THE CHEMISTRY OF STERICALLY CROWDED ARYLOXIDE LIGANDS—VII. SYNTHESIS, STRUCTURE AND SPECTROSCOPIC PROPERTIES OF SOME GROUP 4 AND GROUP 5 METAL DERIVATIVES OF 2,6-DIPHENYLPHENOXIDE

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Abstract—A series of early transition metal organometallic derivatives containing the ancillary ligand 2,6-diphenylphenoxide $(OAr-2,6Ph_2)$ have been synthesized. Compounds of stoichiometry Ti(OAr-2,6Ph_2)₂(R)₂ (R = CH₃, CH₂SiMe₃, CH₂Ph and Ph) and Ti(OAr-2,6Ph)₃(R) (R = CH₃, CH₂SiMe₃) are obtained by treating the corresponding homoleptic alkyl, TiR₄, with the required amount of phenol, HOAr-2,6Ph₂. For the Group 5 metals Nb and Ta, the methyl derivatives M(OAr-2,6Ph₂)₂(CH₃)₃ and M(OAr-2,6Ph₂)₃(CH₃)₂ are obtained via methylation of the corresponding chloro-aryloxides. Besides routine spectroscopic characterization the diphenyl Ti(OAr-2,6Ph₂)₂(Ph)₂ and mono-alkyl Ti(OAr-2,6Ph₂)₃(CH₂SiMe₃) have been structurally characterized by X-ray diffraction techniques. Both molecules contain a pseudo-tetrahedral environment about the titanium atom with short 1.794(3)–1.806(2) Å, Ti-O distances and large, 153–179°, Ti-O-Ar angles. The Ti-C distances appear normal for these types of compounds.

The last few years have seen a considerable research effort into the study of the inorganic and organometallic chemistry associated with 2,6-dialkylphenoxide, (OAr) and 2,6-dialkylthiophenoxide, (SAr) ligation. In the case of the phenoxide ligands a diverse range of chemistry has been supported.¹⁻⁴ The related thiophenoxide ligands have also been extensively used with a wider range of transition metals to generate systems of possible relevance to biological thiolate environments.⁵⁻⁸ Following our work on the sterically very demanding 2,6-di-*tert*-butylphenoxide ligand which has been shown to sometimes undergo the mild activation of the aliphatic carbon-hydrogen bonds of the *tert*-butyl groups,^{9,10} we have begun an investigation of the ligand 2,6-diphenylphenoxide on similar metal systems.¹¹ This ligand has the possibility of forming related six-membered metallacycle rings, albeit this time via activation of an aromatic CH bond. Recent work by our group on molybdenum has confirmed this postulate.¹² We wish to report here our synthesis of a number of Group

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4 and Group 5 metal organometallic derivatives of this ligand as well as their structural and spectroscopic properties. While this work was in progress we became aware that some related studies were being carried out by Dilworth and coworkers^{13,14} to complement the interesting work they had previously completed on the related 2,6diphenylthiophenoxide group.⁵

RESULTS AND DISCUSSION

Synthesis of compounds

Two general synthetic strategies for the synthesis of organometallic derivatives containing 2,6diphenylphenoxide ligation were employed. The first involved the treatment of homoleptic alkyls of titanium and zirconium¹⁵ with the parent phenolic reagent in hydrocarbon solvents. This resulted in the sequential protonolysis of alkyl groups to directly generate mixed alkyl, phenoxides of this ligand. For zirconium the treatment of $Zr(CH_2SiMe_3)_4$ with HOAr-2,6Ph₂ led to the rapid replacement of all alkyl groups and formation of sparingly soluble $Zr(OAr-2,6Ph_2)_4$ in essentially quantitative yields. However, with titanium alkyls the substitution reaction was more controlled and allowed the synthesis in moderate yields of a number of compounds of general formulae $Ti(OAr-2,6Ph_2)_2(R)_2$ (I) and $Ti(OAr-2,6Ph_2)_3(R)$

