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Chemical and Electrochemical Reduction of Titanium(IV) Aryloxides

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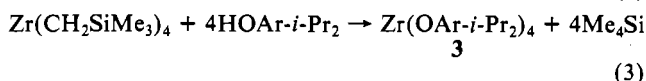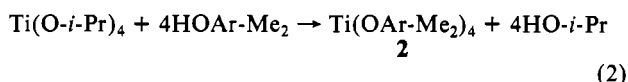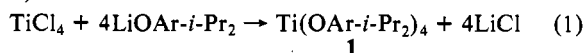
A number of mononuclear, homoleptic aryloxides of Ti(IV) and Zr(IV) have been synthesized and their chemical and electro-chemical reduction behavior investigated. In particular the complex $Ti(OAr-i-Pr_2)_4$ ($OAr-i-Pr_2$ = 2,6-diisopropylphenoxide) undergoes a reversible, one-electron reduction in tetrahydrofuran to the anion $Ti(OAr-i-Pr_2)_4^-$, as demonstrated by both its cyclic voltammogram and electrochemical generation of a solution of the d^1 complex. Furthermore, sodium amalgam reduction allows the high-yield synthesis of the salt complex $[(thf)_2Na\cdot Ti(OAr-i-Pr_2)_4]$. This salt reacts with pyridine to give the purple, neutral complex $Ti(OAr-i-Pr_2)_3(py)_2$. X-ray diffraction studies of $Ti(OAr-i-Pr_2)_4$ and its one-electron-reduced anion have allowed a comparison of the bonding properties of titanium(III) and titanium(IV) in similar coordination environments. Crystal data for $Ti(OAr-i-Pr_2)_4$ at −160 °C: a = 20.811 (8) Å, b = 11.068 (3) Å, c = 19.797 (8) Å, β = 75.48 (2)°, Z = 4, and d_{calcd} = 1.139 g cm^{-3} in space group $I2/a$. Crystal data for $[(thf)_2NaTi(OAr-i-Pr_2)_4]$ at −159 °C: a = 20.888 (13) Å, b = 12.958 (9) Å, c = 19.775 (14) Å, Z = 4, and d_{calcd} = 1.147 g cm^{-3} in space group $P2_12_12_1$. The solid-state structure of $Ti(OAr-i-Pr_2)_4$ shows the titanium atom surrounded by four aryloxides in an almost perfect tetrahedral geometry. The Ti–O distances are short (1.78 Å, average), consistent with significant oxygen-p to metal-d π-bonding. In the salt complex $[(thf)_2Na\cdot Ti(OAr'-i-Pr_2)_4]$ the titanium remains coordinated to four aryloxides, but now two of them are bridging to the sodium atom, which also contains two coordinated thf molecules.

Introduction

The lower valent compounds of titanium have been shown to demonstrate a wide range of inorganic and organometallic reactivity.[1,2] Besides their important involvement in Ziegler–Natta polymerization processes,[3] a large number of studies have implicated reduced titanium species (particularly Ti^{2+}) in the coordination and activation of dinitrogen.[4] Use of suitable ligation (C_5Me_5) has allowed discrete dinitrogen complexes of titanium to be isolated and characterized.[5] Other studies have shown that the reduction of titanium alkoxides[6] or mixed halophenoxides[7] leads to a range of not very well-defined low-valent titanium compounds containing dinitrogen and/or hydride ligation. We wish to report here our initial findings concerning both the chemical and electrochemical reduction of titanium(IV) aryloxides and in particular compounds containing 2,6-dialkylphenoxide ligation, which essentially maintains mononuclearity for the metal-containing species. Furthermore the use of this type of ligation has allowed us to structurally compare the coordination properties of titanium(III) and titanium(IV) in similar coordination environments.

