

Reaction courses for formation of early transition metal phenoxides

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(Received December 1, 1993; in revised form January 19, 1994)

Abstract

The 1:1 and 1:2 reactions of TiCl_4 with $\text{Me}_3\text{SiO}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3$ produced $\text{TiCl}_3[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3](\text{THF})_2$ (**1**) and $\text{TiCl}_2[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3]_2(\text{THF})_2$ (**2**), respectively, bearing six-coordinated geometry around Ti. The compound **2** assumes the *cis*-geometry regarding the two phenoxy groups and THF is coordinated in the *trans* position of the phenoxy groups. Similarly, the 1:1 and 1:2 reactions of NbCl_5 with the trimethylsilyl phenyl ether provided $\text{NbCl}_4[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3](\text{THF})$ (**7**) and $\text{NbCl}_3[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3]_2(\text{THF})$ (**8**), respectively, with octahedron structure. The THF molecule again locates in the *trans* position of a phenoxy group in both cases and the two phenoxy groups of **8** locate in the *cis* position. Tungsten mono-phenoxide, $\text{WCl}_5[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3]$ (**12**), also has octahedron structure. In cases of tungsten bis-phenoxides, $\text{WCl}_4[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3]_2$ (**13**) and $\text{WCl}_4[\text{O}-2,6-(i\text{-C}_3\text{H}_7)\text{C}_6\text{H}_3]_2$ (**14**), the former has *trans* structure while the latter has *cis* structure regarding the phenoxy groups. A unique square pyramidal geometry has been observed in the tetrakis(phenoxy) tungsten, $\text{WCl}[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3]_4$ (**16**).

Key words: Titanium; Niobium; Tungsten; Zirconium; Tantalum

1. Introduction

A series of 2,6-disubstituted phenoxides of Ti, Zr, Hf, Nb, Ta, Mo and W have been synthesized by a convenient route using trimethylsilyl phenyl ether and anhydrous metal halides in THF, as an alternative to cyclopentadienyl derivatives, MX_nCp or MX_nCp_2 . This paper describes the reaction courses for the formation of mono- and bis-phenoxides of these metals and the stereochemistry of the resulting complexes. Although MX_nCp or MX_nCp_2 has been used widely for the preparation of a variety of organometallic compounds, their Lewis acidity is not high enough as an initiator for polymerization of α -olefins, dienes, and acetylene derivatives. Therefore, here we examine the introduction of phenoxy group(s) in place of cyclopentadienyl group(s) to the metal. Only one example is reported for the synthesis of a similar niobium compound, $\text{Nb}(\text{OR})$

Cl_4 ($\text{R} = \text{Me}, \text{Et}, \text{SiMe}_3$), starting from alkoxysilane [1]. The use of the unsubstituted phenoxy group usually results in a complex mixture due to their great tendency to aggregate by themselves.

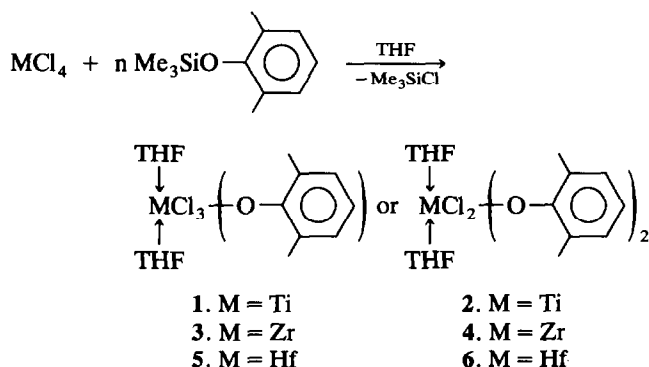
2. Results and discussion

2.1. Reaction courses for the formation of titanium, zirconium and hafnium phenoxides

The 1:1 reaction of $\text{TiCl}_4(\text{THF})_2$ with 2,6-dimethylphenoxy(trimethyl)silane in THF at ambient temperature for 2 h was found to afford a pure sample of a new compound, $\text{TiCl}_3[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3](\text{THF})_2$ (**1**) in 90% yield releasing Me_3SiCl as monitored by the NMR spectra. After the usual workup, the resulting product was purified by recrystallization from THF/hexane to give red crystals of **1** in 71% yield (m.p. 122°C). A bis(phenoxy) derivative, $\text{TiCl}_2[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3]_2(\text{THF})_2$ (**2**) was also available by refluxing a mixture of $\text{TiCl}_4(\text{THF})_2$ and $\text{SiMe}_3\text{-O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3$ (1:2.5 ratio) in THF for 8 h [2]. Recrystallization of the product

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from THF/hexane gave a titanium compound **2** (m.p. 85°C) as dark-red crystals in 70% yield.



Analogously, the corresponding zirconium and hafnium derivatives, $\text{MCl}_3[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3](\text{THF})_2$ (**3**: M = Zr, m.p. 142°C (dec); **5**: M = Hf, m.p. 161°C (dec)) were obtained in high purity by stirring the 1:1 mixture in THF for 3 h, and these were isolated as colorless crystals in 67–71% yields. Bis(phenoxy) derivatives of zirconium [**4**, m.p. 153°C (dec)] and hafnium [**6**, m.p. 170°C (dec)] were also available by refluxing the 1:6 mixture in THF for 8 h. Further addition of 2,6-dimethylphenoxy(trimethyl)silane to MCl_4 (M = Ti, Zr, Hf) or $\text{MCl}_2[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3]_2(\text{THF})_2$ did not form the tris- or tetrakis-phenoxy of these metals.

In order to elucidate the exact geometries of $\text{TiCl}_3[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3](\text{THF})_2$ (**1**), $\text{TiCl}_2[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3]_2(\text{THF})_2$ (**2**) and $\text{ZrCl}_2[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3]_2(\text{THF})_2$ (**4**), the X-ray structure analyses have been performed. An ORTEP drawing illustrated in Fig. 1(a) shows the molecular structure of **1** and Fig. 1(b) shows the molecular structure of **2** together with partial atomic labeling. In both complexes, the central Ti atoms have six-coordinated geometries and two phenoxy groups of **2** locate in the *cis* position. As the remaining two chlorine atoms occupy the *trans* position in both complexes, two-coordinated THF molecules assume the *cis* position. The ORTEP drawing of $\text{ZrCl}_2[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3]_2(\text{THF})_2$ (**4**) showed geometry similar to complex **2** (Fig. 2). Selected bond distances and angles for complexes **1**, **2** and **4** are listed in Table 1. Crystal data and experimental parameters are listed in Table 2. The Cl(1)–Ti–Cl(2) angles show slight deformations of two chloride ligands from the exact *trans* position. The central atoms lie on the basal plane defined by O(1), O(3), O(4) atoms for complexes **1**, **2** and **4**. In the complexes **2** and **4**, the O(phenoxy)–M–O(phenoxy) angles are much larger than the right angle while the O(THF)–M–O(THF) angles are smaller than 90°. These characteristics are also found in other six-coordinated Ti complex bearing a bis-phenoxy group in the

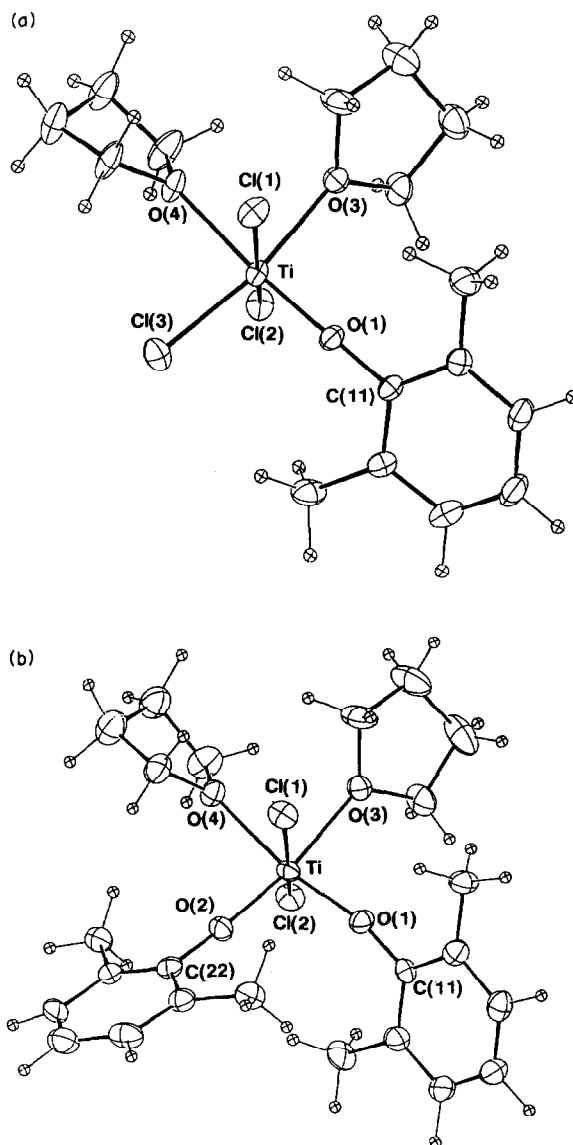
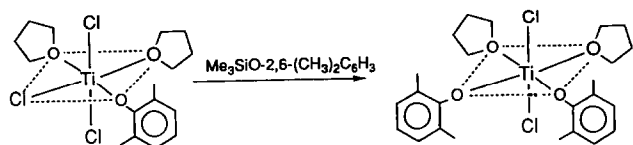


Fig. 1. ORTEP drawings of complexes **1** (a) and **2** (b).

cis position, $\text{Ti}[\text{O}-2,6-(i\text{Pr})_2\text{C}_6\text{H}_3]_2(\text{bipy})_2$ [**3**]. The Ti–O(phenoxy) distances [1.788(11) and 1.789(10) Å] in **2** are comparable or shorter compared with those of $\text{Ti}[\text{O}-2,6-(i\text{Pr})_2\text{C}_6\text{H}_3]_2(\text{bipy})_2$ (1.882 and 1.896 Å), $\text{Ti}[\text{O}-2,6-(t\text{Bu})_2\text{C}_6\text{H}_3]_3$ [1.79(2) Å] [**4**] and $\text{Ti}[\text{O}-2,6-(i\text{Pr})_2\text{C}_6\text{H}_3]_4$ [1.78(1) Å] [**5**] but is longer than that of **1** [1.762(5) Å]. However, the Zr–O bonds (1.904 and 1.906 Å) are a little shorter than those in $\text{Zr}(\text{OAr})_2$ [$\text{C}_8\text{H}_9\text{NC}(\text{CH}_3)\text{C}(\text{CH}_3)\text{NC}_8\text{H}_9$] (2.009 and 1.950 Å) [**6**].