(II) (Scheme 1). The tetra-alkyl substrate TiR₄ was either isolated ($\mathbf{R} = CH_2SiMe_3$) or else generated *in situ* ($\mathbf{R} = CH_3$, CH_2Ph , Ph) before being reacted with HOAr-2,6Ph₂. The phenoxide derivatives (I) and (II) were thermally much more robust than the corresponding homoleptic alkyls, undergoing little noticeable decomposition either in the solid state or hydrocarbon solution at 20-30°C over periods of weeks. These deep red or yellow crystalline materials proved only slightly soluble in hexane but much more soluble in aromatic hydrocarbon solvents.

For the Group 5 metals niobium and tantalum a synthetic route via the mixed chloro, phenoxide intermediates was investigated (Scheme 2). Treatment of the pentahalides MCl_5 (M = Nb, Ta) with HOAr-2,6Ph₂ (2 equivalents) in benzene led to the corresponding trichlorides M(OAr-2,6Ph₂)₂Cl₃ in good yields. It was then found possible to further substitute one more chloride ligand by using LiOAr-2,6Ph₂, again in hydrocarbon solvents, to yield the dihalide derivatives. Treatment of these halide substrates with the alkylating agent LiCH₃ resulted in the formation of the corresponding methyl compounds, M(OAr-2,6Ph₂)₂(CH₃)₃ (III) and $M(OAr-2,6Ph_2)_3(CH_3)_2$ (IV) as yellow (M = Nb) or colorless (M = Ta) crystalline solids (Scheme 2). Treatment of the dimethyl species (IV) with excess LiCH₃ resulted initially in the formation of (III) with loss of LiOAr-2,6Ph₂, but on extended



exposure decomposition, presumably via formation of $M(CH_3)_5$, took place. This reactivity pattern is similar to that found for other 2,6-di-alkylphenoxide complexes of these metals.¹

Spectroscopic properties

Some selected NMR data are collected in Table 1. As is to be expected the ¹H and ¹³C NMR spectra of the 2,6-dipflenylphenoxide ligand itself are not very informative, all resonances being grouped in the δ 6–7.5 ppm and δ 110–160 ppm regions. However, the ligand does have some influence on the NMR resonances of other groups contained in the metal coordination sphere. This is a consequence of the phenyl substituents of the aryloxide ligand which, due to their associated diamagnetic anisotropy, tend to shield some of the proton and carbon nuclei of adjacent groups. This effect was also noticed in dimolybdenum amido and tantalum alkylidyne derivatives of this ligand.¹¹ Table 1 contains some selected ¹H and ¹³C NMR data for the organometallic compounds obtained in this study. Hence, considering the methyl derivatives one finds that the M-CH₃ protons resonate at values of δ 0.53 (Ia), -0.41 (IIa), 0.09 (IIIa), -0.26 (IIIb), 0.18(IVa) and -0.21 ppm (IVb) compared to values of δ 1–2 ppm typically found for methyl derivatives of these metals containing other 2,6-dialkylphenoxide ligands. Similar upfield shifts of the resonances of other protons in the alkyl ligands are also evident (Table 1).

Solid state structures of Ti(OAr-2,6Ph₂)₂(Ph)₂ (Id) and Ti(OAr-2,6Ph₂)₃(CH₂SiMe₃) (IIb)