Results and Discussion

We have recently shown that use of the ligand 2,6-di-*tert*-butylphenoxide (OAr') allows the isolation of a number of interesting mononuclear derivatives of both the group 4[18] and 5 metals.[8,9] With Ti, Zr, and Hf a maximum of only three of these extremely bulky groups could be attached to the metal atom, giving compounds of stoichiometry $M(OAr')_3X$ (X = halide) and in the case of titanium a blue, mononuclear, paramagnetic complex, $Ti(OAr')_3$.[9] Use of the sterically less demanding 2,6-diisopropyl- and 2,6-dimethylphenol ($HOAr-i-Pr_2$ and $HOAr-Me_2$) allows the ready synthesis of the homoleptic compounds $M(OAr^*)_4$ (M = Ti, Zr) in excellent yields by a number of different synthetic routes (eq 1–3).

$$TiCl_4 + 4LiOAr-i-Pr_2 \rightarrow Ti(OAr-i-Pr_2)_4 + 4LiCl \quad (1)$$
$$\mathbf{1}$$

$$Ti(O-i-Pr)_4 + 4HOAr-Me_2 \rightarrow Ti(OAr-Me_2)_4 + 4HO-i-Pr$$
$$\mathbf{2}$$
$$(2)$$

$$Zr(CH_2SiMe_3)_4 + 4HOAr-i-Pr_2 \rightarrow Zr(OAr-i-Pr_2)_4 + 4Me_4Si$$
$$\mathbf{3}$$
$$(3)$$

The reaction between $TiCl_4$ and substituted phenols in the presence of a base (pyridine) was not a suitable method of syn-thesis, giving a mixture of products. Compounds **1–3** are yellow (M = Ti) or white (M = Zr) moisture-sensitive crystalline materials. In both the ^1H and ^{13}C NMR spectra only one set of aryloxide resonances is observed. This fact together with the lack of any M_2-containing species in the mass spectra was taken as an indication of the mononuclearity of the compounds. This was later confirmed by an X-ray diffraction study of $Ti(OAr-i-Pr_2)_4$ (**1**) (vide infra).

An electrochemical study (cyclic voltammetry, coulometry, preparative electrolysis) of **1** in tetrahydrofuran (thf) with 0.2 M tetrabutylammonium hexafluorophosphate (TBAH) as supporting electrolyte reveals the presence in the cyclic voltammogram of a single, reversible one-electron reduction at −1.35 V (vs. Ag pseudoreference electrode) (Figure 1). The reversibility of the electron transfer was judged by the ratio $i_{p,a}/i_{p,c}$ = 1 for scan rates between 20 and 500 mV/s, with the peak spread of the wave being identical with that of the Cp_2Fe^+/Cp_2Fe couple under identical conditions. Controlled-potential reduction at $E_{p,c}$ results in the formation of a light green solution, which exhibits an identical cyclic voltammogram except that the wave is now an oxidation. Electrochemical reoxidation of these solutions regenerates yellow solutions of $Ti(OAr-i-Pr_2)_4$ displaying an cyclic voltammogram indistinguishable from that of the original sample. These data are hence consistent with the reaction shown (eq 4) in which

$$Ti(OAr-i-Pr_2)_4 + e^- \rightleftarrows Ti(OAr-i-Pr_2)_4^- \quad (4)$$
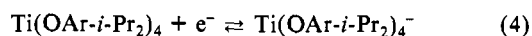
electron transfer between the Ti(IV) and Ti(III) species is completely reversible in the thf/TBAH solution.

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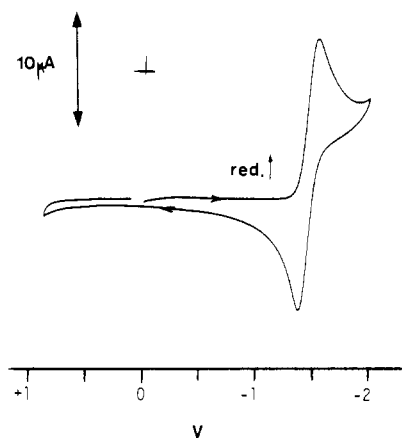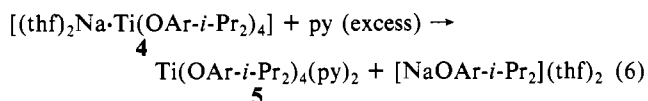[†] Purdue University.
[‡] Indiana University.

Figure 1. Cyclic voltammogram of Ti(OAr-*i*-Pr$_2$)$_4$ (**1**) in thf/0.2 M TBAH using a Pt-disk electrode. The scan rate is 25 mV/S, and potentials are relative to a Ag pseudoreference electrode. Under these experimental conditions the Cp$_2$Fe$^+$/Cp$_2$Fe couple lies at +0.47 V.

