CHEMISTRY LETTERS, pp. 2167-2170, 1990.

Facile Synthesis of Group 4-6 Transition Metal Phenoxides and X-Ray Structures of $TiCl_2[O\text{-}2,6\text{-}(CH_3)_2C_6H_3]_2(THF)_2$ and $NbCl_3[O\text{-}2,6\text{-}(CH_3)_2C_6H_3]_2(THF)$

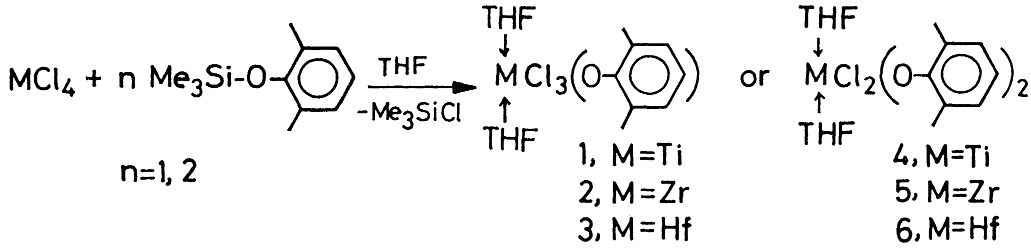
Nobuko KANEHISA, Yasushi KAI,* Nobutami KASAI, Hajime YASUDA,*[†]
Yuushou NAKAYAMA,[††] Kazuo TAKEI,[††] and Akira NAKAMURA*[††]
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita 565
[†]Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 724
[††]Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka 560

Reactions of Group 4-6 metal halides with 2,6-dimethylphenoxy-(trimethyl)silane in THF afford pure compounds of type $MX_l[O\text{-}2,6\text{-}(CH_3)_2C_6H_3]_m(THF)_n$ (M=Ti, Zr, Hf with l=3, m=1, n=2 or l=2, m=2, n=2; M=Nb, l=4, m=1, n=1 or l=3, m=2, n=1; M=W, l=5, m=1, n=0 or l=4, m=2, n=0) in >75% yields. Geometries of $TiCl_2[O\text{-}2,6\text{-}(CH_3)_2C_6H_3]_2(THF)_2$ and $NbCl_3[O\text{-}2,6\text{-}(CH_3)_2C_6H_3]_2(THF)$ were determined by the X-Ray diffraction method.

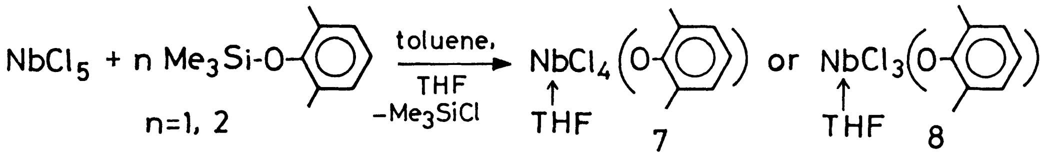
The use of bulky aryloxy or alkoxy metal compounds of Group 4-6 as an alternative of cyclopentadienyl compounds, MX_nCp and MX_nCp_2, is of current interest in organometallic chemistry.1-3) We wish to report herein a facile method for synthesis of a new series of pure mono- and bis-(phenoxy)metal halides4) and their structures.

