yellow orange products (69% yield). ^{1}H NMR (C_6D_6): 7.08 (s, 4H, aromatic H), 7.04 (s, 4H, aromatic H), 4.81 (d, $^2J_{HH}$ = 15 Hz, 2H, CH_2), 3.74 (d, $^2J_{HH}$ = 15 Hz, 2H, CH_2), 2.18 (s, 6H, Ph—*Me*), 2.08 (s, 6H, Ph—*Me*), 1.45 (s, 18H, CMe_3), 1.37 (s, 18H, CMe_3). ^{13}C NMR (C_6D_6, δ): 161.4, 160.9, 136.6, 136.4, 135.6, 134.1, 132.0, 131.7, 129.3, 128.7, 126.5, 126.2 (carbons on the phenyl ring), 36.0 (t, J_{CH} = 125 Hz, CH_2), 35.3, 34.7 (s, CMe_3), 30.4, 30.2 (q, J_{CH} = 127 Hz, Ph—*Me*), 21.0 (q, J_{CH} = 125 Hz, CMe_3). Found: C, 76.5; H, 8.5. Calc. for $C_{46}H_{60}O_4 \cdot 1/2C_6H_{14}$: C, 76.6; H, 8.8%.

Method b. The $Ti(NMe_2)_4$ (1.0 g, 5.5 mmol) solution in toluene (10 cm^3) was cooled to 0°C and then added to 2,2′-methylene-bis(6-*t*-butyl-4-methylphenol) (3.74 g, 11.0 mmol) in toluene (10 cm^3). The solution was stirred at room temperature for 16 h followed by removing solvent and $HNMe_2$ *in vacuo* and recrystallized from hexane. A pale yellow product was isolated (2.5 g, 67% yield).

Method c. (O—CH_2—O)$TiCl_2$ (0.71 g, 1.7 mmol) and Na/Hg (17.1 g, 0.499%, 3.7 mmol) were mixed in toluene (60 cm^3) and stirred for 10 h followed by filtering the solution through Celite. A pale yellow product was obtained by crystallization from toluene (0.20 g, 17% yield).

Bis[(η^2-2,2′-methylene-bis(6-t-*butyl*-4-*methylphenoxide*))(μ,η^1,η^1-2,2′-methylene-bis(6-t-*butyl*-4-*methylphenoxide*))]*dizirconium* (**2**)

In a 30 cm^3 Schlenk flask, $ZrCl_4$ (0.30 g, 1.3 mmol) and 2,2′-methylene-bis(6-*t*-butyl-4-methylphenoxylithium) (0.955 g, 2.7 mmol) were mixed and toluene (25 cm^3) was added *via* cannula at 0°C. The solution was stirred at room temperature for 1 h and filtered through Celite. A white solid was obtained from the filtrate by recrystallization (0.30 g, 30% yield). ^{1}H NMR (C_6D_6): 7.00 (m, 16H, aromatic H), 4.18 (d, $^2J_{HH}$ = 15 Hz, 4H, CH_2), 3.99 (d, $^2J_{HH}$ = 15 Hz, 4H, CH_2), 2.18 (s, 12H, Ph—*Me*), 2.12 (s, 12H, Ph—*Me*), 1.46 (s, 36H, CMe_3), 1.43 (s, 36H, CMe_3).

2,2′-*Methylene-bis*(6-t-*butyl*-4-*methylphenoxide*) *tris*(*dimethylamide*)*tantalum* (**3**)

In separate Schlenk flasks, $Ta(NMe_2)_5$ (0.398 g, 1.17 mmol) was dissolved in toluene (10 cm^3) and 2,2′-methylene-bis(6-*t*-butyl-4-methylphenol) (0.47 g, 1.17 mmol) was dissolved in toluene (15 cm^3). The 2,2′-methylene-bis(6-*t*-butyl-4-methylphenol)/toluene solution then was transferred to the $Ta(NMe_2)_5$/toluene solution *via* cannula at room temperature. The solution then was stirred for another 10 h. The solution was dried totally under vacuum to remove toluene and $HNMe_2$. The solid residue then was redissolved in hot hexane (10 cm^3) and cooled to -30°C slowly. Pale yellow solid was obtained (0.634 g, 83% yield). ^{1}H NMR (C_6D_6, δ): 7.15, 6.96 (m, 4H, proton on the phenyl group), 4.00 (d, 1H, $^2J_{HH}$ = 14 Hz, CH*H*), 3.65 (d, 1H, $^2J_{HH}$ = 14 Hz, C*H*H), 3.45 (s, 6H, NMe_2), 3.30 (s, 6H, NMe_2), 2.17 (s, 6H, Ph—*Me*), 1.47 (s, 18H, CMe_3). ^{1}H NMR (toluene-d_8, 120°C, δ): 7.10, 6.89 (m, 4H, proton on the phenyl group), 3.92 (d, 1H, $^2J_{HH}$ = 14 Hz, CH*H*), 3.65 (d, 1H, $^2J_{HH}$ = 14 Hz, C*H*H), 3.39 (s, 12H, NMe_2), 2.14 (s, 6H, Ph—*Me*), 1.43 (s, 18H, CMe_3). ^{13}C NMR (C_6D_6, δ): 157.6, 138.3, 132.9, 125.9 (carbons on the phenyl ring), 47.5 (q, $^1J_{CH}$ = 129 Hz, NMe_2, 43.7 (q, $^1J_{CH}$ = 135 Hz, NMe_2), 37.3 (dd, $^1J_{CH}$ = 119, 119 Hz, *C*HH), 35.0 (s, —CMe_3), 30.2 (q, $^1J_{CH}$ = 126 Hz, CH_3), 21.1 (q, $^1J_{CH}$ = 125 Hz, CMe_3). Found: C, 53.2; H, 7.3; N, 5.6. Calc. for $C_{29}H_{48}N_3O_2Ta$: C, 53.4; H, 7.4; N, 6.4%.