Attempts to isolate derivatives of the monoanion proved successful. Hence addition of sodium amalgam (1.1 equiv of Na/Ti) to a yellow thf solution of Ti(OAr-*i*-Pr$_2$)$_4$ rapidly generated a deep green solution. Removal of solvent gave almost quantitative yields of a light blue complex, [(thf)$_2$Na·Ti(OAr-*i*-Pr$_2$)$_4$] (**4**). Microanalytical data alone could not determine the number of thf solvent molecules, but a single-crystal diffraction study of **4** showed the presence of two (vide infra). When **4** is dissolved in thf/TBAH, solutions of **4** exhibit cyclic voltammograms similar to that of electrochemically reduced **1** while a broad signal is observed in the EPR spectrum, presumably due to the d^1 monoanion.

These results indicate that in thf dissociation of aryloxide anion is not favorable (eq 5) and contrasts with the case of the isolated,
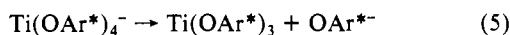
$$Ti(OAr^*)_4^- \rightarrow Ti(OAr^*)_3 + OAr^{*-} \qquad (5)$$

blue Ti(OAr')$_3$ (OAr' = 2,6-di-*tert*-butylphenoxide) where association of more bulky OAr' does not occur.[9] However, neutral Ti(III) derivatives of OAr-*i*-Pr$_2$ can be obtained on addition of a neutral donor ligand such as pyridine. Hence, light blue-green toluene solutions of (**4**) immediately turn purple on addition of pyridine. Removal of solvent followed by extraction then yields the extremely air- and moisture-sensitive compound Ti(OAr-*i*-Pr$_2$)$_3$(py)$_2$ (**5**) as deep purple crystals from hexane. The superior coordination properties of pyridine compared to thf has hence facilitated aryloxide dissociation (eq 6).

$$[(thf)_2Na·Ti(OAr\text{-}i\text{-}Pr_2)_4] + py \text{ (excess)} \rightarrow$$
$$\underset{\textbf{4}}{}$$
$$Ti(OAr\text{-}i\text{-}Pr_2)_4(py)_2 + [NaOAr\text{-}i\text{-}Pr_2](thf)_2 \qquad (6)$$
$$\underset{\textbf{5}}{}$$

An alternate route to Ti(III) complexes of 2,6-diisopropylphenoxide (OAr-*i*-Pr$_2$) involved reaction of TiCl$_3$(NMe$_2$)$_2$ with LiOAr-*i*-Pr$_2$ directly. With the more sterically demanding 2,6-di-*tert*-butylphenoxide this method led to the isolation of the blue, paramagnetic Ti(OAr-*t*-Bu$_2$)$_3$.[9] However, with LiOAr-*i*-Pr$_2$ only an insoluble brown powder was obtained from benzene solution. Microanalysis indicated the presence of chloride ion in this product, which we believe to be a mixed haloaryloxide of titanium(III), Li$_x$Ti(OAr-*i*-Pr$_2$)$_3$Cl$_x$. However, suspensions of this brown solid react immediately with pyridine to give deep purple solutions of Ti(OAr-*i*-Pr$_2$)$_3$(py)$_2$ (**5**).

Although the complex Ti(OAr-Me$_2$)$_4$ (**2**) exhibits electrochemical behavior similar to that of **1**, its chemical reduction with Na/Hg leads to an ill-defined soluble green solid. The cyclic voltammogram of this complex consists only of broad irreversible waves. However, when the complex is treated with pyridine, deep purple solutions are obtained, but as yet the products of this reaction have proved difficult to characterize.