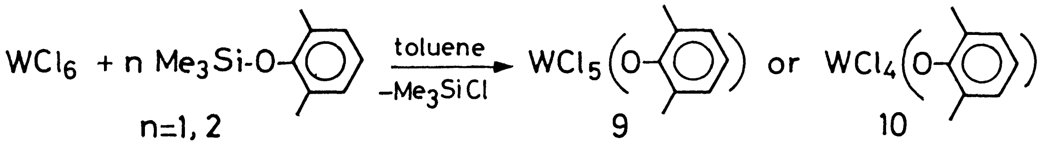
The 1:1 reaction of $TiCl_4(THF)_2$ with 2,6-dimethylphenoxy(trimethyl)silane in THF at 60 °C for 2 h was found to afford a pure sample of a new compound, $TiCl_3[O\text{-}2,6\text{-}(CH_3)_2C_6H_3](THF)_2$ (**1**) in 90% yield releasing Me_3SiCl as monitored by NMR spectra. After the usual work-up, the resulting product was purified by recrystallization from THF/hexane to give red crystals of **1** in 79% yield (mp 122 °C). Analogously, the corresponding zirconium and hafnium derivatives, $MCl_3[O\text{-}2,6\text{-}(CH_3)_2C_6H_3](THF)_2$ [**2**, M=Zr, mp 142 °C(dec) and **3**, M=Hf, mp 161 °C(dec)], were first obtained in high purity by refluxing the 1:1 mixture in THF for 6 h, and these were isolated as colorless crystals in 55-65% yields. Bis(phenoxy) derivatives, $MCl_2[O\text{-}2,6\text{-}(CH_3)_2C_6H_3]_2(THF)_2$, were also available by refluxing a mixture of the corresponding metal halides and $C_6H_3(CH_3)_2O\text{-}Si(CH_3)_3$ (1:2.5 ratio) in THF for 10 h. Recrystallization of the product from THF/hexane gave a titanium compound (**4**, mp 85 °C) as dark-red crystals, a zirconium derivative [**5**, mp 153 °C(dec)] and a hafnium derivative (**6**, 170 °C) as colorless crystals in ca. 75% yield.

All the products are analytically pure as identified by elemental analysis, NMR and mass spectroscopic studies. Thus, the present method is found to be superior to the conventional methods (i.e. reaction with a substituted bulky phenoxysodium5) or reaction of bulky phenols in the presence of an amine6)) with respect to the easiness in handling, purity of both mono- and bis-(phenoxy)metal compounds and yield.

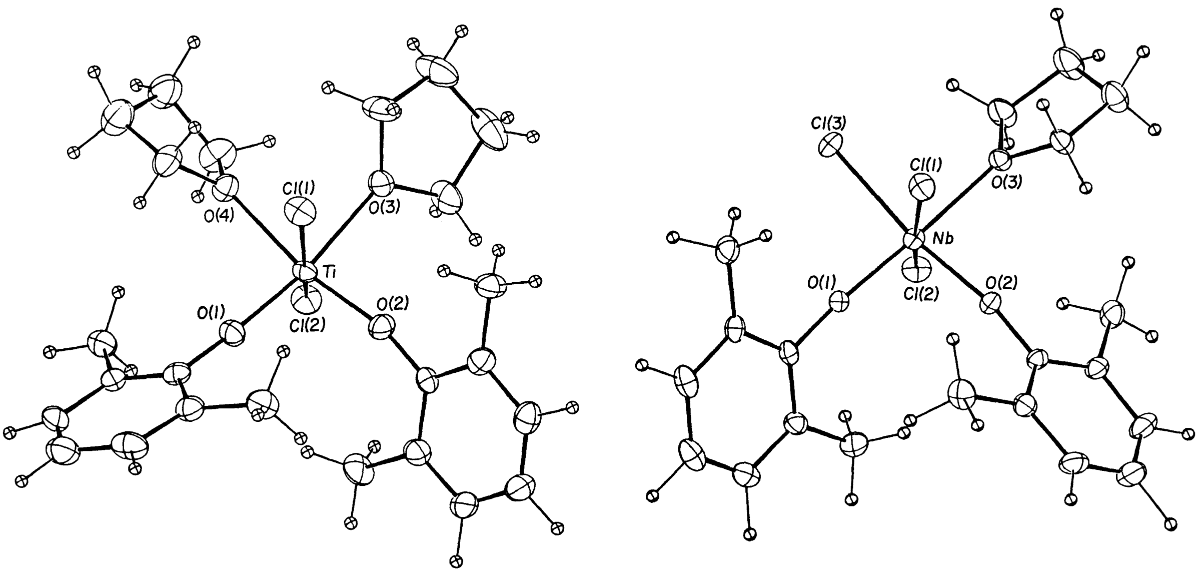


The present method is also useful for the synthesis of Group 5 niobium and Group 6 tungsten phenoxides. The 1:1 and 1:2 reactions of anhydrous $NbCl_5$ with 2,6-dimethylphenoxy(trimethyl)silane in toluene at 80 °C for 2-6 h followed by the addition of 20 equimol of THF gave $NbCl_4[O\text{-}2,6\text{-}(CH_3)_2C_6H_3](THF)$ (**7**) and $NbCl_3[O\text{-}2,6\text{-}(CH_3)_2C_6H_3]_2(THF)$ (**8**), respectively 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 products from THF/hexane provides **7** (mp 143 °C) and **8** (mp 178 °C) as red crystals in 82% and 75%, respectively. In essentially the same manner, both $WCl_5[O\text{-}2,6\text{-}(CH_3)_2C_6H_3]$ (**9**, mp 151 °C) and $WCl_4[O\text{-}2,6\text{-}(CH_3)_2C_6H_3]_2$ (**10**, mp 166 °C) were successfully prepared as dark-blue crystals.