These results indicate that complex **1** changes to **2** by the attack of 2,6-dimethyl(phenoxy)silane to the Cl(3) atom of **1**, nevertheless the Cl(3)–Ti bond distance [2.277(3) Å] in **1** is significantly shorter than the

Cl(1)–Ti [2.327(3) Å] and Cl(2)–Ti [2.330(3) Å] bond lengths due to the *trans* effect of the THF molecule.



2.2. Reaction courses in the formation of niobium- and tantalum-phenoxides

The present method is also useful for the synthesis of Group 5 niobium- and tantalum-phenoxide. The 1:1 reaction of anhydrous NbCl_5 with 2,6-dimethylphenoxy(trimethyl)silane in toluene at 80°C for 2 h followed by the addition of 20 equivol of THF gave $\text{NbCl}_4[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3](\text{THF})$ (**7**) in quantitative yield. Direct addition of NbCl_5 to THF must be avoided since cationic ring opening polymerization of THF occurs promptly. Recrystallization of the product from THF/hexane provides **7** (m.p. 143°C) as red crystals in 66% yield. Using essentially the same method, the 1:2 reaction of NbCl_5 with 2,6-dimethylphenoxy(trimethyl)silane in toluene at 80°C for 2 h followed by the addition of THF gave $\text{NbCl}_3[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3]_2(\text{THF})$ (**8**) as red crystals (m.p. 178°C) in 75% yield. Direct reaction of 2,6-dimethylphenoxy(trimethyl)silane with **7** (1.5:1 ratio) in THF also provides the same compound as revealed by the NMR measurements. However, further addition of 2,6-dimethylphenoxy(trimethyl)silane to **8** did not form higher analogs such as

TABLE 1. Interatomic bond distances (Å) and bond angles (°) for non-hydrogen atoms in complexes **1**, **2** and **4**

	1	2	4
Bond distance			
Ti(Zr)–Cl(1)	2.327(3)	2.374(4)	2.476(5)
Ti(Zr)–Cl(2)	2.330(3)	2.374(4)	2.456(5)
Ti(Zr)–Cl(3)	2.277(3)		
Ti(Zr)–O(1)	1.762(5)	1.788(9)	1.906(9)
Ti(Zr)–O(2)		1.788(9)	1.904(8)
Ti(Zr)–O(3)	2.168(5)	2.202(9)	2.275(9)
Ti(Zr)–O(4)	2.171(6)	2.197(9)	2.288(10)
Bond angle			
Cl(1)–Ti(Zr)–Cl(2)	166.9(1)	1.65.0(2)	163.3(2)
Cl(1)–Ti(Zr)–Cl(3)	92.7(1)		
Cl(1)–Ti(Zr)–O(1)	95.9(2)	96.0(3)	96.0(3)
Cl(1)–Ti(Zr)–O(2)		93.3(3)	93.3(3)
Cl(1)–Ti(Zr)–O(3)	85.0(1)	83.8(3)	82.9(3)
Cl(1)–Ti(Zr)–O(4)	84.7(2)	83.4(2)	83.5(3)
Cl(2)–Ti(Zr)–Cl(3)	95.6(1)		
Cl(2)–Ti(Zr)–O(1)	93.1(2)	94.3(3)	95.2(3)
Cl(2)–Ti(Zr)–O(2)		95.8(3)	96.9(3)
Cl(2)–Ti(Zr)–O(3)	85.0(1)	85.6(3)	84.9(3)
Cl(2)–Ti(Zr)–O(4)	85.3(2)	84.4(2)	83.1(3)
Cl(3)–Ti(Zr)–O(1)	97.4(2)		
Cl(3)–Ti(Zr)–O(3)	169.7(2)		
Cl(3)–Ti(Zr)–O(4)	88.4(2)		
O(1)–Ti(Zr)–O(2)		99.2(4)	100.3(4)
O(1)–Ti(Zr)–O(3)	92.8(2)	88.8(4)	88.9(3)
O(1)–Ti(Zr)–O(4)	174.2(2)	169.3	168.7(4)
O(2)–Ti(Zr)–O(3)		171.7(4)	170.4(3)
O(2)–Ti(Zr)–O(4)		169.3(4)	168.7(4)
O(3)–Ti(Zr)–O(4)	81.4(2)	80.6(3)	79.9(3)
Ti(Zr)–O(1)–Cl(11)	173.4(5)	165.7(8)	166.6(8)
Ti(Zr)–O(2)–Cl(21)		170.0(9)	170.8(8)
Ti(Zr)–O(3)–Cl(34)	123.8	128.3(9)	128.1(10)
Ti(Zr)–O(4)–Cl(41)	124.5(6)	125.9(9)	127.2(10)

$\text{NbCl}_2[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3]_3(\text{THF})$, since **8** was completely inert to 2,6-dimethylphenoxy(trimethyl)silane. In a similar way, $\text{TaCl}_4[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3](\text{THF})$ (**10**) (m.p. 163°C) and $\text{TaCl}_3[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3]_2(\text{THF})$ (**11**) (m.p. 170°C) were prepared as yellow crystals.

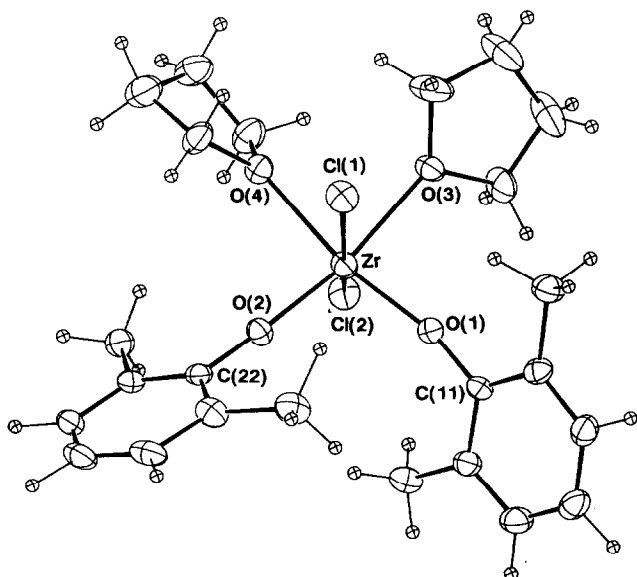
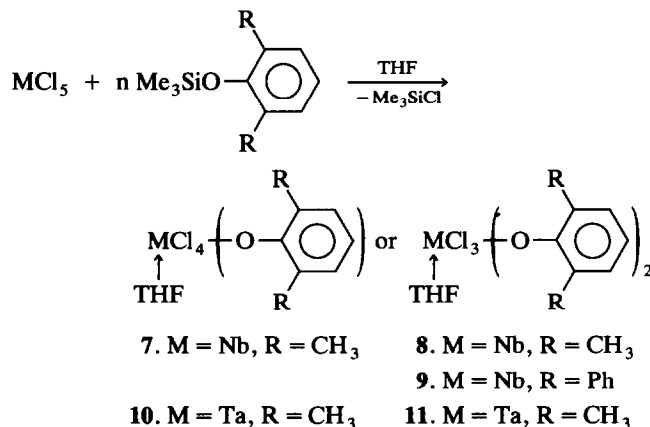


Fig. 2. ORTEP drawing of complex **4**.

The exact structures were determined by the X-ray analyses of **7** and **8**. The Nb atom in **7** has six-coordinated geometry with the THF molecule in the *trans* position to the phenoxy group (Fig. 3(a)). Four chlorine atoms locate in the meridian position. The selected bond distances and angles of **7**, **8** and **9** are summarized in Table 3 and the crystal data are given in Table 4. The Nb–O(1)–C(11) angle of **7** is exactly 180°. This is ascribable to the strong P π (oxygen)–d π (metal) interaction existing in the compounds. The Nb–O(1) distance (1.819 Å) is significantly shorter than the sum of the covalent radii. Actually, the Nb–O(1)–C(11) angle decreases with increase in number of phenoxide groups attached. The Nb–O(1)–C(11) angle of NbCl₄[O-2,6-(CH₃)₂C₆H₃]₂(THF) decreases to 173.2° in the case of NbCl₃[O-2,6-(CH₃)₂C₆H₃]₂(THF) (**8**) (Fig. 3(b)) and that of NbCl₃[O-2,6-(C₆H₅)₂C₆H₃]₂(THF) (**9**) is only 146.0° (Fig. 4). The Nb–O(1)–C(11) angle of **7** is larger than that of Ti-monophenoxide (173.4°) and the corresponding angle of Ti-bis(phenoxide) (165.7°). A similar phenomenon was observed in the Nb–O(2)–C(21) angle. The Nb–O(2)–C(21) angle of **8** (170.2°) is larger than that of **7** (154.5°). However, the Cl(1)–Nb–Cl(2) angles were little affected by changing the identity of the phenoxide groups. The

O(1)–Nb–O(2) bond angles of **8** (96.3°) and **9** (99.7°) are comparable with those of a Ti analog **2** (99.2°) and a Zr analog **4** (100.3°).