Solid-State Structures of Ti(OAr-*i*-Pr$_2$)$_4$ (1) and [(thf)$_2$Na·Ti(OAr-*i*-Pr$_2$)$_4$] (4). Table I contains the crystallographic data for these two compounds while Tables II–V contain the fractional

Table I. Crystallographic Data for Compounds 1 and 4

	1	4
formula	TiC$_{48}$H$_{68}$O$_4$	TiC$_{56}$H$_{48}$O$_6$Na
fw	757.96	924.17
space group	*I2/a*	*P2$_1$2$_1$2$_1$*
a, Å	20.811 (8)	20.888 (13)
b, Å	11.068 (3)	12.958 (9)
c, Å	19.797 (8)	19.775 (14)
β, deg	75.48 (2)	
Z	4	4
V, Å^3	4414.3	5352.7
d$_{calcd}$, g/cm^3	1.139	1.147
cryst size, mm	0.14 × 0.14 × 0.16	0.24 × 0.20 × 0.22
cryst color	yellow	blue-green
radiation	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
linear abs coeff, cm^{-1}	2.289	2.088
temp, °C	−160	−159
detector aperture	3.0 mm wide × 4.0 mm high; 22.5 cm from crystal	
sample to source dist, cm	23.5	23.5
takeoff angle, deg	2.0	2.0
scan speed, deg/min	4.0	4.0
scan width, deg	2.0 + 0.692 tan θ	2.0 + 0.692 tan θ
bkgd counts, s	8	8
2θ range, deg	6–45	6–45
no. of data collcd	3150	4000
no. of unique data	2871	3911
no. of unique data with F$_o$ > 2.33σ(F)	2364	1810
R(F)	0.0704	0.0689
R$_w$(F)	0.0739	0.0657
goodness of fit	1.641	0.968
largest Δ/σ	0.05	0.05

Table II. Fractional Coordinates and Isotropic Thermal Parameters for Ti(OAr-*i*-Pr$_2$)$_4$ (1)

atom	10^4x	10^4y	10^4z	10B$_{iso}$, Å^2
Ti(1)	7500^a	2051 (1)	5000^a	26
O(2)	7847 (1)	1129 (3)	4261 (1)	35
C(3)	8156 (2)	246 (4)	3812 (2)	29
C(4)	8849 (2)	256 (4)	3584 (2)	29
C(5)	9138 (2)	−659 (5)	3136 (3)	39
C(6)	8768 (3)	−1531 (5)	2916 (3)	44
C(7)	8087 (2)	−1505 (5)	3144 (3)	40
C(8)	7766 (2)	−634 (4)	3595 (2)	31
C(9)	9257 (2)	1219 (5)	3831 (2)	35
C(10)	9474 (3)	799 (6)	4466 (3)	58
C(11)	9849 (3)	1638 (6)	3272 (3)	46
C(12)	7013 (2)	−626 (5)	3868 (3)	42
C(13)	6666 (4)	−802 (15)	3319 (5)	169
C(14)	6802 (4)	−1447 (8)	4487 (6)	115
O(15)	6855 (1)	2972 (3)	4834 (1)	35
C(16)	6449 (2)	3916 (4)	4778 (2)	31
C(17)	6237 (2)	3998 (5)	4160 (3)	42
C(18)	5867 (3)	5000 (5)	4085 (4)	62
C(19)	5699 (4)	5860 (6)	4592 (4)	73
C(20)	5898 (3)	5748 (5)	5203 (3)	53
C(21)	6277 (2)	4767 (4)	5309 (2)	37
C(22)	6407 (3)	3031 (6)	3601 (3)	49
C(23)	5792 (5)	2367 (11)	3547 (4)	120
C(24)	6765 (4)	3512 (7)	2894 (4)	84
C(25)	6501 (3)	4667 (5)	5975 (3)	48
C(26)	7032 (3)	5559 (6)	6008 (3)	54
C(27)	5912 (4)	4817 (7)	6616 (3)	72

^{a} These parameters were not varied.

coordinates and some selected bond distances and angles. ORTEP views along with the numbering scheme are given in Figures 2 and 3.

One of the most widely studied properties of early-transition-metal alkoxides, and particularly those of the group 4 metals, is the molecular complexities of the compounds both in solution and in the solid state.[10,11] For small alkoxides such as methoxide and

Table III. Fractional Coordinates and Isotropic Thermal Parameters for [Ti(OAr-*i*-Pr₂)₄·Na(thf)₂] (4)