2,2′-*Methylene-bis*(6-t-*butyl*-4-*methylphenoxide*)-*bis*(*dimethylamide*)*zirconium* (**4**)

Tetrakis(dimethylamide)zirconium (0.29 g, 1.1 mmol) and 2,2′-methylene-bis(6-*t*-butyl-4-methylphenol) (0.36 g, 1.1 mmol) were mixed in a 30 cm^3 Schlenk flask and toluene (20 cm^3) was added *via* cannula. The yellow solution was stirred at room temperature for 18 h. The solvent was removed under vacuum and slight heat. The residue was recrystallized from toluene and 0.30 g of product was obtained (53% yield). ^{1}H NMR (C_6D_6): 7.05 (s, 2H, aromatic H); 7.00 (s, 2H, aromatic H), 3.75 (d, $^2J_{HH}$ = 14 Hz, CH_2), 3.53 (d, $^2J_{HH}$ = 14 Hz, CH_2), 3.15 (s, 6H, N*Me*), 3.01 (s, 6H, N*Me*), 2.18 (s, 6H, Ph—*Me*), 1.54 (s, 18H, CMe_3). ^{1}H NMR (toluene-d_8, 110°C, δ): 6.90 (m, 4H, proton on the phenyl group), 3.65 (d, 1H, $^2J_{HH}$ = 14 Hz, CH*H*), 3.54 (d, 1H, $^2J_{HH}$ = 14 Hz, C*H*H), 3.10 (s, broad, 12H, NMe_2), 2.10 (s, 6H, Ph—*Me*), 1.50 (s, 18H, CMe_3). ^{13}C NMR (C_6D_6, δ): 157.6, 136.9, 133.6, 128.3, 128.2, 126.5 (carbons on the phenyl ring), 45.6 (q, J_{HH} = 127 Hz, NMe_2), 43.9 (q, J_{HH} = 127 Hz, NMe_2), 39.4 (t, J_{CH} = 125 Hz, CH_2), 35.0 (s, CMe_3), 30.2 (q, $J_{CH} = 125$ Hz, Ph—*Me*), 21.0 (q, $J_{CH} = 125$ Hz, C*Me*$_3$).

2,2′-*Methylene-bis*(6-t-*butyl*-4-*methylphenoxide*) *tantalum-trichloride* (**5**)

2,2′-Methylene-bis(6-*t*-butyl-4-methyphenoxylithium) (0.64 g, 1.8 mmol) and $TaCl_5$ (0.40 g, 1.1 mmol) were mixed in a 30 cm^3 Schlenk flask and cooled to -20°C. Toluene was precooled to -20°C and transferred to the solid mixture *via* cannula. The solution was slowly warmed to room temperature and stirred for another 3 h. The golden solution was filtered through Celite to remove salt and the filtrate was dried. The solid was washed with hexane to leave pale yellow solid (0.424 g, 61% yield). ^{1}H NMR (C_6D_6) : 7.00 (s, 4H, aromatic H), 5.20 (d, $^2J_{HH} = 13$ Hz, C*H*$_2$), 3.45 (d, $^2J_{HH} = 13$ Hz, C*H*$_2$), 2.05 (s, 6H, Ph—*Me*), 1.55 (s, 18H, C*Me*$_3$).

2,2′-*Methylene-bis*(6-t-*butyl*-4-*methylphenoxide*)-*bis* (*dimethylamide*)*tantalumchloride* (**6**)

2,2′-Methylene-bis(6-*t*-butyl-4-methylphenoxide)tris(dimethylamide)tantalum (0.275 g, 0.42 mmol) was dissolved in toluene (200 cm^3) and trimethylsilylchloride (0.046 g, 0.42 mmol) was added *via* syringe. The flask was closed and heated to 95°C for 40 min. The solvent and trimethylsilyldimethylamide were removed under vacuum and slight heat. The pale yellow residue was recrystallized from hexane (0.18 g, pale yellow solid, 66% yield). ^{1}H NMR (C_6D_6) : 7.00 (s, 2H, aromatic H), 6.90 (s, 2H, aromatic H), 3.83 (d, $^2J_{HH} = 15$ Hz, 1H, C*H*$_2$), 3.56 (s, 12H, N*Me*$_2$), 3.40 (d, $^2J_{HH} = 15$ Hz, 1H, C*H*$_2$), 2.18 (s, 6H, Ph—*Me*), 1.50 (s, 18H, C*Me*$_3$).