The 1:2 addition of **7** with trimethylsilyl phenyl ether again provides the compound with six-coordinated geometry around the Nb atom (Fig. 3(b)). In this case, one of the meridian chlorine atoms of **7** reacted with the phenoxysilane to afford the *cis*-bis(phenoxide) type compound and a THF molecule is coordinated in the *trans* position of the phenoxide group. If the coordination site of THF does not change during the reaction, we can readily conclude that Nb-mono(phenoxide) transfers to Nb-bis(phenoxide) by the attack of the Cl atom with phenoxysilane as illustrated below. The Nb–O bond distances in complexes **7**, **8** and **9** (1.819, 1.829 and 1.855 Å, respectively) are shorter than those in the complex, Nb[O-2,6-(¹C₃H₇)₂C₆H₃]₂[OC₆H₄C₃H₇C(CH₃)CH₂CPh=CPh] (1.943, 1.873 and 1.882 Å) [7].

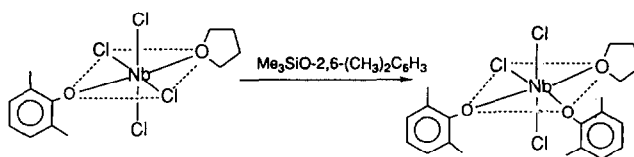


TABLE 2. Crystal data and experimental parameters for X-ray determination of **1**, **2** and **4**

	1	2	4
Formula	TiCl ₃ O ₃ C ₁₆ H ₂₅	TiCl ₂ O ₄ C ₂₄ H ₃₄	ZrCl ₂ O ₄ C ₂₄ H ₃₄
Formula weight	419.7	505.3	548.7
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Pna</i> 2 ₁	<i>Cc</i>	<i>Cc</i>
Temperature (°C)	20	20	20
<i>a</i> (Å) ^a	17.389(3)	16.794(4)	16.660(9)
<i>b</i> (Å)	10.610(1)	13.498(2)	13.647(2)
<i>c</i> (Å)	10.8358(2)	11.421(1)	11.589(2)
β (°)		90.72(1)	91.11(2)
<i>V</i> (Å ³)	1998.9(5)	2588.8(7)	2634.0(8)
<i>Z</i>	4	4	4
<i>D</i> _{calcd} (g cm ⁻³)	1.394	1.296	1.383
<i>F</i> (000) ^e	872	1064	1136
μ (Mo-K α) (cm ⁻¹)	8.5	2.9	6.4
Crystal size (mm)	0.45 × 0.38 × 0.5	0.63 × 0.38 × 0.30	0.20 × 0.25 × 0.20
2 θ range (°) ^b	4 < 2 θ < 60	4 < 2 θ < 60	3 < 2 θ < 60
Scan width, 2 θ ^c	1.0 + 0.35 tan θ	1.0 + 0.35 tan θ	1.103 + 0.35 tan θ
Scan speed (° min ⁻¹)	4	4.0	8.0–16.0
Background count (s)	5	5	50% of peak scan
Reflections measured	3058	3771	3997
Reflections observed ^c	2345	1948	2266
Radiation damage	no	no	no
No. of variables	308	415	415
GOF ^d	2.793	3.040	4.579
<i>R</i> ^e	0.053	0.084	0.060
<i>R</i> _w ^f	0.074	0.092	0.086

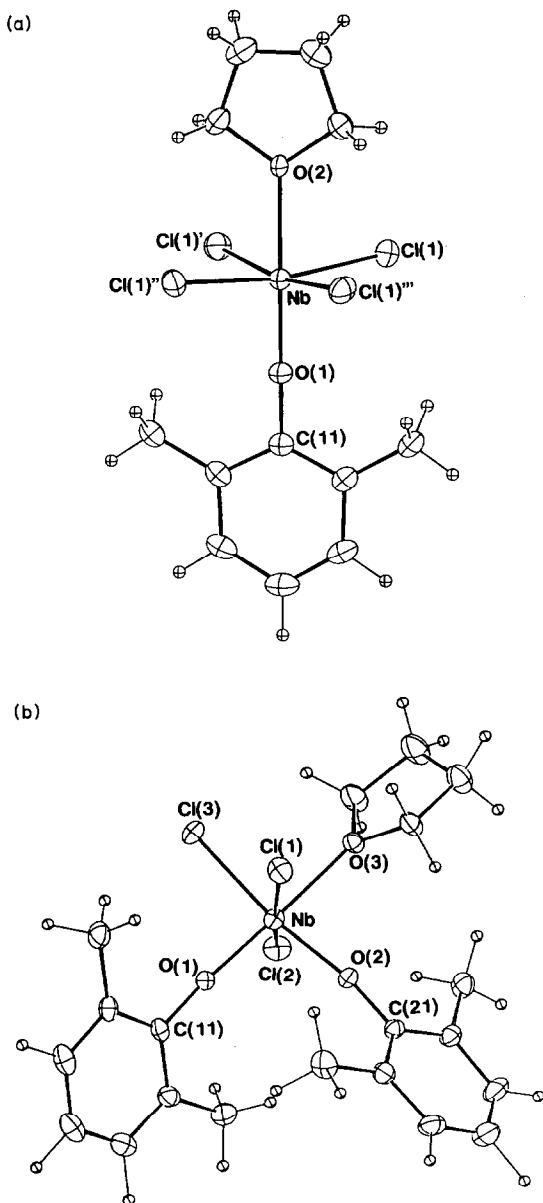
^a Least-squares refinement of the θ values for 25 reflections with $2\theta > 25^\circ$. ^b Intensity data were collected on a Rigaku four-circle diffractometer using graphite-monochromatized Mo-K α radiation by the θ - 2θ scan method. ^c $|F_o| > 3\sigma(F_o)$. ^d $[\sum w(|F_o| - |F_c|)^2 / (n - m)]^{1/2}$, where *n* and *m* are the no. of reflections used and variables refined, respectively. ^e $R = \sum(|F_o| - |F_c|) / \sum |F_o|$. ^f $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$, $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ and $g = 0.003$.

2.3. Reaction courses for the formation of tungsten mono- and bis phenoxides

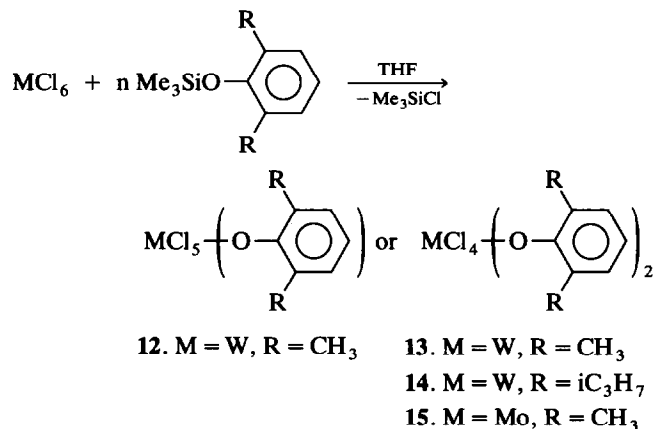
A 1:1 reaction of anhydrous WCl_6 with 2,6-dimethylphenoxy(trimethyl)silane in toluene at $-78^\circ C$ followed by heating to ambient temperature resulted in the formation of $WCl_5[O-2,6-(CH_3)_2C_6H_3]$ (**12**) as deep-purple crystals (m.p. $244^\circ C$). Similarly, the 1:2 reaction of WCl_6 with phenoxy silane in refluxing toluene for 2 h gave $WCl_4[O-2,6-(CH_3)_2C_6H_3]_2$ (**13**) as dark blue crystals (m.p. $162^\circ C$). In essentially the same way. The 1:2 reaction of WCl_6 with 2,6-diisopropylphenoxy(trimethyl)silane was carried out to obtain

TABLE 3. Interatomic bond distances (Å) and bond angles ($^\circ$) for non-hydrogen atoms in complexes **7**, **8** and **9**

	7	8	9
<i>Bond distances</i>			
Nb-Cl(1)	2.351(2)	2.366(3)	2.360(2)
Nb-Cl(2)		2.391(3)	2.363(2)
Nb-Cl(3)		2.388(3)	2.384(3)
Nb-O(1)	1.819(8)	1.829(6)	1.855(5)
Nb-O(2)		1.854(6)	1.883(5)
Nb-O(3)	2.207(7)	2.194(6)	2.217(7)
O(1)-C(11)	1.40(1)	1.360(11)	1.377(9)
O(3)-C(31)	1.465(9)	1.483(13)	1.513(20)
<i>Bond angles</i>			
Cl(1)-Nb-Cl(1)(Cl(3))	89.6(1)	88.7(1)	88.1(1)
Cl(1)-Nb-Cl(1)''	89.5(1)		
Cl(1)-Nb-Cl(1)'(Cl(2))	169.8(1)	168.8(1)	168.9(1)
Cl(1)-Nb-O(1)	95.1(1)	95.0(2)	91.3(2)
Cl(1)-Nb-O(2)		92.5(2)	95.5(2)
Cl(1)-Nb-O(3)	84.9(1)	84.5(2)	83.0(2)
O(1)-Nb-O(3)	180.0	177.4	172.0(2)
O(1)-Nb-O(2)		96.3(3)	99.7(2)
Nb-O(1)-C(11)	180.0	173.2(6)	146.0(5)
Nb-O(2)-C(21)		170.2(5)	154.2(5)
Nb-O(3)-C(31)	124.8(4)	122.6(6)	121.7(6)



the 1:2 addition compound, $WCl_4[O-2,6-(iPr)_2C_6H_3]_2$ (**14**), as deep-blue crystals. However, we have failed to isolate $MoCl_4[O-2,6-(CH_3)_2C_6H_3](THF)$ because of the predominant formation of the complex mixture, but the isolation of bis-phenoxide, $MoCl_3[O-2,6-(CH_3)_2C_6H_3]_2(THF)$ (**15**) was successful as purple crystals in 15% yield (mass spectrum: m/z 444 ($M^+ - THF$)).



