Towards supported catalyst models: the synthesis, characterization, redox chemistry, and structures of the complexes $Ti(OAr')_4$ (Ar' = C₆H₄(2-*t*-Bu), C₆H(2,3,5,6-Me)_4)

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Reaction of substituted phenoxides with TiCl₄ affords the species Ti(OAr')₄ (Ar' = C₆H₄(2-t-Bu), **1**; Ar' = C₆H(2,3,5,6-Me)₄, **2**). The compound Ti(OC₆H₄(2-t-Bu))₄, **1**, crystallizes in the tetragonal space group $P\bar{4}2_1c$, with a = 15.203(4) Å, c = 8.026(3) Å, Z = 2, and V = 1855(2) Å³. The compound Ti(OC₆H(2,3,5,6-Me)₄)₄, **2**, crystallizes in the orthorhombic space group *Pbcn*, with a = 16.539(7) Å, b = 16.136(6) Å, c = 27.716(12) Å, Z = 8, and V = 7397(9) Å³. The geometry of the Ti coordination sphere in these complexes is best described as pseudo-tetrahedral. In the case of **1** strict crystallographic $\bar{4}$ symmetry is imposed. The complex **2** exhibits reversible cyclic voltammetric behaviour consistent with a one electron reduction to the Ti(III) analogue. Chemical reduction of **2** employing sodium amalgam affords the quantitative formation of (C₆H(2,3,5,6-Me)₄O)₂Ti(μ -OC₆H(2,3,5,6-Me)₄)₂Na(THF)₂, **3**. The reaction of **3** with [(COD)Rh(μ -Cl)]₂ does not afford the Ti(III)/Rh(I) early–late heterobimetallic (ELHB) complex (C₆H(2,3,5,6-Me)₄O)₂Ti(μ -OC₆H(2,3,5,6-Me)₄)₂Rh(COD). The nature of all products is not known; however, redox chemistry, in which electron transfer from Ti(III) to Rh(I) occurs is evidenced by the generation of **2** and Rh(0). In addition, ligand transfer reactions giving uncharacterized Rh-alkoxides are suggested by the spectral data. The implications and ramifications for the synthesis of alkoxide bridged ELHB models of bimetallic heterogeneous catalyst systems are discussed.

Key words: titanium phenoxides, redox chemistry, structures.

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Les réactions de phénolates substitués avec le TiCl₄ fournissent les espèces Ti(OAr')₄ [Ar' = C₆H₄(2-*t*-Bu) (1) et Ar' = C₆H(2,3,5,6-Me)₄ (2)]. Le composé Ti(OC₆H₄(2-*t*-Bu))₄ (1) cristallise dans le groupe d'espace tétragonal $P42_1c$, avec a = 15,203(4) et c = 8.026(3) Å, Z = 2 et V = 1855(2) Å³. Le composé Ti(OC₆H(2,3,5,6-Me)₄)₄ (2) cristallise dans le groupe d'espace orthorhombique *Pbcn*, avec a = 16.539(7), b = 16.136(6) et c = 27.716(12) Å, Z = 8 et V = 7397(9) Å³. Dans ces complexes, la meilleure façon de décrire la sphère de coordination du Ti est de la considérer comme pseudo-tétraédrique. Dans le cas du composé 1, une symétrie cristallographique $\tilde{4}$ stricte est imposée. Le complexe 2 présente un comportement voltampérométrique cyclique réversible qui est en accord avec une réduction impliquant un électron et conduisant à l'analogue Ti(III). La réduction chimique du composé 2 à l'aide d'amalgame de sodium conduit à une formation quantitative du (C₆H(2,3,5,6-Me)₄O)₂Ti(μ -OC₆H(2,3,5,6-Me)₄)₂Na(THF)₂(3). La réaction du produit 3 avec du [(COD)Rh(μ -Cl)]₂ ne fournit pas le complexe hétérobimétallique de la fin des premiers termes (ELHB) du Ti(III)/Rh(I), (C₆H(2,3,5,6-Me)₄O)₂Ti(μ -OC₆H(2,3,5,6-Me)₄)₂Rh(COD). La nature de tous les produits n'est pas connue; toutefois, la génération du composé 2 ainsi que du Rh(0) fournit des données expérimentales supportant une chimie d'oxydoréduction impliquant un transfert d'électron du Ti(III) au Rh(I). De plus, les données spectrales suggèrent l'existence de réactions de transferts de ligands conduisant à des alcoolates de Rh qui n'ont pas été caractérisés. On discute des implications de ces résultats et de leurs ramifications pour la synthèse d'ELBM pontés par le biais d'alcoolates qui seraient des modèles de systèmes catalytiques bimétallique hétérogènes. *Mot clés* : phénolates de titane, chimie d'oxydoréduction, structures.