In order to more fully characterize the coordination properties of the 2,6-diphenylphenoxide ligand in these systems, X-ray diffraction analyses of the diphenyl compound (Id) and mono-trimethylsilylmethyl derivative (IIb) were carried out. Although a complete data set was also collected on the trimethyl Ta(OAr-2,6Ph₂)₂(CH₃)₃, the structure proved impossible in our hands to solve.¹⁶ Attempts to solve the structure of the niobium analogue by Dilworth and co-workers were also unsuccessful.¹³ Figures 1 and 2 contain the ORTEP views of (Id) and (IIb) respectively while Tables 2 and 3 contain some selected bond distances and angles. The diphenyl compound (Id) was found to contain one molecule of benzene per unit cell. It can be seen that both compounds (Id and IIb) contain a pseudo-tetrahedral arrangement of oxygen and carbon atoms about the titanium metal center. The five Ti-O distances lie in the narrow range of 1.794(3)-1.806(2) Å and can be compared with distances of 1.780(3) and 1.781(3) Å in Ti(OAr- $2,6Pr_2^i)_4^{17}$ and 1.782(8), 1.802(7) and 1.810(9) in $Ti(OAr-2,6Bu_2^t)_3 I^{18}$ In the less crowded diphenyl (Id) the Ti-O-Ar angles are 153.0(3) and 162.2(3)° while in the much more sterically congested Ti(OAr-2,6Ph₂)₃(CH₂SiMe₃) (IIb) this angle opens up to values of 164.6(2), 170.7(2) and 179.1(2)°. These latter values are on average significantly larger than found in the stoichiometrically related iodide compound $Ti(OAr-2,6Bu'_2)_{3}I$; 155.2(4), 158.2(4) and 159.1(4)°.18

The short Ti—O distances found in these compounds are consistent with the presence of considerable oxygen-*p* to metal-*d* π -bonding. The almost linear Ti—O—Ar angles also can be attributed to this effect and are characteristic of the coordination of 2,6-dialkylphenoxide ligands to early transition metal centers¹⁹ and allow some relief of the steric congestion at the metal caused by the bulky substituents. Similar structural

Compound	¹ H NMR $(\delta)^a$	¹³ C NMR $(\delta)^a$	
$Ti(OAr-2,6Ph_2)_2(CH_3)_2$ (Ia)	0.53 (s, Ti–CH ₃)	66.1 (Ti–CH ₃), $^{1}J = 125 \text{ Hz}$	
$Ti(OAr-2,6Ph_2)_2(CH_2SiMe_3)_2$ (Ib)	0.85 (s, Ti-CH ₂); -0.05 (SiMe ₃)	90.0 (Ti-CH ₂), ${}^{1}J = 112$ Hz; 6.6 (SiMe ₃)	
$Ti(OAr-2,6Ph_2)_2(CH_2Ph)_2$ (Ic)	1.87 (s, Ti– CH_2)	99.2 (Ti- CH_2), ¹ J = 131 Hz	
$Ti(OAr-2,6Ph_2)_2(Ph_2)$ (Id)		202.9 (Ti $-C_6H_5$)	
$Ti(OAr-2,6Ph_2)_3(CH_3)$ (IIa)	-0.41 (s, Ti-CH ₃)	66.7 (Ti–CH ₃), $^{1}J = 129 \text{ Hz}$	
$Ti(OAr-2,6Ph_2)_3(CH_2SiMe_3)$ (IIb)	0.27 (s, Ti-CH ₂); -0.77 (SiMe ₃)	101.0 (Ti-CH ₂) 5.6 (SiMe ₃)	
$Nb(OAr-2,6Ph_2)_2(CH_3)_3$ (IIIa)	$0.09 (s, Nb-CH_3)$	52.0 (Nb-CH ₃)	
$Ta(OAr-2,6Ph_2)_2(CH_3)_3$ (IIIb)	-0.26 (s, Ta-CH ₃)	58.7 (Ta-CH ₃)	
$Nb(OAr-2,6Ph_2)_3(CH_3)_2$ (IVa)	0.18 (s, Nb-CH ₃)	62.0 (Nb-CH ₃)	
Ta(OAr-2,6Ph ₂) ₃ (CH ₃) ₂ (IVb)	-0.21 (s, Ta-CH ₃)	64.8 (Ta-CH ₃)	

Table 1. Selected spectroscopic data

^{*a*} In C₆D₆ at 30° C.