The ORTEP drawings and crystal data for compounds **12** and **13** have been reported previously (Fig. 5(a,b)) [8]. The compound **12** is six-coordinated regarding the tungsten atom and the $W-O-C(11)$ angle is exactly 180° . The $W-O(1)-C(11)$ and $W-O(2)-C(22)$ angles of **13** are again 179° due to strong $p\pi(\text{oxygen})-d\pi(\text{metal})$ interaction. The molecular structure of **13** includes phenoxide groups in the *trans* position ($O(1)-W-O(2)$)

Fig. 3. The molecular structures of complexes **7** (a) and **8** (b).

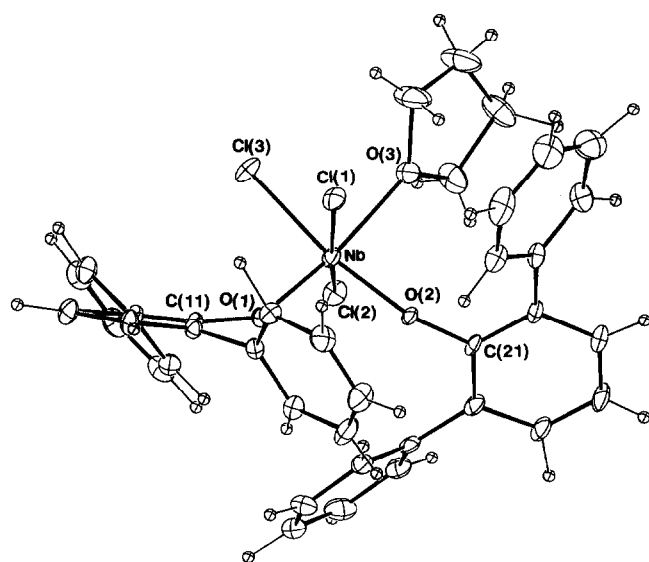


Fig. 4. The molecular structure of complex 9.

angle, 180°) in sharp contrast to the *cis*-position of an analogous complex, $\text{WCl}_4[\text{O}-2,6-(\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_3]_2$ [9]. This conflict may arise from the steric bulkiness of the 2,6-substituents. To examine this situation, we used 2,6-diisopropylphenoxy(trimethyl)silane in place of 2,6-dimethyl substituted phenoxysilane. The reaction was carried out under essentially the same conditions as described for 13 and $\text{WCl}_4[\text{O}-2,6-(i\text{Pr})_2\text{C}_6\text{H}_3]_2$ (14) was obtained in high yield. The X-ray structure of this molecule revealed the location of bis(phenoxide) in the *cis* position (Fig. 6(a)). Selected bond distances and angles of 12 and 14 are summarized in Table 5 and crystal data are given in Table 6. Therefore, we can estimate that the *cis* or *trans* arrangement of bis(phenoxide) in 13 and 14 is controlled by the steric bulkiness of the 2,6-substituents. Thus, the use of bulky 2,6-substituents usually leads to *cis*-geometry regarding the two phenoxy groups. Further addition of 2,6-dimethylphenoxy(trimethyl)silane did not form tris- or

TABLE 4. Crystal data and experimental parameters for X-ray determination of complexes 7, 8 and 9

	7	8	9
Formula	$\text{NbCl}_4\text{O}_2\text{C}_{12}\text{H}_{17}$	$\text{NbCl}_3\text{O}_3\text{C}_{20}\text{H}_{26}$	$\text{NbCl}_3\text{O}_3\text{C}_{40}\text{H}_{34} + 1/2(\text{hexane})$
Formula weight	428.0	513.7	762.0(805.1)
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	<i>Cmcm</i>	<i>P1</i>	<i>P1</i>
Temperature (°C)	23	20	20
<i>a</i> (Å) ^a	7.979(3)	9.639(9)	10.996(5)
<i>b</i> (Å)	17.094(4)	15.396(6)	18.009(4)
<i>c</i> (Å)	12.536(2)	8.763(4)	10.643(3)
α (°)		98.68(4)	90.30(2)
β (°)		98.61(9)	102.36(3)
γ (°)		75.45(6)	102.63(2)
<i>V</i> (Å ³)	1709.7(8)	1235.8(15)	2006.0(12)
<i>Z</i>	4	2	2
<i>D</i> _{calcd} (g cm ⁻³)	1.663	1.379	1.261(1.332)
<i>F</i> (000) ^e	856	524	780
$\mu(\text{Mo-K}\alpha)$ (cm ⁻¹)	13.0	8.1	5.3
Crystal size (mm)	0.25 × 0.40 × 0.30	0.25 × 0.25 × 0.25	0.25 × 0.25 × 0.30
2 θ range (°)	6 < 2 θ < 55	3 < 2 θ < 60	3 < 2 θ < 60
Scan width 2 θ ^o	1.630 + 0.30 tan θ	0.84 + 0.35 tan θ	1.732 + 0.35 tan θ
Scan speed (° min ⁻¹)	8–16	8.0–16.0	8–16.0
Background count (s)	50% of peak scan	50% of peak scan	50% of peak scan
Reflections measured	1146	7218	12196
Reflections observed ^c	702	4483	8023
Radiation damage	no	no	no
No. of variables	60	349	616
GOF ^d	2.27	4.937	6.781
<i>R</i> ^e	0.053	0.080	0.091
<i>R</i> _w ^f	0.038	0.130	0.143

^a Least-squares refinement of the θ values for 25 reflections with $2\theta > 25^\circ$. ^b Intensity data were collected on a Rigaku four-circle diffractometer using graphite-monochromatized Mo-K α radiation by the θ -2 θ scan method. ^c $|F_o| > 3\sigma(F_o)$. ^d $[\sum w(|F_o| - |F_c|)^2 / (n - m)]^{1/2}$, where *n* and *m* are the no. of reflections used and variables refined, respectively. ^e $R = \sum(|F_o| - |F_c|) / \sum |F_o|$. ^f $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$, $w = 4F_o^2 / \sigma^2(F_o^2)$.

tetrakis(phenoxide) since the resulting $WCl_4[O-2,6-(CH_3)_2C_6H_3]_2$ was completely inert to the phenoxysilane. The W–O distance of 1.82 Å is shortest in the tungsten-phenoxide hitherto reported, *i.e.* $WCl_3[O-2,6-(^1C_3H_7)_2C_6H_3]_3$ (1.832, 1.836 and 1.848 Å) [10], $W[O-2,6-(^1C_3H_7)_2C_6H_3]_4$ (1.849, 1.851, 1.851 and 1.866 Å) [11] and $W[2,6-(CH_3)_2C_6H_3]_4$ (1.843 Å) [11].

In contrast to these bond distances, very long W–O distances were reported in $WCl_3[O-2,6-(C_6H_5)_2C_6H_3][P(CH_3)_2C_6H_5]$ (1.887 and 1.853 Å) and $WCl_2[O-2,6-(C_6H_5)_2C_6H_3]_2[P(CH_3)_2C_6H_5]$ (1.996 Å) [9].

During the course of synthesizing a carbene complex, we have found that treatment of $WCl_4[O-2,6-(CH_3)_2C_6H_3]_2$ (16) with $LiCH_2Bu$ in hexane produced $WCl[O-2,6-(CH_3)_2C_6H_3]_4$ in 18% yield as dark red crystals. This complex is presumably formed by the reduction of $WCl_4[O-2,6-(CH_3)_2C_6H_3]_2$ followed by the disproportionation of the resulting $WCl_3[O-2,6-(CH_3)_2C_6H_3]_2$. The X-ray analysis revealed a novel square-pyramidal structure of 16 where the Cl atom locates at the apical position and phenoxide groups locate at the basal position (Fig. 6(b)). Similar W^V phenoxide complexes are known in cases of $WCl_3[O-2,6-(C_6H_5)_2C_6H_3]_2(THF)$, $WCl_3[O-2,6-(C_6H_5)_2C_6H_3]_2[P(CH_3)_2C_6H_5]$ and $WCl[O-2,6-(C_6H_5)_2C_6H_3]_4(Et_2O)$ [12], but these complexes assume a six-coordinated octahedron structure. Similar tungsten tetra(phenoxide), $W[O-2,6-(CH_3)_2C_6H_3]_4$ and $W[O-2,6-(^1C_3H_7)_2C_6H_3]_4$ are reported to exhibit tetrahedron structure.