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Introduction

In recent years our research has focused on the synthesis, characterization, and reactivity studies of complexes containing both early, oxophilic metals and late, electron-rich metal centres (1-19). Our interest in such species is prompted by the observation of strong metal-support interactions (SMSI) in heterogeneous catalyst systems (20). This phenomenon arises when late metals are dispersed on an early metal support such as titania. The result is a dramatic alteration of the reactivity patterns compared to dispersions of the same metal on other, non-Lewis acidic supports. The cause of the perturbations in reactivity is not clear, but one possibility that has some experimental support, is the direct role of the early metal in substrate activation (20). Alternatively, it has also been suggested that the support may act as an electron sink and thus the effects of the proximity of a Ti(III) centre on the reactivity of a late metal have come into question (20). In our efforts to study such questions, we have prepared several reducible early-late heterobimetallic (ELHB) species. Our initial efforts in this area involved the use of chelating phosphinethiolate ligands giving complexes of the form shown below (2–4). Structural data support the notion of dative interactions between the electron-rich, late metal and the d^0 Ti(IV) centres. Such metal-metal interactions may provide a vehicle for direct electron communication between the early and late metal centres, and thus may be related to the observations of SMSI. The implied role of reduced Ti centres in SMSI led us to study the redox chemistry of these heterobimetallics. These complexes undergo reversible chemical reduction affording the formally Ti(III)/M(I) (M = Cu, Rh) species. In the case of CP₂Ti(μ -SCH₂CH₂CH₂PPh₂)₂Rh, the observation of coupling of the unpaired electron on Ti to Rh and P further suggests the possibility of a transannular, metal-metal communication (4).

Although these initial systems continue to be of interest, we are actively pursuing synthetic routes to other reducible ELHB compounds that may be more appropriate models for the metal centres in the heterogeneous systems where SMSI are observed. Thus, we have initiated efforts to prepare complexes in which a Ti centre is placed in an oxo environment (17, 18); the reason being that such a Ti environment will more effectively mimic the Ti centres of the support material, TiO₂. In this report, we describe some efforts to that end. The synthesis, characterization, electrochemical and structural studies of two complexes

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M = Rh, n = 1; M = Ni, n = 0

of the general formula $Ti(OAr')_4$ are presented. Chemical reduction of these species with Na affords the Ti(III) species, $Ti(OAr')_4Na(THF)_2$. Attempts to derivatize this reduced material via metal ion exchange employing $[(COD)Rh(\mu-CI)]_2$ failed to yield the desired Ti(III)/Rh(I) ELHB species. Rather, electron transfer occurred affording Ti(IV) and Rh(0). The results of these studies are presented and discussed and the utility of Ti(III) aryloxides for reduced ELHB complex synthesis is considered.

Experimental section

All preparations were done under an atmosphere of dry, O_2 -free N_2 in a Vacuum Atmospheres' Inert Atmosphere glove box. The quality of the atmosphere was maintained employing a 5 cfm blower with a deoxygenation/drying catalyst column and a molecular sieve prepurifier canister. Solvents were reagent grade, distilled from the appropriate drying agents under N_2 , and degassed by the freeze-thaw method at least three times prior to use. ¹H and ¹³C{¹H} NMR experiments were performed using a Bruker AC-300 MHz spectrometer employing trace amounts of protonated solvent as the internal reference. Chemical shifts are reported relative to Si(CH₃)₄. Cyclic voltammetry was recored on a BAS CV-27 employing THF as the solvent, Bu₄NBF₄ as the supporting electrolyte, and Ag/AgCl as the reference electrode. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. Crystalline samples were shipped in ampoules sealed under an atmosphere of N₂.

Preparation of $LiOAr'(Ar' = C_6H_4(2-t-Bu), C_6H(2,3,5,6-Me)_4)$

These salts are prepared in a similar manner and thus a general route is described. HOAr' is stirred in hexane at 0°C while an equivalent of 2.5 M *n*-BuLi is slowly added. The reaction is allowed to stir while warming to 25°C over a 2 h period. The solvent is removed and the residue is washed with hexane. These solids were isolated and manipulated in a dry box and were used without further purification.

Preparation of $Ti(OAr')_4(Ar' = C_6H_4(2-t-Bu), 1; C_6H(2,3,5,6-Me)_4, 2)$

These compounds were prepared in a similar manner and thus only one description is given. To a slurry of $LiOC_6H_4(2-t-Bu)$ (8.23 g, 52.7 mmol) in hexane (50 mL) was slowly added TiCl₄ (2.00 g, 1.16 mL, 10.5 mmol). The reaction was vigorously stirred for 12 h, during which time the mixture became yellow. Filtration of the solution followed by removal of the solvent yields a yellow powder. This material is extracted into benzene, filtered, and the solvent removed.