Fig. 1. ORTEP view of Ti(OAr-2,6Ph₂)₂(Ph)₂ (Id) emphasizing the central coordination sphere and Ti—Ph groups.

features were reported by Dilworth for Ti(OAr-2,6Ph₂)₂Cl₂.¹³ The Ti—C(phenyl) distances of 2.070(5) and 2.106(5) Å in Ti(OAr-2,6Ph₂)₂(C₆H₅)₂ (**Id**) are slightly shorter than the distance of 2.272(14) Å reported for the metallocene derivative Cp₂Ti(C₆H₅)₂.²⁰ The Ti—C distance of 2.051(4) Å in (**IIb**) is also slightly shorter than found in the mono-cyclometallated complex Ti(OC₆H₃Bu' CMe₂CH₂)(OAr-2,6Bu'₂)(CH₂SiMe₃)(py), 2.131(6) Å.⁹ However, we do not believe these shorter distances in these derivatives of 2,6-diphenylphenoxide are significant.

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk and glove box techniques. Solvents were distilled under nitrogen from sodium benzophenone and stored under nitrogen. The halides $TiCl_4$, NbCl₅ and $TaCl_5$ were obtained commercially (Alfa) as was 2,6-diphenylphenol (HOAr-2,6Ph₂, Aldrich). ¹H and ¹³C NMR spectra were recorded on a Varian Associates XL-200 spectrometer. Microanalyses were obtained in-house at Purdue University.

Preparations

Due to similarities of the procedures used full details of the synthesis of only representative compounds will be given. Considerable difficulty in obtaining good microanalyses of derivatives of 2,6diphenylphenoxide was experienced. Typically carbon percentages were suppressed probably due to the formation of metal carbides. However, full microanalytical data that were obtained on all new compounds are reported.

Ti(OAr-2,6Ph₂)₂(CH₃)₂ (**Ia**). To a solution of IMgCH₃ (0.11 mol) in diethylether (250 cm³) cooled to -78° C was slowly added TiCl₄ (0.026 mol) in hexane (15 cm³). The resulting yellow mixture con-



Fig. 2. ORTEP view of Ti(OAr-2,6Ph₂)₃(CH₂SiMe₃) (IIb) emphasizing the central coordination sphere and alkyl group.

taining Ti(CH₃)₄ was stirred for 1 h at -78° C before HOAr-2,6Ph₂ (13.9 g, 2 equiv per Ti) was added slowly as a tolucne (50 cm³) solution. The color of the mixture darkened to orange and methane was evolved. After being allowed to warm slowly to room temperature, all solvent was removed *in vacuo* to yield a dark solid residue. Extraction of the residue with a 50/50 hexane/

benzene mixture and evaporation gave the crude product as an off-yellow crystalline powder. Reextraction with hexane and cooling to -15° C gave the pure product as lemon-yellow crystals. Yield = 6.28 g (42%). Found : C, 79.7; H, 5.5. Calc. for TiC₃₈H₃₂O₂: C, 80.3; H, 5.7%.

 $Ti(OAr-2,6Ph_2)_2(CH_2SiMe_3)_2$ (**Ib**). To a yellow solution of $Ti(CH_2SiMe_3)_4$ (1.0 g) in benzene (20

Table 2. Selected bond distances and angles for $Ti(OAr-2,6Ph_2)_2(C_6H_5)_2 \cdot C_6H_6$