In order to elucidate the exact geometries of $TiCl_2[O\text{-}2,6\text{-}(CH_3)_2C_6H_3]_2(THF)_2$ (4) and $NbCl_3[O\text{-}2,6\text{-}(CH_3)_2C_6H_3]_2(THF)$ (**8**) the X-ray structure analyses have been proceeded on these complexes.7) The ORTEP views in Fig. 1 show the comparative molecular structures of **4** and **8** together with the partial atomic labelings. In both complexes, the central metal atoms Ti and Nb have six-coordinated geometries with two phenoxy groups in *cis* positions. As the chlorine atoms occupy *trans* positions in both complexes, two THF ligands of the complex **4** are in *cis*. Selected bond distances and angles for **4** and **8** are listed in Table 1. Two Cl-M-Cl (M=Ti,Nb) angles show the slight deformations of two chloride ligands from the exact *trans* position. Central metal atoms lie on the basal plane defined by O(1), O(2), O(3), O(4) atoms for **4**, and by O(1), O(2), O(3), Cl(3) for **8**, respectively, because the sum of bond angles around the metal atoms in basal planes is exactly 360° in both complexes. O(phenoxy)-M-O(phenoxy) angles are much larger



4 **8**

Fig. 1. Molecular structures of $TiCl_2[O\text{-}2,6\text{-}(CH_3)_2C_6H_3]_2(THF)_2$ (**4**) and $NbCl_3[O\text{-}2,6\text{-}(CH_3)_2C_6H_3]_2(THF)$ (**8**).

Table 1. Selected bond distances (Å) and angles (deg) for **4** and **8**

4		**8**	
Ti - Cl(1)	2.374(7)	Nb - Cl(1)	2.366(3)
Ti - Cl(2)	2.347(7)	Nb - Cl(2)	2.391(3)
Ti - O(1)	1.788(11)	Nb - Cl(3)	2.388(3)
Ti - O(2)	1.789(10)	Nb - O(1)	1.829(6)
Ti - O(3)	2.201(11)	Nb - O(2)	1.854(6)
Ti - O(4)	2.195(11)	Nb - O(3)	2.194(6)
Cl(1) - Ti - Cl(2)	165.0(3)	Cl(1) - Nb - Cl(2)	168.8(1)
Cl(1) - Ti - O(1)	93.3(4)	Cl(1) - Nb - Cl(3)	88.7(1)
Cl(1) - Ti - O(2)	95.9(4)	Cl(1) - Nb - O(1)	95.0(2)
Cl(1) - Ti - O(3)	83.9(3)	Cl(1) - Nb - O(2)	92.5(2)
Cl(1) - Ti - O(4)	83.5(3)	Cl(1) - Nb - O(3)	84.5(2)
Cl(2) - Ti - O(1)	95.8(4)	Cl(2) - Nb - Cl(3)	86.4(1)
Cl(2) - Ti - O(2)	94.4(4)	Cl(2) - Nb - O(1)	95.2(2)
Cl(2) - Ti - O(3)	85.5(3)	Cl(2) - Nb - O(2)	90.8(2)
Cl(2) - Ti - O(4)	84.4(3)	Cl(2) - Nb - O(3)	85.0(2)
O(1) - Ti - O(2)	99.2(5)	Cl(3) - Nb - O(1)	92.7(2)
O(1) - Ti - O(3)	171.8(5)	Cl(3) - Nb - O(2)	170.8(2)
O(1) - Ti - O(4)	91.5(5)	Cl(3) - Nb - O(3)	84.7(2)
O(2) - Ti - O(3)	88.7(4)	O(1) - Nb - O(2)	96.3(3)
O(2) - Ti - O(4)	169.3(5)	O(1) - Nb - O(3)	177.4(3)
O(3) - Ti - O(4)	80.6(4)	O(2) - Nb - O(3)	86.3(2)