NMR studies of the formation of (O—CH$_2$—O) Ti(NMe$_2$)$_2$

A J. Young® NMR tube was loaded with 20 mg of **1**, 8 mg of $Ti(NMe_2)_4$ and 0.5 cm^3 of benzene-d_6. The sample was heated at 64°C and monitored by ^{1}H NMR spectroscopy. The reaction was complete within 36 h. ^{1}H NMR (C_6D_6, δ, 22°C) : 7.16, 7.12, 7.05 (aromatic protons), 4.19 (d, $^2J_{HH} = 15$ Hz, C*H*$_2$), 3.43 (d, $^2J_{HH} = 15$ Hz, C*H*$_2$), 3.26 (s, 6H, N*Me*), 2.76 (s, 6H, N*Me*), 2.18 (s, 6H, Ph—*Me*), 1.54 (s, 18H, C*Me*$_3$). ^{13}C NMR (C_6D_6, δ) : 158.9, 137.0, 131.4, 129.7, 129.5, 125.8 (carbons on the phenyl ring), 44.5 (q, $J_{CH} = 127$ Hz, N*Me*$_2$), 44.3 (q, $J_{CH} = 127$ Hz, N*Me*$_2$), 35.0 (s, *C*Me$_3$), 32.9 (t, $J_{CH} = 123$ Hz, *C*H$_2$), 30.3 (q, $J_{CH} = 125$ Hz, Ph—*Me*), 21.0 (q, $J_{CH} = 128$ Hz, C*Me*$_3$).

X-ray crystal structure determination Ti(O—CH$_2$—O)$_2$ (**1**).

The operating procedure has been reported previously [18]. The crystal was mounted on a glass fiber using silicon grease and transferred to the goniostat and cooled to -171°C for characterization and data collection. The data were collected using a standard moving crystal-moving detector technique with fixed background at each extreme of the scan. Data were corrected for Lorentz and polarization effects and equivalent reflections were averaged. The structure was readily solved by direct methods (MULTAN78) and Fourier techniques. Hydrogen atoms were clearly visible in a difference Fourier phased on the non-hydrogen atoms and were allowed to vary isotropically in the final cycles of refinement. The final $R(F) = 0.0377$ for the 4398 number of unique reflection with $F > \sigma\ 2.33(F)$.

$Zr_2(\eta^2$-O—CH$_2$—O)$_2(\mu,\eta^1,\eta^1$-O—CH$_2$—O)$_2$ (**2**). The crystal was mounted using silicon grease and transferred to the goniostat where it was cooled to -173°C for characterization and data collection. The structure was solved using a combination of direct methods (MULTAN78) and Fourier techniques. One of the *t*-butyl groups had a two-fold disorder, modeled as atoms C(49) through (C54). In the final cycles of refinement the non-hydrogen atoms were varied with anisotropic thermal parameters to give a final $R(F) = 0.056$ for the 614 total variables using all of the unique data. Data having $F < 3\sigma(F)$ were given zero weight. The largest peak in the final difference map was 0.87 and the deepest hole was -0.54 e A^{-3}. The molecule lies on a crystallographic center of symmetry, i.e. the asymmetric unit contains 1/2 the title formula.

Ta(O—CH$_2$—O)(NMe$_2$)$_3$ (**3**). The crystal was mounted, transferred to a goniostat and was cooled to -169°C for characterization and data collection. A preliminary search revealed a primitive monoclinic cell. Following intensity data collection, the space group was determined as *P*21/*n*.

The structure was solved using a combination of direct methods (MULTAN78) and Fourier techniques. The position of the tantalum atom was obtained from an initial E-map. The position of the remaining non-hydrogen atoms were obtained from subsequent iterations of a least-squares refinement followed by a difference-Fourier calculation. Some of the hydrogens were observed including at least one on each of the methyl groups, which allowed all hydrogens to be included in fixed idealized positions. Hydrogen thermal parameters were fixed at one plus the isotropic thermal parameter of the carbon atom to which it was bonded.

In the final cycles of refinement, the non-hydrogen atoms were varied with anisotropic thermal parameters to give a final $R(F) = 0.028$ for the 317 total variables using all of the unique data. Data having $F < 3\sigma(F)$ were given zero weight. The largest peak in the final difference map was a tantalum residual of 1.74 and the deepest hole was -1.0 e A^{-3}.

Atomic coordinates have been deposited with the Cambridge Crystallographic Data Centre.

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Note added in proof: The synthesis of (**1**) has previously been reported: Okuda, J., Fokken, S., Kang, H.-C. and Massa, W., *Unem. Ber.*, 1995, **128,** 221.

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