Recrystallization from pentane affords crystalline compound (yield: 5.85 g, 85%), 1: ¹H NMR (*d*₆-benzene): δ (ppm), 7.37 (d of d, H_d), $|J_{H-H}^3| = 7.1$ Hz, $|J_{H-H}^5| = 1.3$ Hz, 7.19 (d of d, H_a), $|J_{H-H}^3| = 7.8$ Hz, $|J_{H-H}^5| = 1.6$ Hz, 6.91 (d of d of d, H_c), $|J_{H-H}^3| = 7.4$ Hz, 6.80 (d of d of d, H_b), 1.49 (s, 9H). ¹³C{¹H} NMR (*d*₆-benzene): 127.09, 123.31, 123.21, 35.03, 30.33 ppm. *Anal.* calcd.: C 74.52; H 8.13; found; C 74.50; H 8.20, **2**: ¹H NMR (*d*₆-benzene): δ (600 (s, 1H), 2.35 (s, 6H), 2.05 (s, 6H). ¹³C{¹H} NMR (*d*₆-benzene): δ (ppm), 134.15, 128.52, 125.77, 122.82, 19.95, 13.31. *Anal.* calcd.: C 74.52; H 8.13; found: C 74.40; H 8.00.

Generation of $(C_6H(2,3,5,6-Me)_4O)_2Ti(\mu-OC_6H(2,3,5,6-Me)_4)_2$ $Na(THF)_2$, **3**

To a yellow THF solution of 2 (0.070 g, 0.109 mmol) was added sodium amalgam (1.1 equiv. of Na). The mixture was stirred at 25°C for 2 h and the blue THF solution decanted from the amalgam. EPR (THF) g = 1.986.

Reaction of **3** with $[(COD)Rh(\mu-Cl)]_2$

To a THF solution of **3** (0.054 mmol generated as above) was added $a THF solution of <math>[(COD)Rh(\mu-Cl)]_2$ (0.023 g, 0.054 mmol). With the addition of the Rh species the color of the solution changed from blue to greenish/brown. On standing for 24 h the solution became orange/brown and Rh metal plated on the surface of the flask. Monitoring of the reaction was accomplished by EPR and ¹H NMR. No EPR signal was observed. ¹H NMR data show resonances attributable to **1** and other uncharacterized diamagnetic products.

X-ray data collection and reduction

Diffraction experiments for compound 1 were performed on a four-circle Syntex P21 diffractometer with graphite-monochromatized Mo K α radiation ($\lambda = 0.71069$ Å) while the diffraction data for 2 was collected on a four-circle Rigaku AFC6 diffractometer also equipped with a graphite monochromator. The initial orientation matrices were obtained from 15 to 20 machine-centred reflections selected from a rotation photograph in the case of 1 and obtained by a zig-zag search routine in the case of 2. These data were used to determine the crystal systems. Partial rotation photographs around each axis were consistent with a tetragonal crystal system for 1 while intensity measurements of equivalent reflections confirmed the Laue symmetry as mmm for the orthorhombic crystal system of 2. The final lattice parameters and the orientation matrices were determined from 30 and 25 high-angle data $(20^{\circ} < 2\theta < 25^{\circ})$ for 1 and $(20^{\circ} < 2\theta < 24^{\circ})$ for 2, respectively. The observed extinctions and ultimate structure refinements confirmed the space groups $P42_1c$ for 1 and Pbcn for 2. h, k, -l were collected $(4.5^{\circ} < 2\theta < 45.0^{\circ})$ for 1, while 2 and h, k, -l data were collected $(4.5^{\circ} < 2\theta < 50.0^{\circ})$. In each case, three standard reflections were recorded regularly during data collection. The intensities of the standards showed no statistically significant change over the duration of the data collection. The data were processed using the TEXSAN program package.

Structure solution and refinement

Non-hydrogen atomic scattering factors were taken from the literature tabulations (21-23). The heavy atom positions were determined using direct methods. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinement was carried out by using full-matrix least-squares techniques on F, minimizing the function $w(|F_0| - |F_c|)^2$ where the weight, w, is defined as $4F_0^2/2\sigma(F_0^2)$ and F_0 and F_c are the observed and calculated structure factor amplitudes. In the final cycles of the refinement of 1, the titanium, oxygen, and methyl carbon atoms were assigned anisotropic temperature factors, while for 2 only the titanium atom was refined anisotropically. In both cases the phenyl ring carbon atoms were refined as rigid groups with individual isotropic thermal parameters. The hydrogen atom positions were calculated assuming a C-H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. The hydrogen atom contributions were calculated, but not refined. The residual electron densities, in each case, were of no chemical significance. Crystal data and data collection parameters are summarized in Table 1. Tables of positional parameters (Table 2) and selected bond distances and angles (Table 3) are reported. Thermal parameters (Table S1), hydrogen atom parameters (Table S2), and calculated and observed structure factors (Table S3) have been deposited.2