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å²
Ti(1)	-7297 (1)	-3101 (2)	-8310 (1)	13
Na(2)	-6754 (3)	-1881 (5)	-9679 (3)	24
O(3)	-7311 (5)	-1702 (7)	-8679 (4)	20
C(4)	-7643 (8)	-792 (12)	-8618 (8)	21 (3)
C(5)	-8184 (8)	-636 (13)	-9023 (8)	23 (4)
C(6)	-8475 (8)	332 (13)	-8997 (8)	21 (3)
C(7)	-8242 (9)	1067 (13)	-8570 (9)	29 (4)
C(8)	-7729 (9)	906 (13)	-8153 (8)	31 (4)
C(9)	-7427 (7)	-49 (12)	-8160 (8)	20 (3)
C(10)	-8430 (8)	-1457 (13)	-9512 (8)	28 (4)
C(11)	-9139 (9)	-1686 (15)	-9377 (9)	36 (4)
C(12)	-8314 (9)	-1158 (14)	-10249 (9)	35 (4)
C(13)	-6867 (9)	-251 (13)	-7715 (9)	25 (4)
C(14)	-6235 (8)	-10 (14)	-8075 (9)	29 (4)
C(15)	-6882 (8)	288 (13)	-7031 (9)	31 (4)
O(16)	-6751 (5)	-3408 (8)	-9089 (5)	20
C(17)	-6383 (7)	-4186 (11)	-9342 (7)	10 (3)
C(18)	-6634 (8)	-4908 (12)	-9807 (8)	19 (3)
C(19)	-6218 (7)	-5578 (12)	-10110 (7)	14 (3)
C(20)	-5569 (8)	-5620 (13)	-9947 (8)	23 (4)
C(21)	-5348 (7)	-4951 (12)	-9449 (8)	18 (3)
C(22)	-5730 (7)	-4202 (11)	-9143 (7)	15 (3)
C(23)	-7337 (8)	-4916 (13)	-9965 (8)	26 (3)
C(24)	-7611 (9)	-5974 (14)	-9958 (9)	35 (4)
C(25)	-7448 (10)	-4417 (16)	-10663 (10)	53 (5)
C(26)	-5471 (7)	-3458 (12)	-8620 (8)	21 (3)
C(27)	-5257 (8)	-2468 (14)	-8952 (9)	30 (4)
C(28)	-4941 (8)	-3892 (13)	-8183 (9)	30 (4)
O(29)	-6815 (5)	-3400 (8)	-7547 (5)	16
C(30)	-6464 (7)	-3988 (11)	-7127 (7)	12 (3)
C(31)	-6132 (7)	-3525 (12)	-6591 (8)	20 (3)
C(32)	-5775 (8)	-4147 (12)	-6152 (8)	19 (3)
C(33)	-5747 (8)	-5221 (12)	-6256 (8)	20 (3)
C(34)	-6062 (7)	-5676 (12)	-6792 (8)	20 (3)
C(35)	-6450 (7)	-5070 (12)	-7225 (7)	16 (3)
C(36)	-6124 (7)	-2357 (11)	-6502 (7)	13 (3)
C(37)	-6216 (8)	-1993 (14)	-5759 (8)	27 (4)
C(38)	-5525 (8)	-1919 (15)	-6796 (9)	38 (4)
C(39)	-6807 (8)	-5559 (12)	-7809 (8)	18 (3)
C(40)	-6465 (8)	-6472 (13)	-8117 (9)	33 (4)
C(41)	-7467 (8)	-5933 (13)	-7554 (8)	25 (4)
O(42)	-8145 (5)	-3562 (7)	-8332 (5)	20
C(43)	-8659 (8)	-3721 (12)	-7954 (8)	19 (3)
C(44)	-8807 (7)	-3104 (14)	-7405 (8)	21 (3)
C(45)	-9346 (8)	-3314 (13)	-7001 (8)	30 (4)
C(46)	-9728 (9)	-4158 (15)	-7149 (10)	37 (4)
C(47)	-9588 (9)	-4788 (14)	-7696 (9)	32 (4)
C(48)	-9067 (7)	-4588 (12)	-8100 (8)	20 (3)
C(49)	-8390 (7)	-2160 (12)	-7217 (7)	19 (3)
C(50)	-8021 (7)	-2351 (12)	-6565 (8)	23 (3)
C(51)	-8769 (9)	-1147 (14)	-7186 (9)	31 (4)
C(52)	-8915 (7)	-5221 (12)	-8729 (8)	22 (3)
C(53)	-9093 (8)	-4591 (13)	-9364 (9)	24 (4)
C(54)	-9267 (9)	-6259 (14)	-8731 (9)	35 (4)
O(55)	-6347 (5)	-2298 (8)	-10723 (5)	26
C(56)	-6579 (9)	-1777 (16)	-11327 (9)	41 (4)
C(57)	-6124 (11)	-2130 (18)	-11875 (11)	56 (5)
C(58)	-5630 (10)	-2702 (16)	-11583 (12)	56 (5)
C(59)	-5828 (9)	-2964 (15)	-10886 (9)	35 (4)
O(60)	-6506 (6)	-189 (8)	-9909 (6)	28
C(61)	-5858 (10)	82 (16)	-10068 (10)	43 (5)
C(62)	-5806 (11)	1226 (17)	-10039 (11)	55 (5)
C(63)	-6413 (10)	1570 (16)	-9685 (10)	51 (5)
C(64)	-6883 (10)	735 (16)	-9863 (10)	46 (5)