than the right angle in both complexes while the O(THF)-Ti-O(THF) or O(THF)-Nb-Cl(3) angles are smaller than 90°. These aspects are also found in other six coordinated Ti complex with bis-phenoxy groups in *cis* position, $Ti[O-2,6-(i\text{-}Pr)_2C_6H_3]_2(bipy)_2$.[8] The Ti-O(phenoxy) distances [1.788(11) and 1.789(10)Å] in **4** are comparable with those of the bis-(2,6-di-isopropylphenoxy) analogue.[8] The Nb-O(phenoxy) distances in **8** [1.829(6) and 1.854(6)Å] are significantly longer than those in the above Ti complexes. The longer Nb-O(2) distance as compared with Nb-O(1) is the result of stronger *trans* influence of Cl atom than THF ligand. Ti- and Nb-O(THF) distances in **4** and **8** are similar to each other.

The present work was supported by a Grant-in Aid for Scientific Research (No. 1490012) from the Ministry of Education, Science and Culture.

References

1) I. P. Rothwell, *Polyhedron*, **4**, 177 (1985).
2) K. C. Wallace, A. H. Liu, J. C. Dewan, and R. R. Schrock, *J. Am. Chem. Soc.*, **110**, 4964 (1988).
3) T. V. Lubben and P. T. Wolczanski, *J. Am. Chem. Soc.*, **109**, 424 (1987).
4) For a preliminary report, see H. Yasuda, K. Takei, and A. Nakamura, 56th National Meeting of the Chemical Society of Japan, Tokyo, April, 1988, Abstr. 2B01.
5) For example, I. P. Rothwell, *Acc. Chem. Res.*, **21**, 153 (1988).
6) For example, A. Flamini, D. J. Cole-Hamilton, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, **1978**, 454.
7) Crystal data of $TiCl_2[O-2,6-(CH_3)_2C_6H_3]_2(THF)_2$ (**4**): $C_{24}H_{34}O_4Cl_2Ti$, $F.W.$=505.3, monoclinic, space group Cc, a=16.794(4), b=13.498(2), c=11.421(1)Å, β=90.72(1)°, V=2588.8(7)Å^3, Z=4, D_c=1.296 g cm^{-3}, $F(000)$=1064, $\mu(MoK\alpha)$=2.9 cm^{-1}. Crystal data of $NbCl_3[O-2,6-(CH_3)_2C_6H_3]_2(THF)$ (**8**): $C_{20}H_{26}O_3Cl_3Nb$, $F.W.$=513.7, triclinic, space group $P\bar{1}$, a=9.639(9), b=15.396(6), c=8.763(4)Å, α=98.68(4), β=98.61(9), γ=75.45(6)°, V=1235.8(15)Å^3, Z=2, D_c=1.380 g cm^{-3}, $F(000)$=524, $\mu(MoK\alpha)$=8.1 cm^{-1}. The X-ray diffraction data were measured by the use of four-circle diffractometer with graphite monochromatized Mo$K\alpha$ radiation. A total of 3771 reflections for **4** and 7218 for **8** were collected by the θ-2θscan technique up to 2θ of 60°. The crystal structures were solved by the heavy atom method and refined by the full-matrix least-squares using the observed reflections [$|F_o|>3\sigma(F_o)$] of 1948 for **4** and 4483 for **8**, respectively. The refinements were proceeded by supposing anisotropic thermal parameters for nonhydrogen atoms and isotropic ones for hydrogen atoms. The final discrepancy factors R (R_w) are 0.085 (0.100) for **4** and 0.080 (0.130) for **8**. In the crystal lattice of **8**, a diffused electron density was found around the crystallographic inversion center. The crystal was obtained from the mixed solution of THF and hexane. Therefore, the residual density may be attributed to the THF packed in disorder. The ^{1}H NMR spectra of **8** also support that the nearly equivalent amount of THF to the main fragment is included in the crystal lattice. The assignment of the density peaks to each atom of the THF molecule was unsuccessful, which resulted the limited total accuracy of the molecular structure of **8**.
8) L. D. Durfee, P. E. Fanwick, I. P. Rothwell, K. Folting, and J. C. Huffman, *J. Am. Chem. Soc.*, **109**, 4720 (1987).

(Received August 27, 1990)