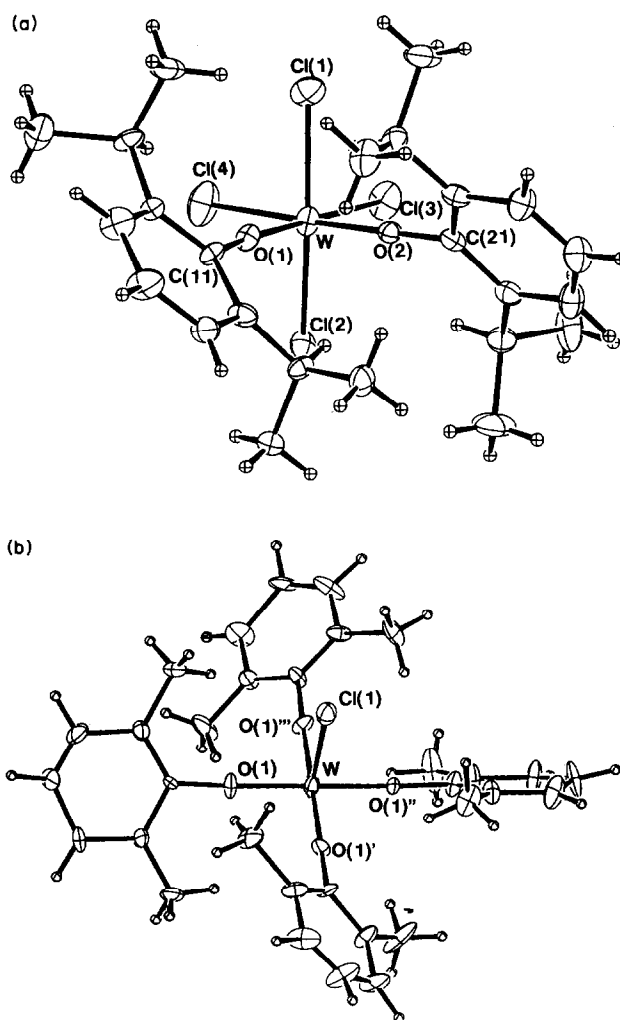


Fig. 6. ORTEP drawings of complexes 14 (a) and 16 (b).

2.4. 1H NMR studies of metal mono- and bis-phenoxide

Table 7 shows the chemical shifts of methyl protons in mono- and bis-phenoxy metal compounds. In the mono-phenoxy metal compounds, the chemical shift of the methyl group in 2,6-dimethylphenoxy metal (Ti, Zr, Hf) appeared at δ 2.50–2.70 ppm while those of Ta and Nb complexes appeared at δ 2.78–2.80 ppm and W complex at δ 3.58 ppm (Table 7). Thus, the magnitude of the chemical shift increases with increase in the Lewis acidity of the compounds. This trend was also observed in the bis-phenoxides. Methyl protons in Ti, Zr and Hf derivatives absorb at δ 2.33–2.36 ppm while those of Ta and Nb derivatives absorb at δ 2.44–2.54 ppm and that of W derivative at δ 2.91 ppm.

3. Experimental details

3.1. General

All manipulations were carried out by using a standard Schlenk technique under an argon atmosphere. All

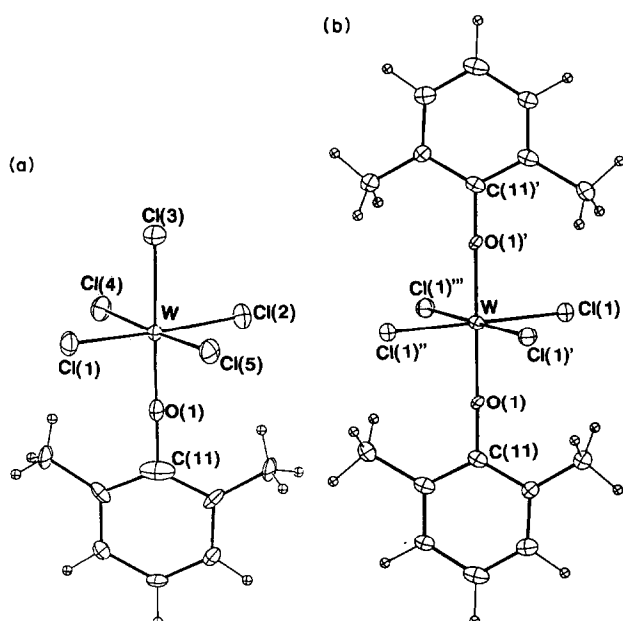


Fig. 5. ORTEP drawings of complexes 12 (a) and 13 (b).

TABLE 5. Interatomic bond distances (Å) and bond angles (°) for non-hydrogen atoms in complexes 12, 14 and 16

	12	14	16
Bond distance			
W-Cl(1)	2.307(3)	2.318(4)	2.427(6)
W-Cl(2)	2.307(3)	2.319(4)	
W-Cl(3)	2.299(9)	2.327(4)	
W-Cl(4)	2.307(3)	2.325(5)	
W-Cl(5)	2.307(3)		
W-O(1)	1.82(2)	1.814(8)	1.844(7)
W-O(2)		1.796(9)	1.855(7)
O(1)-C(11)	1.41(4)	1.39(1)	1.37(1)
O(2)-C(21)		1.40(2)	1.37(1)
Bond angle			
Cl(1)-W-Cl(2)	176.9(3)	171.1(2)	
Cl(1)-W-Cl(3)	88.4(1)	89.9(2)	
Cl(1)-W-Cl(4)	88.4(1)	86.5(2)	
Cl(1)-W-Cl(5)	90.4(3)		
Cl(1)-W-O(1)	91.6(1)	93.4(3)	90.1(8)
Cl(1)-W-O(2)		92.5(3)	90.1(8)
Cl(2)-W-Cl(3)	88.4(1)	87.3(2)	
Cl(2)-W-Cl(4)		86.6(2)	
Cl(2)-W-Cl(5)	89.5(3)		
Cl(2)-W-O(1)	91.6(1)	92.4(3)	
Cl(2)-W-O(2)		94.1(3)	
Cl(3)-W-Cl(4)		89.5(2)	
Cl(3)-W-O(1)	180.0	179.7(3)	
Cl(3)-W-O(2)		88.6(3)	
Cl(4)-W-O(1)	91.6(1)	90.6(3)	
Cl(4)-W-O(2)		177.9(3)	
O(1)-W-O(2)		91.4(4)	90.0
O(1)-W-O(3)			180(2)
W-O(1)-C(11)	180.0	169.8(9)	176(3)
W-O(2)-C(21)		177.7(9)	

solvents were dried over calcium hydride and then over sodium benzophenone ketyl. These were distilled before use. ^1H NMR spectra were recorded on a Jeol JNM-GSX-270 spectrometer. Mass spectra were run on a Jeol DX-300 spectrometer at 40–70 eV.

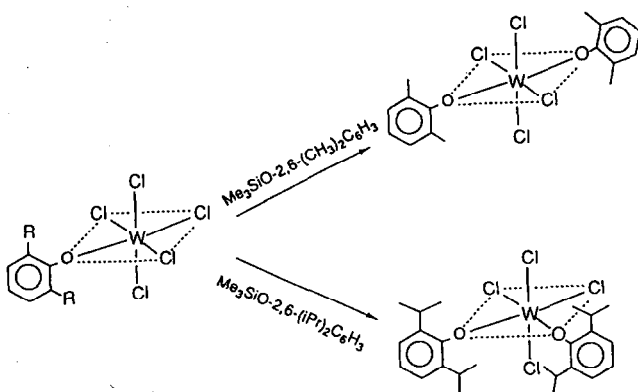


TABLE 6. Crystal data and experimental factors for complexes 14 and 16

	14	16
Formula	$\text{WCl}_4\text{O}_2\text{C}_{24}\text{H}_{28}$	$\text{WClO}_4\text{C}_{32}\text{H}_{36}$
Formula weight	674.15	703.94
Crystal system	Monoclinic	Tetragonal
Space group	$P2_1/n$	$I4$
Temperature (°C)	25°C	1°C
<i>a</i> (Å)	9.697(2)	12.328(1)
<i>b</i> (Å)	17.115(2)	
<i>c</i> (Å)	16.799(2)	10.287(4)
β (°)	91.80(1)	
<i>V</i> (Å ³)	2786.7(8)	1563.5(7)
<i>Z</i>	4	2
<i>D</i> _{calcd} (g cm ⁻³)	1.607	1.495
<i>F</i> (000) (e)	1320	702
μ (Mo-K α) (cm ⁻¹)	46.37	38.89
Crystal size (mm)	0.25 × 0.25 × 0.50	0.35 × 0.35 × 0.38
2 θ range (°)	3 > 2 θ > 55	3 > 2 θ > 55
Scan width 2 θ°	1.73 + 0.35 tan θ	1.21 + 0.35 tan θ
Scan speed (° min ⁻¹)	10.0	10.0
Background (s)	50% of peak scan	50% of peak scan
Reflections measured	7008	1038
Reflections observed	6625	952
Radiation damage	no	no
No. of variables	280	87
GOF	3.93	5.77
<i>R</i>	0.079	0.049
<i>R</i> _w	0.056	0.063

3.2. Synthesis of 2,6-dimethylphenoxy(trimethyl)silane

A solution of BuLi (210 mmol) in hexane (130 ml) was added dropwise to a solution of 2,6-dimethylphenol (25.1 g, 206 mmol) in THF (100 ml) at 0°C. The reaction mixture was warmed up to ambient temperature and stirred for 1 h. To the resulting 2,6-dimethylphenoxyolithium was added dropwise Me_3SiCl (27.4 g, 252 mmol) at 0°C. After stirring the reaction mixture for 1 h, the precipitated salt was removed by filtration. Distillation under reduced pressure (110°C, 24 mmHg) afforded $\text{Me}_3\text{SiO-2,6-(CH}_3)_2\text{C}_6\text{H}_3$ as a colorless oil (36.6 g, 92%). ^1H NMR (CDCl_3 , 30°C): δ 6.8–7.0 (m, 3H, aromatic protons); 2.20 (s, 6H, CH_3); 0.40 (s, 9H, SiMe_3). Mass spectrum: *m/z* 194 (M^+). Spectral data were similar to those reported in the literature [13].