Table IV. Selected Bond Distances (Å) and Angles (deg) for Ti(OAr-*i*-Pr₂)₄ (1)

Ti(1)-O(2)	1.781 (3)	Ti(1)-O(15)	1.780 (3)
O(2)-Ti-O(2)′	110.1 (2)	O(15)-Ti-O(15)′	110.1 (2)
O(2)-Ti-O(15)	110.2 (1)		
Ti-O(2)-C(3)	166.1 (3)	Ti-O(15)-C(16)	164.5 (3)

ethoxide, tetrameric clusters have been observed in the crystals. Solution studies show that tetramers, trimers, and dimers are

Table V. Selected Bond Distances and Angles (deg) for [Ti(OAr-*i*-Pr₂)₄·Na(thf)₂] (4)

Ti(1)-O(3)	1.95 (1)	Na(2)-O(3)	2.31 (1)
Ti(1)-O(16)	1.96 (1)	Na(2)-O(16)	2.30 (1)
Ti(1)-O(16)	1.86 (1)	Na(2)-O(55)	2.30 (1)
Ti(1)-O(42)	1.87 (1)	Na(2)-O(60)	2.30 (1)
O(3)-Ti-O(16)	84.5 (4)	O(3)-Ti(1)-O(42)	105.9 (5)
O(3)-Ti(1)-O(29)	120.3 (5)	O(16)-Ti-O(42)	117.8 (5)
Ti(1)-O(3)-C(4)	140.5 (9)	Ti(1)-O(29)-C(30)	156.5 (9)
Ti(1)-O(16)-C(17)	140.1 (9)	Ti(1)-O(42)-C(43)	143.6 (10)
Ti(1)-O(3)-Na(2)	102.6 (5)	Ti(1)-O(16)-Na(2)	102.9 (5)

commonly formed, with the *tert*-butoxide being shown to be monomeric in solution. The ready formation of oligomers in this way reflects both the electron deficiency of the metal in a [Ti-(OR)₄] unit and also the ability of OR ligands to readily become doubly and triply bridging. Previously no homoleptic phenoxides of the group 4 metals had been structurally characterized although the compound [Ti(OPh)₄·PhOH] has been shown to be dimeric with bridging phenoxo groups, the metal thus achieving an octahedral environment.[12] Compound 1 thus represents the first structurally characterized four-coordinate aryloxide of the group 4 metals. It can be seen that the coordination environment is almost perfectly tetrahedral with O–Ti–O angles of 110.1 ± 0.1° (average). The orientation of the aryl rings is such that a crystallographic C_2 axis is present. The presence of significant oxygen to metal π-bonding is shown by both the very short Ti–O distances of 1.78 Å (average) and large Ti–O–Ar angles of 165° (average). The orientation of the *i*-Pr groups on OAr can be seen to be such that steric interaction with the metal is reduced as much as possible. This is done by forming conformations in which the Me₂C–H bond is pointing almost directly at the metal atom. However, large thermal ellipsoids for some of the methyl carbon atoms indicate that a certain amount of conformational flexibility is present in the solid state.