()				
1.794(3)	Ti(1)—C(40)	2.106(5)		
1.797(3)	Ti(1)C(46)	2.070(5)		
122.99(14)	Ti	153.0(3)		
108.97(18)	Ti-O(21)-C(22)	162.2(3)		
107.14(18)	Ti-C(40)-C(41)	120.7(5)		
106.09(18)	Ti-C(40)-C(45)	126.3(4)		
109.24(18)	Ti-C(46)-C(47)	122.7(4)		
100.01(20)	Ti-C(46)-C(51)	118.9(4)		
	1.794(3) 1.797(3) 122.99(14) 108.97(18) 107.14(18) 106.09(18) 109.24(18) 100.01(20)	$\begin{array}{c} 1.794(3) & Ti(1)-C(40) \\ 1.797(3) & Ti(1)-C(46) \\ 122.99(14) & Ti-O(2)-C(3) \\ 108.97(18) & Ti-O(21)-C(22) \\ 107.14(18) & Ti-C(40)-C(41) \\ 106.09(18) & Ti-C(40)-C(45) \\ 109.24(18) & Ti-C(46)-C(47) \\ 100.01(20) & Ti-C(46)-C(51) \\ \end{array}$		

TiO(1)	1.797(2)	Ti-O(3)	1.802(2)
TiO(2)	1.806(2)	Ti—C(100)	2.051(4)
O(1)-Ti-O(2)	115.42(8)	O(3)-Ti-C(100)	104.7(2)
O(1)TiO(3)	111.27(9)	Ti - O(1) - C(11)	170.7(2)
O(1)-Ti-C(100)	102.5(2)	Ti-O(2)-C(21)	179.1(2)
O(2)-Ti-O(3)	114.39(9)	Ti-O(3)-C(31)	164.6(2)
O(2)TiC(100)	107.2(2)	Ti-C(100)-Si(1)	126.4(2)

Table 3. Selected bond distances and angles for Ti(OAr-2,6Ph₂)₃(CH₂SiMe₃) (IIb)

cm³) was added solid HOAr-2,6Ph₂ (1.24 g, 2 equiv) with vigorous stirring. The resulting mixture was stirred overnight before the solvent was removed *in vacuo* to yield the crude product as a yellow powder. The compound can be readily recrystallized from saturated hexane solution on cooling as large yellow blocks. Yield = 1.08 g (60%). Found: C, 73.2; H, 7.0. Calc. for TiC₄₄H₄₈O₂Si₂: C, 70.8; H, 6.7%.

Ti(OAr-2,6Ph₂)₂(CH₂Ph)₂ (Ic). An essentially identical procedure used for (Ia) except using ClMgCH₂Ph (0.16 mol) and TiCl₄ (0.04 mol) yielded the di-benzyl (Ic) as deep-red crystals from hexane. Yield = 24.6 g (84%). Found : C, 80.9; H, 5.7. Calc. for TiC₅₀H₄₀O₂: C, 83.3; H, 5.5%.

Ti(OAr-2,6Ph₂)₂(Ph)₂·C₆H₆ (Id). Addition of HOAr-2,6Ph₂ (14.8 g, 2 equiv) to a preformed solution of TiPh₄ (PhMgBr, 0.12 mol; TiCl₄, 0.03 mol) using the procedures outlined for (Ia) above yielded a dark brown mixture. The crude product was purified by recrystallization from hexane/ benzene mixture as large yellow blocks. Yield = 3.5 g (17%). Found: C, 82.2; H, 5.5. Calc. for TiC₄₈H₃₆O₂·C₆H₆: C, 84.1; H, 5.5%.

Ti(OAr-2,6Ph₂)₃(CH₃) (IIa). A yellow solution of Ti(OAr-2,6Ph₂)₂(CH₃)₂ (Ia) (0.5 g) and HOAr-2,6Ph₂ (0.22 g) in toluene (10 cm³) was stirred at 25°C. Methane evolution occurred, but no color change was evident. After 30 min the solution was cooled slowly to yield the product as yellow crystals. Yield = 0.50 g (73%). More product could be obtained on cooling the mother liquor. Found : C, 81.4; H, 5.2. Calc. for TiC₅₅H₄₂O₃: C, 82.7; H, 5.3%.