TABLE 7. Chemical shifts (δ , ppm) of methyl protons in 2,6-dimethylphenoxy metal compounds

	<i>n</i> = 1	<i>n</i> = 2	
$\text{TiCl}_{4-n}[\text{O-2,6-(CH}_3)_2\text{C}_6\text{H}_3]_n(\text{THF})_2$	2.70	2.33	
$\text{ZrCl}_{4-n}[\text{O-2,6-(CH}_3)_2\text{C}_6\text{H}_3]_n(\text{THF})_2$	2.53	2.36	
$\text{HfCl}_{4-n}[\text{O-2,6-(CH}_3)_2\text{C}_6\text{H}_3]_n(\text{THF})_2$	2.50	2.33	
$\text{NbCl}_{5-n}[\text{O-2,6-(CH}_3)_2\text{C}_6\text{H}_3]_n(\text{THF})$	2.83	2.54	2.45
$\text{TaCl}_{5-n}[\text{O-2,6-(CH}_3)_2\text{C}_6\text{H}_3]_n(\text{THF})$	2.78	2.52	2.44
$\text{WCl}_{6-n}[\text{O-2,6-(CH}_3)_2\text{C}_6\text{H}_3]_n$	3.58	2.91	

TABLE 8. Final atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms in $\text{TiCl}_3[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3](\text{THF})_2$ (1)^a

Atom	x	y	z	B_{eq} (Å ²)
Ti	0.17659(5)	0.05375(9)	0	3.25
Cl(1)	0.12358(9)	-0.13336(14)	0.0729(3)	4.76
Cl(2)	0.21494(10)	0.26119(15)	-0.0346(3)	4.72
Cl(3)	0.13359(12)	0.0188(3)	-0.1956(3)	5.66
O(1)	0.2703(2)	-0.0058(4)	-0.0204(5)	4.0
O(3)	0.1963(3)	0.0963(5)	0.1931(5)	4.1
O(4)	0.0650(2)	0.1342(4)	0.0432(6)	4.5
C(11)	0.3450(3)	-0.0375(5)	-0.0360(7)	3.5
C(12)	0.3807(4)	-0.1093(6)	0.0559(7)	4.0
C(13)	0.4579(4)	-0.1430(8)	0.0382(9)	5.4
C(14)	0.4975(5)	-0.1006(9)	-0.0667(10)	6.3
C(15)	0.4614(5)	-0.0302(8)	-0.1540(9)	5.5
C(16)	0.3832(4)	0.0029(6)	-0.1437(7)	4.3
C(17)	0.3374(5)	-0.1546(9)	0.1665(8)	5.6
C(18)	0.3423(6)	0.0725(8)	-0.2437(9)	5.9
C(31)	0.1516(6)	0.0483(13)	0.2980(9)	8.0
C(32)	0.1857(7)	0.1021(12)	0.4095(10)	7.2
C(33)	0.2672(6)	0.1393(10)	0.3735(9)	6.6
C(34)	0.2613(5)	0.1717(8)	0.2382(8)	5.3
C(41)	-0.0090(4)	0.0720(7)	0.0190(12)	6.5
C(42)	-0.0673(5)	0.1744(8)	0.0208(12)	6.9
C(43)	-0.0343(5)	0.2665(9)	0.1095(13)	7.2
C(44)	0.0502(5)	0.2613(7)	0.0856(14)	7.2

^a Positional parameters are in fraction of cell edges and B_{eq} is the equivalent isotropic temperature factors calculated from the corresponding anisotropic thermal parameters.

3.3. Synthesis of $\text{TiCl}_3[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3](\text{THF})_2$

To a solution of $\text{TiCl}_4(\text{THF})_2$ (1.82 g, 5.46 mmol) in THF (80 ml) at -78°C was added $\text{Me}_3\text{SiO}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3$ (1.10 g, 5.66 mmol). The reaction mixture was allowed to warm to ambient temperature. After the mixture was evaporated to dryness, the resulting powdery product was recrystallized from THF/hexane to give red crystals of $\text{TiCl}_3[2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3](\text{THF})_2$ (1.81 g, 73%). Anal. Found: C, 43.35; H, 5.92. $\text{C}_{16}\text{H}_{25}\text{Cl}_3\text{O}_3\text{Ti}$ calcd.: C, 45.80; H, 6.01%. $^1\text{H NMR}$ (CDCl_3 , 30°C): δ 6.7–7.1 (m, 3H, aromatic protons); 4.30 (m, 8H, THF); 2.70 (s, 6H, CH_3); 2.03 (m, 8H, THF). Mass spectrum for ^{48}Ti : m/z 274 ($\text{M}^+ - 2\text{THF}$).

3.4. Synthesis of $\text{TiCl}_2[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3]_2(\text{THF})_2$

A mixture of TiCl_4 (4.67 g, 24.6 mmol) and $\text{Me}_3\text{SiO}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3$ (9.54 g, 49.2 mmol) in hexane (80 ml) was refluxed with vigorous stirring for 8 h. After hexane was removed by distillation, the resulting powdery product was recrystallized from THF/hexane to give red crystals of $\text{TiCl}_2[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3]_2(\text{THF})_2$ (0.51 g, 4%). Concentration of the supernatant solution gave second and third crops. Total yield was 70%. Anal. $\text{C}_{24}\text{H}_{34}\text{Cl}_2\text{O}_4\text{Ti}$ calcd.: C, 57.05; H, 6.78%. Found: C, 54.56; H, 6.79. $^1\text{H NMR}$ (CDCl_3 , 30°C): δ 6.8–7.0 (m, 3H, aromatic protons); 4.08 (m, 8H, THF); 2.33 (s, 6H,

CH_3); 1.97 (m, 8H, THF). Mass spectrum for ^{48}Ti : m/z 360 ($\text{M}^+ - 2\text{THF}$).

3.5. Synthesis of $\text{ZrCl}_3[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3](\text{THF})_2$

To a suspension of ZrCl_4 (0.44 g, 1.90 mmol) in toluene (3 ml) at 0°C was added THF (20 ml, 25 mmol). Stirring at ambient temperature allowed ZrCl_4 to dissolve. To the resulting solution was dropwise added $\text{Me}_3\text{SiO}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3$ (0.38 g, 1.97 mmol) at -78°C . The mixture was stirred for 3 h at ambient temperature and was evaporated to dryness. Recrystallization from THF/hexane gave colorless crystals of $\text{ZrCl}_3[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3](\text{THF})_2$ (0.58 g, 67%). Anal. Found: C, 40.35; H, 5.68. $\text{C}_{16}\text{H}_{25}\text{Cl}_3\text{O}_3\text{Zr}$ calcd.: C, 41.51; H, 5.44%. $^1\text{H NMR}$ (CDCl_3 , 30°C): δ 6.6–7.0 (m, 3H, aromatic protons); 4.46 (m, 8H, THF); 2.53 (s, 6H, CH_3); 2.09 (m, 8H, THF). Mass spectrum for ^{90}Zr : m/z 316 ($\text{M}^+ - 2\text{THF}$).

TABLE 9. Final atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms in $\text{TiCl}_2[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3]_2(\text{THF})_2$ (2)^a

Atom	x	y	z	B_{eq} (Å ²)
Ti	0.25	0.28505(15)	0.25	3.70
Cl(1)	0.2163(3)	0.2787(3)	0.4511(3)	5.48
Cl(2)	0.2493(3)	0.3073(3)	0.0462(4)	5.51
O(1)	0.3451(5)	0.3423(7)	0.2717(8)	4.7
O(2)	0.2806(5)	0.1582(7)	0.2468(8)	4.8
O(3)	0.1948(5)	0.4329(6)	0.2570(8)	4.8
O(4)	0.1247(5)	0.2431(7)	0.2233(8)	4.8
C(11)	0.4233(7)	0.3622(9)	0.2931(10)	4.0
C(12)	0.4808(9)	0.3189(10)	0.2196(13)	5.5
C(13)	0.5602(9)	0.3411(11)	0.2421(16)	6.4
C(14)	0.5815(9)	0.4027(13)	0.3377(16)	6.5
C(15)	0.5245(9)	0.4418(10)	0.4085(12)	5.8
C(16)	0.4427(8)	0.4245(11)	0.3852(12)	5.2
C(17)	0.4571(10)	0.2557(12)	0.1162(13)	6.7
C(18)	0.3806(9)	0.4676(12)	0.4648(12)	5.9
C(21)	0.2997(8)	0.0606(11)	0.2643(11)	4.3
C(22)	0.2662(8)	-0.0087(10)	0.1927(13)	4.8
C(23)	0.2837(10)	-0.1093(11)	0.2147(15)	6.5
C(24)	0.3336(10)	-0.1364(13)	0.3054(17)	7.0
C(25)	0.3682(10)	-0.0629(14)	0.3736(15)	6.8
C(26)	0.3552(8)	0.0389(10)	0.3544(12)	5.0
C(27)	0.2103(9)	0.0181(11)	0.0951(14)	5.8
C(28)	0.3940(9)	0.1171(12)	0.4284(13)	6.1
C(31)	0.2300(11)	0.5177(11)	0.1973(14)	7.0
C(32)	0.1858(16)	0.6056(13)	0.2382(16)	9.7
C(33)	0.1112(14)	0.5658(16)	0.292(2)	9.8
C(34)	0.1298(10)	0.4611(14)	0.3301(15)	7.8
C(41)	0.0727(10)	0.2731(14)	0.1225(14)	7.5
C(42)	-0.0107(10)	0.2397(14)	0.1551(19)	8.0
C(43)	0.0053(10)	0.1511(14)	0.2339(16)	8.0
C(44)	0.0819(9)	0.1742(12)	0.2946(15)	6.8

^a Positional parameters are in fraction of cell edges and B_{eq} is the equivalent isotropic temperature factors calculated from the corresponding anisotropic thermal parameters.