Results and discussion

The room temperature reaction of $TiCl_4$ with excess of the lithium salt of either 2-*t*-butylphenol or 2,3,5,6-tetramethylphenol led to the isolation, following the standard workup, of yellow microcrystalline solids. The isolated products are soluble in benzene, THF, diethyl ether, and hexane and are stable at room temperature for prolonged periods in the absence

²A complete set of data may be purchased from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ont., Canada K1A 0S2.

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TABLE 1.	Crystallographic	parameters
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	Value			
Parameter	Molecule 1	Molecule 2		
Formula	C ₄₀ H ₅₂ O ₄ Ti	C ₄₀ H ₅₂ O ₄ Ti		
Crystal color, form	Yellow blocks	Yellow blocks		
a (Å)	15.203(4)	16.539(7)		
b(A)		16.136(6)		
<i>c</i> (Å)	8.026(3)	27.716(12)		
Crystal system	Tetragonal	Orthorhombic		
Space group	$P\bar{4}2_1c$ (No. 114)	<i>Pbcn</i> (No. 60)		
$V(Å^3)$	1855(2)	7397(9)		
Density $(g \text{ cm}^{-3})$ calcd.	1.15	1.16		
Ζ	2	8		
Crystal dimensions (mm)	$0.40 \times 0.30 \times 0.35$	$0.25 \times 0.28 \times 0.32$		
Absolute coefficient, μ (cm ⁻¹)	2.62	2.63		
Radiation, λ (Å)	Μο Κα (0.71069)	Μο Κα (0.71069)		
<i>T</i> (°C)	24	24		
Scan speed (deg/min)	$2.0-5.0 (\theta/2\theta)$	16 (θ/2θ)		
Scan range (deg)	1.0 below $K\alpha_1$	$0.88 + 0.30 \tan \theta$		
	1.0 above $K\alpha_2$			
Background/scan time ratio	0.5	0.5		
Data collected	1447	4189		
2θ range (deg)	4.5-40.0	4.5-50.0		
Index range	h, k, -l	h, k, -l		
Unique data $F_o^2 > 3\sigma(F_o^2)$	955	852		
Variables	60	138		
R (%)	5.3	8.7		
R_{w} (%)	6.5	8.2		
Largest Δ/σ in final least-squares cycle	0.001	0.000		

of moisture and oxygen. The compounds also quickly degrade in protic or halogenated solvents. The ¹H NMR spectrum of the 2-t-butylphenol derivative showed resonances attributable to the expected aromatic and methyl protons indicative of the incorporation of the phenolate into the product 1. The aromatic region of the ¹H NMR spectrum of **1** shows two doublets of doublets and two overlapping doublets of doublets of doublets (Fig. 1). Homonuclear decoupling experiments were used to confirm the coupling constant assignments. Selective irradiation of the methyl resonances permitted the observation of an NOE enhancement which confirmed the assignment of the resonances as shown in Fig. 1. The data are consistent with conformations of the ring substituents which are symmetric about the Ti atom. Similarly, the 2,3,5,6-tetramethylphenol derivative 2 exhibited the expected singlet resonance arising from the aromatic proton of the phenolate as well as the two singlets from the ortho and meta methyl groups. These data, in addition to the combustion analysis data, are consistent with the formulation of the products as $Ti(OAr')_4$ (Ar' = C₆H₄(2-t-Bu), 1; Ar' = $C_6H(2,3,5,6-Me)_4$, 2). These formulations were subsequently confirmed by X-ray crystallographic studies (vide infra).

Similar reactions involving 2,6-di-*i*-propylphenolate and 2,6-di-*t*-butylphenolate have been described by Rothwell and co-workers (24, 25). In the former case, the isolated products were the homoleptic species $M(OC_6H_3(2,6-i-Pr)_2)_4$ (M = Ti, Zr). In the latter case, the yellow products were identified as $M(OC_6H_3(2,6-t-Bu)_2)_3Cl$ (M = Ti, Zr). Attempts to effect further substitution were not successful. The authors surmized that the steric demands of the *ortho t*-butyl groups precluded the formation of Ti(OAr')_4. Clearly, in the case of the present



complexes, the lesser steric demands of 2-*t*-butylphenolate and 2,3,5,6-tetramethylphenolate permit ligand and substitutent conformations which allow the formation of tetraphenolate derivatives.