It can be seen from Figure 3 that the titanium atom remains four-coordinate in the salt complex 4. However, two of the coordinated aryloxides are now involved in forming oxygen bridges between the titanium and the sodium atom to which the thf molecules are bound. Hence both metal atoms have a four-coordinate oxygen environment, sharing two common oxygen atoms. It is interesting to compare the Ti–O bonding in compounds 1 and 4 in view of the differing metal oxidation states. As stated previously the short Ti–O distances in 1 are consistent with significant oxygen-p to metal-d π-bonding. Under T_d symmetry this π-bonding would involve donation to the e (d_{z^2}, $d_{x^2-y^2}$) set of orbitals. However, for reduced complex 4 the extra electron will go into this e set, and one would therefore expect to see (besides a Jahn–Teller distortion) a decrease in oxygen to metal π-bonding. Although the structure of 4 is not as accurate as one would like, it can still be seen that there is an overall increase in Ti–O distances on reduction; compare terminal distances in 4 of 1.86 (2) Å with 1.780 (3) Å in 1. As one would expect, the bridging aryloxides in 4 have even longer Ti–O distances of 1.95 (1) Å. Although less reliable, the Ti–O–Ar angles are also consistent with less π-bonding in 4 than 1; compare 150 (5)° and 165 (1)°, respectively, for the terminal aryloxides. However, the presence of two aryloxides bridging between the titanium and sodium atoms unfortunately complicates the correlation of Ti–O distances between the two compounds.

Electronic Spectra of Complexes. The yellow color of the d⁰ tetrakis(aryloxo) complexes 1 and 2 is caused by an intense absorption centered at 310 (1) or 330 nm (2), which tails off into the visible region (Table VI). This broad band we assign as being due to a ligand to metal charge-transfer transition involving the

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(11) Coffindaffer, T. W.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2906.

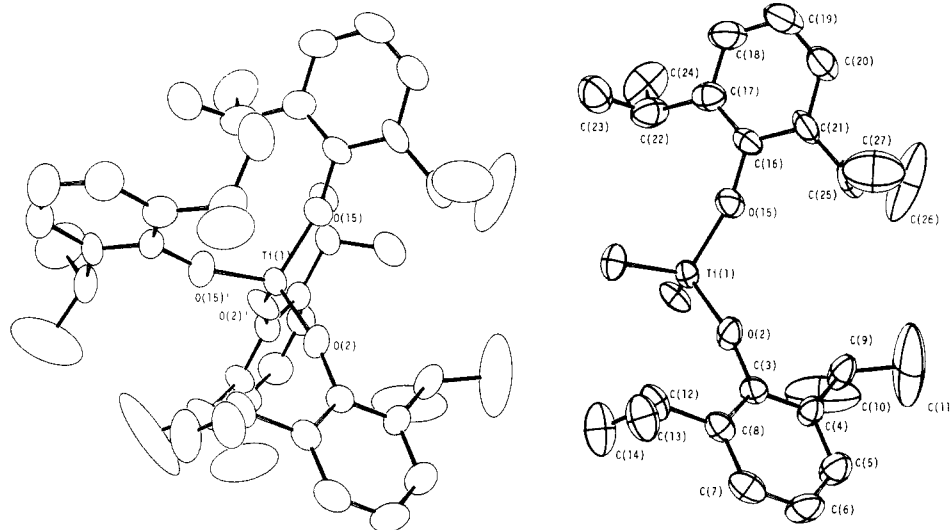(12) Malhotra, K. C.; Martin, R. L. *J. Organomet. Chem.* **1982**, *239*, 159.

Figure 2. ORTEP drawing and numbering scheme for Ti(OAr-*i*-Pr$_2$)$_4$ (**1**). Due to the extremely congested coordination sphere an ORTEP showing only two of the aryloxide rings is also given. The other aryloxides are related by a C_2 axis.
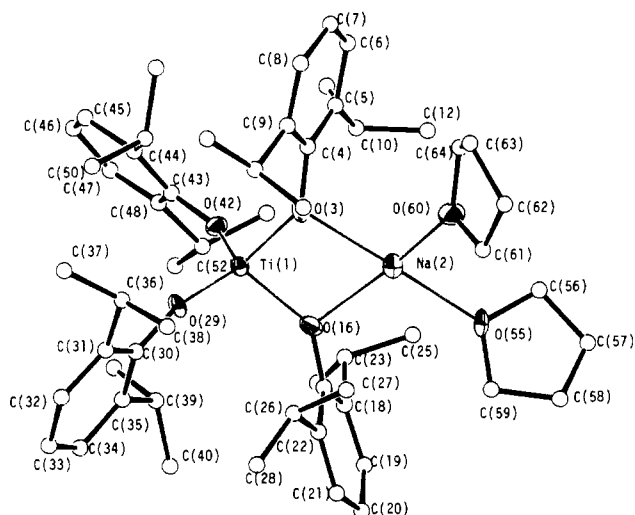

Figure 3. ORTEP view and numbering scheme for [(thf)$_2$Na·Ti(OAr-*i*-Pr$_2$)$_4$] (**4**).