3.6. Synthesis of $ZrCl_2[O-2,6-(CH_3)_2C_6H_3]_2(THF)_2$

$ZrCl_4$ (2.15 g, 9.24 mmol) was dissolved in a mixture of benzene (10 ml) and THF (100 ml, 1.23 mol). To the resulting solution of $ZrCl_4(THF)_2$ was added dropwise $Me_3SiO-2,6-(CH_3)_2C_6H_3$ (10.65 g, 54.92 mmol) at 0°C and then the reaction mixture was refluxed for 8 h. The product was recrystallized from THF/hexane to afford colorless crystals of $ZrCl_2[O-2,6-(CH_3)_2C_6H_3]_2(THF)_2$ (1.94 g, 67%). Anal. Found: C, 50.8; H, 6.33. $C_{24}H_{34}Cl_2O_4Zr$ calcd.: C, 52.54; H, 6.25%. 1H NMR ($CDCl_3$, 30°C): δ 6.6–7.0 (m, 3H, aromatic protons); 4.39 (m, 8H, THF); 2.36 (s, 6H, CH_3); 2.06 (m, 8H, THF). Mass spectrum for ^{90}Zr : m/z 402 ($M^+ - 2THF$).

3.7. Synthesis of $NbCl_4[O-2,6-(CH_3)_2C_6H_3](THF)$

To a suspension of anhydrous $NbCl_5$ (350 mg, 1.30 mmol) in toluene (40 ml) at $-78^\circ C$ was added $Me_3SiO-2,6-(CH_3)_2C_6H_3$ (250 mg, 1.30 mmol). The

TABLE 10. Final atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms in $ZrCl_2[O-2,6-(CH_3)_2C_6H_3]_2(THF)_2$ (4)^a

Atom	x	y	z	B_{eq} (\AA^2)
Zr	0.25	0.28577(7)	0.25	4.25
Cl(1)	0.2107(3)	0.2825(3)	0.4549(3)	5.39
Cl(2)	0.2493(3)	0.3084(4)	0.0397(4)	5.47
O(1)	0.3513(5)	0.3476(7)	0.2763(8)	4.2
O(2)	0.2819(5)	0.1518(6)	0.2506(8)	4.2
O(3)	0.1908(6)	0.4359(7)	0.2536(8)	4.5
O(4)	0.1189(6)	0.2424(8)	0.2168(8)	4.5
C(11)	0.4302(7)	0.3702(9)	0.2991(11)	4.1
C(12)	0.4892(8)	0.3285(10)	0.2293(13)	4.9
C(13)	0.5679(9)	0.3515(13)	0.2540(16)	6.0
C(14)	0.5887(9)	0.4115(13)	0.3482(16)	6.3
C(15)	0.5286(9)	0.4511(11)	0.4150(14)	5.4
C(16)	0.4491(8)	0.4313(10)	0.3912(11)	4.5
C(17)	0.4677(10)	0.2667(12)	0.1272(15)	6.1
C(18)	0.3827(10)	0.4737(13)	0.4650(14)	6.1
C(21)	0.3025(7)	0.0522(9)	0.2698(10)	3.7
C(22)	0.2725(8)	-0.0153(10)	0.1990(12)	4.5
C(23)	0.2915(9)	-0.1128(10)	0.2226(15)	5.8
C(24)	0.3406(11)	-0.1352(12)	0.3133(17)	6.6
C(25)	0.3738(10)	-0.0648(13)	0.3801(15)	6.1
C(26)	0.3568(10)	0.0343(11)	0.3593(12)	5.2
C(27)	0.2170(9)	0.0104(12)	0.0972(15)	5.4
C(28)	0.3941(10)	0.1171(13)	0.4329(13)	6.2
C(31)	0.2270(11)	0.5210(11)	0.1948(14)	6.2
C(32)	0.1830(19)	0.6051(13)	0.2384(18)	9.5
C(33)	0.1119(18)	0.5744(16)	0.293(3)	10.0
C(34)	0.1226(13)	0.4678(15)	0.323(2)	8.6
C(41)	0.0688(11)	0.2665(14)	0.1157(18)	6.7
C(42)	-0.0129(11)	0.2322(16)	0.1435(19)	7.2
C(43)	-0.0013(10)	0.1483(16)	0.2256(18)	7.3
C(44)	0.0747(10)	0.1746(13)	0.2924(17)	6.3

^a Positional parameters are in fraction of cell edges and B_{eq} is the equivalent isotropic temperature factors calculated from the corresponding anisotropic thermal parameters.

TABLE 11. Final atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms in $NbCl_4[O-2,6-(CH_3)_2C_6H_3](THF)$ (7)

Atom	x	y	z	B_{eq} (\AA^2)
Nb	0	0.10268(7)	1/4	3.73
Cl(1)	0.2075(2)	0.0905(1)	0.1179(1)	5.3
O(1)	0	0.2091(4)	1/4	4.2
O(3)	0	-0.0264(4)	1/4	3.7
C(11)	0	0.2907(7)	1/4	3.7
C(12)	0	0.3277(5)	0.3492(7)	4.3
C(13)	0	0.4102(6)	0.3446(8)	5.3
C(14)	0	0.4501(8)	1/4	6.0
C(15)	0	0.2843(5)	0.4519(7)	5.4
C(31)	0	-0.0753(5)	0.3460(7)	6.4
C(32)	0	-0.1555(6)	0.3081(7)	7.4

reaction mixture was stirred at ambient temperature for 12 h. After the solvent was removed by distillation, the residue was recrystallized from THF/hexane to give $NbCl_4[O-2,6-(CH_3)_2C_6H_3](THF)$ (369 mg, 66%) as red crystals. Anal. Found: C, 34.00; H, 4.05. $C_{12}H_{17}Cl_4O_2Nb$ calcd.: C, 33.68; H, 4.00. 1H NMR ($CDCl_3$, 30°C): δ 6.9–7.1 (m, 3H, aromatic protons); 4.92 (m, 4H, THF); 2.83 (s, 6H, CH_3); 2.24 (m, 4H, THF). Mass spectrum for ^{93}Nb m/z 354 ($M^+ - THF$).

TABLE 12. Final atomic coordinates and isotropic temperature factors for non-hydrogen atoms in $NbCl_3[O-2,6-(CH_3)_2C_6H_3]_2(THF)$ (8)

Atom	x	y	z	B_{eq} (\AA^2)
Nb	0.72962(8)	0.31630(5)	0.14411(9)	3.31
Cl(1)	0.7812(4)	0.44889(17)	0.0846(3)	4.42
Cl(2)	0.6400(3)	0.18751(17)	0.1640(4)	4.40
Cl(3)	0.5030(3)	0.4054(2)	0.2165(4)	4.90
O(1)	0.8168(7)	0.3248(4)	0.3443(7)	3.3
O(2)	0.8891(6)	0.2426(4)	0.0575(7)	3.0
O(3)	0.6164(6)	0.3107(5)	-0.0925(7)	3.3
C(11)	0.8966(9)	0.3294(7)	0.4858(9)	3.3
C(12)	0.8839(10)	0.4145(7)	0.5707(11)	3.6
C(13)	0.9699(13)	0.4202(9)	0.7126(12)	4.7
C(14)	1.0637(13)	0.3414(10)	0.7673(12)	5.2
C(15)	1.0707(11)	0.2586(9)	0.6789(13)	4.7
C(16)	0.9855(10)	0.2509(7)	0.5360(11)	3.7
C(17)	0.7807(13)	0.4979(8)	0.5153(13)	4.9
C(18)	0.9886(13)	0.1607(8)	0.4426(14)	5.2
C(21)	1.0127(8)	0.1835(6)	0.0183(10)	2.9
C(22)	1.1447(10)	0.2034(7)	0.0849(11)	3.3
C(23)	1.2727(11)	0.1419(9)	0.0438(14)	4.9
C(24)	1.2673(14)	0.0660(9)	-0.0572(16)	5.8
C(25)	1.1321(13)	0.0486(8)	-0.1243(15)	5.1
C(26)	1.0063(10)	0.1087(6)	-0.0889(11)	3.6
C(27)	1.1536(12)	0.2869(8)	0.1969(13)	5.0
C(28)	0.8612(12)	0.0915(7)	-0.1670(12)	4.5
C(31)	0.6733(11)	0.3338(8)	-0.2255(11)	4.2
C(32)	0.5766(13)	0.3022(10)	-0.3688(13)	5.7
C(33)	0.4419(13)	0.3069(12)	-0.3116(14)	6.7
C(34)	0.4732(12)	0.2938(12)	-0.1402(14)	5.7

3.8. Synthesis of $\text{NbCl}_3[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3]_2(\text{THF})$

The 1:2 reaction of anhydrous NbCl_5 (3.34 g, 12.4 mmol) with $\text{Me}_3\text{SiO}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3$ (4.93 g, 25.4 mmol) in toluene (100 ml) at 80°C for 2 h followed by recrystallization from THF/hexane gave $\text{NbCl}_3[\text{O}-2,6-$

TABLE 13. Final atomic coordinates and equivalent temperature factors for non-hydrogen atoms in $\text{NbCl}_3[\text{O}-2,6-(\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_3]_2(\text{THF})$ (9)