Structural studies

The X-ray crystallographic study of 1 showed that the molecule crystallizes in the space group $P42_1c$ with two independent molecules in the unit cell. The symmetry of the unit cell requires the Ti centre to occupy a site of 4 symmetry. The

TABLE 2. Positional parameters(a) Molecule 1

Atom	<i>x</i>	у	Z	B (eq)
Ti	1/2	1/2	0	3.46(4)
0	0.5037(3)	0.4035(2)	0.1250(4)	4.9(2)
C (1)	0.4679(2)	0.3476(2)	0.2325(4)	3.5(1)
C(2)	0.4189(3)	0.3835(2)	0.3629(5)	5.2(1)
C(3)	0.3813(3)	0.3284(3)	0.4824(4)	6.1(1)
C(4)	0.3927(2)	0.2376(2)	0.4714(4)	6.8(2)
C(5)	0.4417(2)	0.2017(2)	0.3410(5)	5.3(1)
C(6)	0.4793(2)	0.2568(2)	0.2216(4)	3.3(1)
$\mathbf{C}(8)$	0.4932(4)	0.2392(3)	-0.0913(7)	5.4(3)
C(7)	0.5334(4)	0.2169(3)	0.0770(7)	4.1(3)
$\mathbf{C}(9)$	0.6286(4)	0.2498(4)	0.0813(8)	6.8(4)
C(10)	0.5376(4)	0.1158(4)	0.0874(9)	7.1(4)
		(b) Molecule 2		
Atom	x	у	Ζ	<i>B</i> (eq)
 Ti(1)	0.8311(3)	0.1314(3)	0.1196(2)	4.0.(2)
0(1)	0.889(1)	0.056(1)	0.0882(6)	5.1(5)
O(2)	0.7791(9)	0.079(1)	0.1659(5)	3.8(4)
O(3)	0.8946(9)	0.209(1)	0.1432(5)	4.2(4)
O(4)	0.763(1)	0.179(1)	0.0776(5)	3.9(4)
$\mathbf{C}(7)$	1.036(1)	0.124(2)	0.0544(9)	5.4(7)
C(8)	1.166(2)	0.002(2)	0.0360(9)	6 7(8)
C(9)	0.982(2)	-0.230(2)	0.081(1)	8(1)
C(10)	0.962(2) 0.852(1)	-0.111(2)	0.001(1)	52(8)
C(17)	0.852(1)	-0.036(2)	0.2257(9)	4 9(7)
C(18)	0.801(2)	-0.050(2)	0.2237(9) 0.328(1)	9(1)
C(10)	0.601(2)	0.030(2) 0.182(2)	0.320(1)	$\frac{9(1)}{8(1)}$
C(20)	0.005(2)	0.102(2)	0.299(1)	6.2(8)
C(27)	1.038(2)	0.139(2)	0.195(1)	7.1(8)
C(28)	1.050(2) 1.150(2)	0.137(2)	0.103(1) 0.221(1)	6.0(8)
C(20)	0.073(2)	0.230(2)	0.221(1) 0.181(1)	6.5(8)
C(20)	0.973(2) 0.848(1)	0.490(2) 0.375(2)	0.131(1) 0.1481(8)	5,7(7)
C(30)	0.040(1)	0.575(2)	0.1431(3) 0.0773(6)	5.7(7)
C(1)	1.023(1)	0.004(1)	0.0773(0)	5.5(8)
C(2)	1.025(1)	-0.025(1)	0.0023(0)	4.3(7)
C(3)	1.0651(6)	-0.110(1)	0.0341(3)	2.9(0)
C(4)	1.072(1)	-0.110(1)	0.0009(3)	3.4(0)
C(3)	0.990(1)	-0.1373(7)	0.0739(3)	3.8(0)
C(0)	0.9333(8)	-0.081(1)	0.0840(3)	4.0(6)
C(11)	0.733(1)	0.077(1)	0.2128(4)	3.7(6)
C(12)	0.760(6)	0.0190(9)	0.2433(0)	3.0(0)
C(13)	0.703(1)	0.0127(8)	0.2911(0)	4.2(7)
C(14)	0.703(1)	0.005(1)	0.3085(4)	5.4(7)
C(15)	0.0072(8)	0.123(1)	0.2780(7)	4.9(0)
. C(10)	0.693(1)	0.1296(8)	0.2301(6)	4.5(7)
C(21)	0.949(1)	0.257(1)	0.1649(5)	4.4(7)
C(22)	1.023(1)	0.2303(7)	0.1833(6)	3.2(6)
C(23)	1.0789(8)	0.288(1)	0.2000(5)	3.2(6)
C(24)	1.061(1)	0.372(1)	0.1984(5)	5.8(7)
C(25)	0.987(1)	0.3992(7)	0.1800(6)	5.4(8)
C(26)	0.9309(8)	0.341(1)	0.1632(5)	3.3(6)
C(31)	0.732(1)	0.181(1)	0.0327(4)	3.5(6)
C(32)	0.7641(8)	0.236(1)	-0.0008(7)	3.2(6)
C(33)	0.733(1)	0.240(1)	-0.0475(6)	4.5(7)
C(34)	0.669(1)	0.188(1)	-0.0606(4)	6.4(8)
C(35)	0.6367(9)	0.132(1)	-0.0270(7)	7.0(8)
C(36)	0.668(1)	0.1288(9)	0.0196(6)	3.4(5)
C (37)	0.637(2)	0.070(2)	0.056(1)	7.4(9)
C(38)	0.567(2)	0.078(2)	-0.042(1)	11(1)
C(39)	0.767(2)	0.293(2)	-0.085(1)	9(1)
C (40)	0.830(2)	0.292(2)	0.0133(9)	5.6(7)