Ti(OAr-2,6Ph₂)₃(CH₂SiMe₃) (**IIb**). A mixture of Ti(CH₂SiMe₃)₄ (1.0 g) and HOAr-2,6Ph₂ (1.86 g, 3 equiv) in toluene (30 cm³) was refluxed for 4 h. The solvent was removed to give the crude product as a yellow powder which was recrystallized from a toluene/hexane mixture. Yield = 0.6 g (27%). Found: C, 79.6; H, 6.0. Calc. for TiC₅₈H₅₀SiO₃: C, 80.8; H, 5.8%.

Nb(OAr-2,6Ph)₂(Cl₃). A solution of HOAr-2,6Ph₂ (18.16 g) in benzene was added slowly to a

solution of NbCl₅ (9.96 g) also in benzene. The resulting mixture was stirred for 3 h before the solvent, along with generated HCl, was removed *in vacuo* to leave the crude product as an orange solid. Recrystallization from a saturated toluene solution gave the pure product. Yield = 24.0 g (94.4%). Found: C, 62.5; H, 4.3; Cl, 14.2. Calc. for Nb, $C_{36}H_{26}O_2Cl_3$: C, 62.7; H, 3.8; Cl, 15.4%.

Ta(OAr-2,6Ph₂)₂Cl₃. This was obtained as a yellow solid using an identical procedure using TaCl₅ instead of NbCl₅. Found: C, 56.9; H, 3.9; Cl, 12.2. Calc. for Ta, $C_{36}H_{26}O_2Cl_3$: C, 55.6; H, 3.4; Cl, 13.7%.

Nb(OAr-2,6Ph₂)₃Cl₂. Addition of LiOAr-2,6Ph₂ (0.37 g) to a solution of Nb(OAr-2,6Ph₂)₂Cl₃ (1.0 g) in benzene gave a yellow-orange suspension. After being stirred overnight the mixture was filtered and the filtrate stripped to yield the crude product as a yellow-orange solid. (Recrystallization from saturated hexane solutions gave the pure product.) Yield = 1.25 g (96.2%). Found : C, 72.3; H, 4.6; Cl, 7.1. Calc. for NbC₅₄H₃₉O₃Cl₂ : C, 72.1; H, 4.4; Cl, 7.9%.

Ta(OAr-2,6Ph₂)₃Cl₂. An identical procedure using Ta(OAr-2,6Ph₂)₂Cl₃ gave the product as a pale yellow solid. Found : C, 64.2; H, 4.4; Cl, 8.7. Calc. for TaC₅₄H₃₉O₃Cl₂: C, 65.6; H, 4.0; Cl, 7.2%.

Nb(OAr-2,6Ph₂)₂(CH₃)₃ (**IIa**). Slow addition of LiCH₃ (190 mg, 3 equiv) to a solution of Nb(OAr-2,6Ph₂)₂Cl₃ (2.0 g) in benzene causes a lightening of the solution from orange to pale yellow. Filtration and removal of the solvent *in vacuo* gave the product as a yellow powder. Recrystallization from hexane yielded the pure products as well formed yellow crystals. Yield = 1.1 g (68.1%). Found : C, 70.7; H, 5.4. Calc. for NbC₃₉H₃₅O₂; C, 74.5; H, 5.6%.

Ta(OAr-2,6Ph₂)₂(CH₃)₃ (**IIIb**). An identical procedure using Ta(OAr-2,6Ph₂)₂Cl₃ yielded (**IIb**) as well formed, white blocks from hexane. Found : C, 65.0; H, 5.1. Calc. for TaC₃₉H₃₅O₂: C, 65.3; H, 4.9%.

Nb(OAr-2,6Ph₂)₃(CH₃)₂ (IVa). Obtained from

Nb(OAr-2,6Ph₂)₃Cl₂ and LiCH₃ (2 equiv) in benzene. Recrystallized from hexane on cooling. Found : C, 78.3; H, 5.4. Calc. for NbC₅₆H₄₅O₃: C, 78.3; H, 5.3%.