Atom	x	y	z	$B_{\text{eq}} (\text{Å}^2)$
Nb	0.40489(7)	0.19644(4)	0.48516(6)	2.79
Cl(1)	0.2182(2)	0.20413(13)	0.55533(18)	3.48
Cl(2)	0.5788(3)	0.16310(13)	0.4191(2)	3.63
Cl(3)	0.4726(3)	0.13843(15)	0.68088(19)	4.44
O(1)	0.4884(5)	0.2923(3)	0.5603(5)	2.4
O(2)	0.3465(5)	0.2228(3)	0.3154(4)	2.4
O(3)	0.2959(6)	0.0789(4)	0.4207(6)	3.7
C(11)	0.5191(7)	0.3398(4)	0.6697(6)	2.3
C(12)	0.6267(8)	0.3386(4)	0.7641(6)	2.6
C(13)	0.6448(8)	0.3801(5)	0.8819(7)	3.0
C(14)	0.5580(9)	0.4196(5)	0.9033(7)	3.6
C(15)	0.4549(9)	0.4227(5)	0.8046(8)	3.6
C(16)	0.4334(7)	0.3849(4)	0.6866(7)	2.5
C(21)	0.3232(8)	0.2132(5)	0.1842(6)	2.7
C(22)	0.4222(8)	0.2414(5)	0.1218(7)	3.2
C(23)	0.3984(9)	0.2229(6)	-0.0104(7)	4.0
C(24)	0.2873(10)	0.1811(7)	-0.0767(7)	4.5
C(25)	0.1856(9)	0.1559(6)	-0.0146(7)	3.9
C(26)	0.2008(8)	0.1723(5)	0.1179(6)	3.0
C(31)	0.1990(17)	0.0273(8)	0.4819(15)	8.6
C(32)	0.1685(17)	-0.0447(8)	0.4233(17)	8.5
C(33)	0.2260(14)	-0.0409(7)	0.3087(16)	7.3
C(34)	0.3334(12)	0.0325(7)	0.3271(12)	5.9
C(51)	0.7298(7)	0.3004(5)	0.7461(7)	2.8
C(52)	0.7888(9)	0.2609(6)	0.8483(9)	4.0
C(53)	0.8908(9)	0.2301(6)	0.8368(11)	4.6
C(54)	0.9369(10)	0.2367(7)	0.7316(11)	4.8
C(55)	0.8807(9)	0.2751(6)	0.6273(10)	4.5
C(56)	0.7778(9)	0.3055(6)	0.6358(8)	3.7
C(61)	0.3306(7)	0.3982(4)	0.5810(7)	2.6
C(62)	0.3575(8)	0.4233(5)	0.4651(8)	3.5
C(63)	0.2629(12)	0.4452(7)	0.3728(9)	5.1
C(64)	0.1428(9)	0.4438(7)	0.3939(10)	4.3
C(65)	0.1147(9)	0.4183(6)	0.5070(10)	4.6
C(66)	0.2074(8)	0.3945(5)	0.6012(8)	3.1
C(71)	0.5451(8)	0.2912(5)	0.1897(7)	2.9
C(72)	0.6619(9)	0.2804(6)	0.1708(8)	3.8
C(73)	0.7737(10)	0.3316(7)	0.2274(12)	5.1
C(74)	0.7719(10)	0.3946(6)	0.3001(9)	4.6
C(75)	0.6580(9)	0.4059(5)	0.3204(9)	3.9
C(76)	0.5452(9)	0.3547(5)	0.2645(8)	3.5
C(81)	0.0911(8)	0.1506(6)	0.1753(7)	3.4
C(82)	0.0577(9)	0.2022(7)	0.2538(8)	4.1
C(83)	-0.0507(11)	0.1815(9)	0.2990(11)	6.1
C(84)	-0.1319(11)	0.1127(10)	0.2662(13)	6.6
C(85)	-0.1018(11)	0.0578(9)	0.1877(14)	7.1
C(86)	0.0111(10)	0.0790(7)	0.1462(11)	5.1
C(91)	0.1775(17)	0.3815(11)	-0.0001(14)	8.3
C(92)	0.1013(13)	0.4366(8)	-0.0643(11)	6.2
C(93)	0.0368(12)	0.4727(7)	0.0304(10)	5.6

TABLE 14. Final atomic coordinates and equivalent temperature factors for non-hydrogen atoms in $\text{WCl}_4[\text{O}-2,6-(\text{C}_3\text{H}_7)\text{C}_6\text{H}_3]_2$ (14)

Atom	x	y	z	$B_{\text{eq}} (\text{Å}^2)$
W	0.47807(07)	0.21657(04)	0.30644(04)	3.77(3)
Cl(1)	0.2391(04)	0.2124(03)	0.2986(02)	6.1(2)
Cl(2)	0.7129(04)	0.2294(03)	0.3335(02)	5.5(2)
Cl(3)	0.4629(05)	0.1584(03)	0.4310(02)	6.7(3)
Cl(4)	0.4543(06)	0.3386(03)	0.3654(03)	7.9(3)
O(1)	0.4908(09)	0.2619(05)	0.2093(05)	3.6(5)
O(2)	0.4934(08)	0.1208(05)	0.2640(05)	3.1(5)
C(11)	0.5060(13)	0.2833(09)	0.1304(07)	3.1(6)
C(12)	0.4176(14)	0.3396(08)	0.0981(08)	3.7(8)
C(13)	0.4332(19)	0.3572(11)	0.0181(09)	6(1)
C(14)	0.535(02)	0.3228(13)	-0.0248(09)	7(1)
C(15)	0.6214(16)	0.2698(11)	0.0086(09)	5(1)
C(16)	0.6096(15)	0.2445(09)	0.0874(08)	4.2(8)
C(21)	0.5024(15)	0.0470(09)	0.2281(08)	3.4(7)
C(22)	0.4109(15)	0.0295(09)	0.1644(08)	3.8(8)
C(23)	0.424(02)	-0.0443(11)	0.1323(09)	6(1)
C(24)	0.521(02)	-0.0969(10)	0.1606(10)	6(1)
C(25)	0.6110(18)	-0.0766(10)	0.2213(10)	5(1)
C(26)	0.6033(15)	-0.0042(09)	0.2590(08)	3.8(8)
C(51)	0.3012(16)	0.3720(10)	0.1456(08)	4.3(9)
C(52)	0.1704(17)	0.3291(12)	0.1286(10)	7(1)
C(53)	0.277(02)	0.4595(11)	0.1308(11)	7(1)
C(61)	0.7136(14)	0.1913(08)	0.1224(08)	3.8(8)
C(62)	0.8525(16)	0.2255(10)	0.1382(10)	6(1)
C(63)	0.7313(16)	0.1166(09)	0.0724(09)	5(1)
C(71)	0.3026(17)	0.0850(09)	0.1321(10)	4.6(9)
C(72)	0.315(02)	0.1000(10)	0.0429(10)	7(1)
C(73)	0.1571(18)	0.0599(12)	0.1500(12)	9(1)
C(81)	0.7008(16)	0.0158(09)	0.3270(10)	4.7(9)
C(82)	0.848(02)	0.0220(13)	0.2993(13)	9(1)
C(83)	0.693(02)	-0.0398(11)	0.3952(11)	9(1)

$(\text{CH}_3)_2\text{C}_6\text{H}_3]_2(\text{THF})$ (4.17 g, 66%) as red crystals. Anal. Found: C, 46.43; H, 5.29. $\text{C}_{20}\text{H}_{26}\text{Cl}_3\text{O}_3\text{Nb}$ calcd.: C, 46.76; H, 5.10%. ^1H NMR (CDCl_3 , 30°C): δ 6.7–7.0 (m, 6H, aromatic protons); 4.66 (m, 4H, THF); 2.54 (s, 6H, CH_3); 2.45 (s, 6H, CH_3); 2.14 (m, 4H, THF). Mass spectrum for ^{93}Nb : m/z 440 ($\text{M}^+ - \text{THF}$).

TABLE 15. Final atomic coordinates and equivalent temperature factors for non-hydrogen atoms in $\text{WCl}_4[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3]_4$ (16)

Atom	x	y	z	$B_{\text{eq}} (\text{Å}^2)$
W(1)	0	0	0	3.64(4)
Cl(1)	0	0	0.2359(5)	4.8(2)
O(1)	0.1059(6)	0.1069(6)	-0.000(3)	3.6(4)
C(1)	0.185(1)	0.184(1)	0.008(3)	3.3(6)
C(2)	0.169(2)	0.275(1)	-0.073(2)	4.8(9)
C(3)	0.246(2)	0.358(2)	-0.075(2)	6(1)
C(4)	0.337(2)	0.343(1)	0.020(4)	6(1)
C(5)	0.354(2)	0.256(2)	0.074(2)	6(1)
C(6)	0.275(1)	0.171(1)	0.080(2)	4.0(8)
C(7)	0.073(2)	0.290(2)	-0.152(3)	9(1)
C(8)	0.292(2)	0.067(2)	0.166(2)	6(1)

3.9. Synthesis of $WCl_4[O-2,6-(CH_3)_2C_6H_3]_4$

To a solution of $WCl_4[O-2,6-(CH_3)_2C_6H_3]_2$ (1.15 g, 2.03 mmol) in THF (150 ml) at $-78^\circ C$ was added an 0.38 M solution of $LiCH_2Bu$ in hexane (11.0 ml, 4.16 mmol). The reaction mixture was allowed to warm to ambient temperature. The color of the solution turned to red brown from deep purple. Then the solvent was removed *in vacuo*. The extraction from the residue by toluene and cooling the extract to $-20^\circ C$ gave dark red brown crystals of $WCl_4[O-2,6-(CH_3)_2C_6H_3]_4$ in 18% yield. M.p. $> 300^\circ C$. FAB mass spectrum for ^{184}W : m/z 708 (M^+).

3.10. X-Ray structural determination of the complexes

The integrated intensity data were measured on a Rigaku four-circle diffractometer with graphite monochromatized $Mo-K\alpha$ ($\lambda = 0.71069 \text{ \AA}$) radiation. The data measurements were processed using MSC/AFC software. The final atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms in the complexes **1**, **2**, **4**, **7**, **8**, **9**, **14** and **16** are listed in Tables 8–15. The determination and refinement of the crystal structures were carried out using TEXSAN software.

The crystal structures were solved by a heavy-atom method. Successive Fourier synthesis found in Patterson maps clearly revealed the remaining non-hydrogen atoms. The structures were refined anisotropically by a full-matrix least-squares method (XRAY-76).

Acknowledgment

The authors are indebted to Grant-in-Aid for Scientific Research (No. 4455018 and No. 1490012) from the Ministry of Education, Science and Culture.

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