TABLE 3.	Selected	bond	distances	and	angles*
	(<i>a</i>)	Mole	cule 1		

Atom	Ato	m	Distance		Aton	1	Atom	Distance
Ti	0		1.779(3)		C(7)		C(6)	1.546(6)
0	C(1)	1.327(5)		C(8)		C(7)	1.521(8)
C(7)	C(9	ý)	1.532(8)		C(7)		C(10)	1.541(8)
Atom	Atom	Atom	Angle	<u> </u>	Atom	Atom	Atom	Angle
	 т:		108 6(1)					111 2(2)
C(10)	Γ		108.0(1)		0	C(1)		111.3(2)
C(10)	C(I)	C(0)	111.9(4)		U T	C(1)	C(2)	117.2(3)
C (1)	C(1)	C(0)	122.8(3)			0	C(1)	151.9(3)
C(8)	C(I)	C(9)	109.1(5)		C(8)	C(7)	C(10)	106.7(5)
C(7)	C(6)	C(1)	120.1(3)		C(8)	C(7)	C(6)	111.4(4)
C(7)	C(6)	C(5)	119.9(3)		C(9)	C(7)	C(10)	106.6(5)
C(1)	C(6)	C(5)	120.0(3)		C(9)	C(7)	C(6)	111.0(4)
			(<i>b</i>) N	Iolecul	le 2			
Atom	Ato	m	Distance		Aton	1	Atom	Distance
Ti	O(1))	1.78(2)		Ti		O(2)	1.76(2)
Ti	0(3	ý	1.76(2)		Ti		O(4)	1.79(2)
<u>o(1)</u>	C	ý	1.31(2)		O(2)		o(1)	1.37(2)
O(3)	CO	, 1)	1.33(2)		O(4)		C(31)	1.35(2)
C(7)	C(2)	· /	1.53(2) 1.52(3)		C(8)		C(3)	1.50(2)
C(n)	C(2)	<i>)</i>	1.52(5) 1.51(2)		C(0)	、 、	C(5)	1.30(3)
C(9))) \	1.51(5)		C(10	,	C(0)	1.48(3)
C(17)	C(1.	2) 5)	1.50(3)		C(18)	C(13)	1.56(3)
C(19)	C(1,	5)	1.51(3)		C(20)	C(16)	1.49(3)
C(27)	C(22	2)	1.50(3)		C(28))	C(23)	1.53(3)
C(29)	C(2	5)	1.48(3)		C(30))	C(26)	1.54(3)
C(37)	C(30	6)	1.48(3)		C(38)	C(35)	1.51(4)
C(39)	C(3)	3)	1.47(3)		C(40))	C(32)	1.46(3)
Atom	Atom	Atom	Angle		Atom	Atom	Atom	Angle
O(1)	– — – Ti	O(2)	107.1(8)		0(2)	C(11)	C(12)	117(2)
Ōù	Ti	$\overline{O(3)}$	110.2(7)		O(2)	C(1)	C(16)	123(1)
O(1)	Ti	O(4)	108.2(7)		O(2)	Ti	O(3)	1111(7)
C(17)	C(12)	C(11)	100.2(7)		O(2)	Т	O(3)	111.1(7)
C(17)	C(12)	C(12)	121(2) 110(2)		O(2)		O(4)	109 4(9)
C(17)	O(12)	C(13)	162(1)		O(3)		O(4)	100.4(0)
11	O(1)	C(1)	162(1)		C(18)	C(13)	C(12)	123(2)
11	O(2)	$C(\Pi)$	149(1)		C(18)	C(13)	C(14)	117(2)
11	O(3)	C(21)	170(1)		11	O(4)	C(31)	149(1)
O(1)	C(1)	C(2)	121(2)		C(19)	C(15)	C(14)	118(2)
O(1)	C(1)	C(6)	119(1)		C(19)	C(15)	C(16)	121(2)
C(2)	C(1)	C(6)	120(1)		C(7)	C(2)	C(1)	119(2)
C(20)	C(16)	C(11)	117(2)		C(7)	C(2)	C(3)	121(2)
C(20)	C(16)	C(15)	123(2)		C(8)	C(3)	C(2)	122(2)
O(3)	C(21)	C(22)	125(1)		C(8)	C(3)	C(4)	118(2)
O(3)	C(21)	C(26)	115(1)		C(27)	C(22)	C(21)	118(2)
C(0)	C(21)	C(20)	110(1)		C(27)	C(22)	C(21)	110(2)
C(9)	C(3)	C(4)	119(2)		C(27)	C(22)	C(23)	122(2)
C(9)	C(3)		121(2)		$C(2\delta)$	C(23)	C(22)	120(2)
C(10)	C(6)	C(1)	120(2)		C(28)	C(23)	C(24)	120(2)
C(10)	C(6)	C(5)	120(2)		C(29)	C(25)	C(24)	116(2)
C(29)	C(25)	C(26)	124(2)		C(30)	C(26)	C(21)	123(2)
C(30)	C(26)	C(25)	117(2)		O(4)	C(31)	C(32)	119(2)
O(4)	C(31)	C(36)	121(1)		C(40)	C(32)	C(31)	120(2)
C(40)	$\dot{C(32)}$	C(33)	120(2)		C(39)	C(33)	C(32)	122(2)
C(39)	C(33)	C(34)	117(2)		C(38)	C(35)	C(34)	119(2)
C(38)	C(35)	C(36)	121(2)		C(37)	C(36)	C(31)	118(2)
C(27)	C(35)	C(25)	122(2)		C(37)	C(30)	C(31)	110(2)
$\mathcal{C}(\mathcal{I})$	C(30)	C(33)	122(2)					