Ta(OAr-2,6Ph₂)₃(CH₃)₂ (**IVb**). Obtained by reacting Ta(OAr-2,6Ph₂)₃Cl₂ with LiCH₃ (2 equiv) in benzene. An identical procedure to that used for (**IIa**) yielded the product as a white crystalline solid. Found : C, 70.3; H, 4.7. Calc. for TaC₅₆H₄₅O₃: C, 71.0; H, 4.8%.

Crystallographic studies

Crystal data are summarized in Table 4. One of the structures was determined at the Indiana University Molecular Structure Center while the second was determined in-house at Purdue.

 $Ti(OAr-2,6Ph_2)_2(Ph)_2 \cdot C_6H_6$ (Id). General oper-

ating procedures and a listing of programs have been published previously.²¹ A suitable small crystal was selected and transferred to the goniostat for characterization and data collection. Attempts at cooling the crystal to our usual operating temperature of -150° C resulted in fracturing of the crystal, possibly due to a phase transition. At about -94° C the crystal was stable, and this temperature was used for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited monoclinic symmetry and extinctions corresponding to the space group $P2_1/c$.

The structure was solved by direct methods, all non-hydrogen atoms were readily located after some initial difficulty resulting from the placement of the Ti atom almost on a twofold screw axis. After initial refinement the hydrogen atoms were located

	(Id)	(IIb)
Formula	TiC ₄₈ H ₃₆ O ₂ ·C ₆ H ₆	TiC ₆₁ H ₅₇ SiO ₃
fw	770.82	914.12
Space group	$P2_1/c$	ΡĪ
a, Å	10.959(2)	11.923(2)
b. Å	36.309(1)	11.887(3)
c, Å	10.859(2)	19.446(5)
α°		90.19(2)
₿°	110.29(1)	92.69(2)
v°	_	115.96(2)
Z	4	2
V. Å ³	4053.16	2474.0
Density (calc.) $g \text{ cm}^{-3}$	1.263	1.227
Crystal size	$0.30 \times 0.30 \times 0.40$	$0.65 \times 0.36 \times 0.24$
Crystal color	orange	yellow
Radiation	ΜοΚα	ΜοΚα
	$(\lambda = 0.71069 \text{ Å})$	$(\lambda = 0.71069 \text{ Å})$
Linear abs coeff., cm ⁻¹	2.48	2.37
Temp. deg. C	-94	167
Detector aperture	3.0 mm wide \times 4.0 mm high	$(1.5 + \tan \theta)$ mm wide 4.0 mm high
Takeoff angle deg	2.0	4 90
Scan speed deg min ⁻¹	5.0	variable
Scan width deg	1.2 + dispersion	$0.8 \pm 0.35 \tan \theta$
bkad counts s	6	50% of scan time
2θ range, deg.	6-45	4-45
Unique data	5321	6442
Unique data with		
$Fo > 3.00 \sigma$	3754	5151
R(F)	0.0647	0.052
Rw(F)	0.0651	0.076
Goodness of fit	1.171	1.515
Largest Λ/σ	0.05	0.11

Table 4. Crystal structure determination data

and refined. The full matrix least-squares refinement was completed using anisotropic thermal parameters on all non-hydrogen atoms and isotropic thermal parameters on the hydrogen atoms. The final difference map was essentially featureless, the largest peak was 0.6 e/Å. The asymmetric unit contained one molecule of benzene solvent. The atoms in the solvent are numbered C(52) through to C(57).

Ti(OAr-2,6Ph₂)₃(CH₂SiMe₃) (**IIb**). A suitable crystal was located and mounted in a 0.5 mm capillary surrounded by epoxy resin. Data collection and refinement were carried out using the standard procedures of the Purdue Crystallographic facility.¹¹

Hydrogens were located such that the hydrogencarbon bond was 0.95 Å and the angles were correct. For methyl groups, one hydrogen was located in the Fourier map, its position was idealized, and the remaining hydrogen positions were calculated based on it. Hydrogen temperature factors and positions were not refined.

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