*Bond distance in Å, bond angles in degrees. Estimated standard deviations in the least significant figure are given in parentheses.



FIG. 2. ORTEP drawing of molecule 1, 20% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity.

consequence of this crystallographically imposed symmetry is that the asymmetric unit contains only a single 2-*t*-butylphenolate ligand. Three other symmetry related ligands complete the coordination sphere of the Ti and maintain the strict 4 symmetry. An ORTEP drawing of molecule **1** is shown in Fig. 2. The closest approach between independent molecules is 2.539 Å (H8—H9).

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A crystallographic study of **2** shows that the compound crystallizes in the space group *Pbcn* with eight molecules in the unit cell. The closest approach between molecules is found to be 2.205 Å (H47—H47). In this case, no crystallographic symmetry is imposed on the individual molecules and thus, the contents of the asymmetric unit is a single molecule of **2**. An ORTEP drawing of **2** is shown in Fig. 3.

Generally, Lewis acidic complexes readily form aggregates both in solution and in the solid state. For example, the complex [Ti(OPh)₄·HOPh] has been shown to be a dimer (26). Smaller homoleptic alkoxide complexes of the early metals form higher aggregates, the nuclearity of which can be dependent on solvent, alkyl substituents and the metal (26). The mononuclearity of **1** and **2** is attributed to the bulk of the ligands. Similar complexes have been previously described where bulky substituents stabilize mononuclear complexes despite the Lewis acidity of the metal centre.

The coordination spheres of the Ti atoms of both 1 and 2 are pseudo-tetrahedral in geometry. In the case of 1, the imposed symmetry results in O—Ti—O' angles of 108.6(1) and 111.3(2)°. In a similar manner, the O—Ti—O' angles about the Ti in 2 fall between 107.1(8)–111.8(7)°. The range of the angles about Ti can be attributed to the orientations of the aryl moieties. The conformation or packing arrangement of the aryl rings appears to be an accommodation of the steric demands of the *ortho* substituents. Closer proximity of these substituents to adjacent rings corresponds to the slightly larger O—Ti—O' angles. The Ti—O distance observed in 1 is 1.779(3) Å while in 2 the Ti—O distances range between 1.76(2) and 1.79(2) Å. These distances are comparable to that of 1.78(1) Å for Ti(OC₆H₃-



FIG. 3. ORTEP drawing of molecule 2, 20% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity.

(2,6-i-Pr)₂)₄ (24) and 1.80(1) Å found for Ti(OC₆H₃(2,6-t-Bu)₂)₃I (24). The Ti—O distances found in 1 and 2 are shorter than both the terminal Ti-O bond distances of 1.86(2) Å found in the related Ti(III) species $(2,6-i-Pr)_2C_6H_3O_2Ti(\mu-OC_6H_3(2,6-i-Pr)_2C_6H_3O_2)$ $i-Pr_{2}_{4}Na(THF)_{2}$ (25) and the Ti—O distance of 1.807(8) Å found in Ti(OC₆H₃(2,6-t-Bu)₂)(THF)₂Cl₂ (27). This is consistent with the greater π -acceptor ability of Ti(IV) compared to that of Ti(III). The relatively short Ti---O distances are consistent with the proposition of Ti—O $d\pi$ — $p\pi$ bonding. Such π interactions between a Lewis acidic titanium centre and oxygen, nitrogen, and phosphorus donors has been previously suggested (16-19). The Ti-O-C angle found in 1 is 151.9(3)°. For 2 the corresponding angles are 149(1), 149(1), 162(1), and 170(1)°. The corresponding angles in $Ti(OC_6H_3)$ $(2,6-i-Pr)_{2}_{4}$ were found to be 166.1(3) and 164.5(3)° (24) while in $Ti(OC_6H_3(2,6-t-Bu)_2)(THF)_2Cl_2$ the Ti-O-C angle is 174.2(9)° (27). Presumably, the broad range observed for the Ti-O-C angles is a reflection of the structural compromise between the steric demands of the substituted phenoxides and the Lewis acidity of the metal centre. Bond distances and angles within the aryl substituents are as expected and require no further comment.

Redox chemistry

Cyclic voltammetric studies of **2** were performed in THF employing Bu₄NBF₄ as the supporting electrolyte and a Ag/AgCl electrode as the reference. The results are illustrated in Fig. 4. A quasi-reversible wave is observed at -1.19 V relative to Ag/AgCl. The peak separation of 220 mV is substantially greater than that expected for a completely reversible one-electron transfer, nonetheless repetitive scans at scan rates between 20 and 500 mV/s showed no decay in the current. The potential at which the redox chemistry occurs is consistent with a Ti(IV)/Ti(III) redox couple suggesting that the reduced species being generated is [Ti(OC₆H(2,3,5,6-Me)₄)₄]⁻. Chemical reduction of **2** is achieved employing sodium. The EPR spectrum of the blue THF solution of **3** shows a single centre band resonance at g = 1.986, consistent with the



FIG. 4. Cyclic voltamogram of 2 in THF employing NBu_4BF_4 as the supporting electrolyte. The potential shown are referenced to Ag/AgCl electrode. The scan speed employed was 250 mV/s.



generation of a metal-based radical. The *extremely* air-sensitive Ti(III) species **3** is formulated as $(C_6H(2,3,5,6-Me)_4O)_2Ti(\mu-OC_6H(2,3,5,6-Me)_4)_2Na(THF)_2$ by analogy to the products of reduction of some related homoleptic early metal aryl-oxides described by Rothwell and co-workers (24).

Attempts to employ this anion as a metalloligand and effect complexation to Rh were undertaken. Reaction of 3 with [(COD)Rh(µ-Cl)]₂ was performed in THF under strictly anaerobic conditions. Upon addition of the Rh species the solution becomes greenish/brown. Ultimately a grey precipitate appears and the solution becomes orange/brown. Monitoring of the reaction by EPR shows loss of the resonance attributable to 3. The NMR of the final solution indicates the presence of 2 and other diamagnetic products. In addition Rh metal plates out on the surface of the flask. These data suggest a redox reaction in which the Ti(III) species 3 is oxidized to 2 with concurrent reduction of the Rh(I) to Rh(0). Alternatively, Rh-aryloxide species may be formed in ligand transfer reactions. Similar thiolate ligand transfers from Ti to Rh have been previously described (28). The formation of Rh-aryloxide species may account for the observation of other diamagnetic products; however, no single Rh-containing species could be isolated from the reaction mixtures. It may be that the reaction of **3** with Rh(I) chloride proceeds through the desired ELHB species $[(C_6H(2,3,5,6-Me)_4O)_2Ti(\mu-OC_6H(2,3,5,6-Me)_4)_2Rh(COD)];$ however, no evidence for the existence of this Ti(III)/Rh(I) intermediate has been observed (Scheme 1). This is in contrast to

thiolato- and phosphido-bridged systems where Ti(III)/Rh(I) ELHB complexes can be isolated and unequivocally characterized (2-4, 16).

It appears that the oxidation potential of the Ti(III) species **3** is too negative to permit the use of this species as a metalloligand for Rh(I). It may be possible to shift the redox potential in a positive direction by tuning the nature of the substituents on the phenoxides. Presumably more electron-withdrawing substituents will help to stabilize Ti(III) and thus inhibit electron transfer. Alternatively strong electron-donor ligands on Rh would make the Rh centre less electron accepting and thus also serve to inhibit electron transfer from Ti(III). These approaches are being pursued in continuing efforts to mimic the heterogeneous catalyst systems.

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