Table VI. Electrochemical and Electronic Spectral Data^a

compd	$E_{1/2}$/V	λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1}))
Ti(OAr-*i*-Pr$_2$)$_4$ (**1**)	−1.35 (reducn)	310 (12 500)
Ti(OAr-Me$_2$)$_4$ (**2**)	−1.42 (reducn)	330 (8000)
Ti(OAr-*i*-Pr$_2$)$_4^-$ (**4**)	−1.40 (oxidn)	970 (149)
Ti(OAr-*i*-Pr$_2$)$_3$(py)$_2$ (**5**)	−0.05 (oxidn)^b	580 (575)
	−1.60 (reducn)^c	920 (114)

^{a} In volts vs. a Ag pseudoreference electrode. ^{b} Irreversible, $E_{p,a}$ quoted. ^{c} Irreversible, $E_{p,c}$ quoted.

oxygen lone pair (2p) electrons. A relatively sharp absorption band is also present centered around 275 nm, and this we assign as due to the lowest lying π–π* transition of the aryloxide aromatic rings.[13] In the case of the colorless zirconium compound Zr-(OAr-*i*-Pr$_2$)$_4$ (**3**) the 275-nm band is still present, but the LMCT band has been drastically blue-shifted below 250 nm and cannot be accurately assigned.

The greenish blue color of solutions of the one-electron-reduced complex (**4**) is due to a very broad, weak transition at 970 nm, which corresponds to the $E_g \rightarrow T_{2g}$ (d–d) transition. Strong LMCT bands are still present below 320 nm. Hence a value of Δ_t for titanium(III) surrounded by aryloxide ligation can be

assigned as 10 300 cm^{-1}. Analogous monomeric complexes of the type TiX$_4^-$ are unknown, although spectroscopic data are available on TiX$_6^{3-}$ salts.[14]

The five-coordinate complex Ti(OAr-*i*-Pr$_2$)$_3$(py)$_2$ (**5**) is stoichiometrically related to a series of complexes TiX$_3$(L)$_2$ (X = halide, L = neutral donor ligand) originally studied by Fowles.[15,16] The typical structure of these complexes is trigonal bipyramidal with trans, axial ligands L. Two d–d transitions are theoretically predicted and observed between 14 000 and 16 000 cm^{-1} (^{2}E″ → ^{2}A$_1'$) and between 5000 and 8000 cm^{-1} (^{2}E″ → ^{2}E′). For deep purple **5**, two bands are again observed at 580 nm (17 300 nm^{-1}) and 920 nm (10 870 cm^{-1}). Hence, presumably this compound adopts an analogous structure with trans-pyridine atoms. The slightly higher energy of these bands compared to those of the chloro analogues is not readily explained.

Experimental Section

All manipulations were carried out by using standard techniques to preclude exposure to either moisture or oxygen. Analyses were carried out by either Galbraith Microanalytic Service or the internal service at Purdue. Lithium aryloxides were synthesized as described previously.[8,9] ^{1}H and ^{13}C NMR spectra were obtained on a Varian Associates XL-200 while EPR measurements were made in the nonaqueous cavity of a Varian Associates E-line Century Series spectrometer.

Cyclic voltammograms were obtained on a BioAnalytical Systems, Inc., Model CV-1A instrument. Potential control for coulometric experiments was performed with a potentiostat purchased from BioAnalytical Systems, Inc. A three-compartment (H) cell was used with a Pt-disk or Pt-gauze working electrode, Pt-wire auxiliary electrode, and Ag/AgCl pseudoreference electrode[9] to which all potentials refer. Scan rates were 25 mV/S. Under these conditions the Cp$_2$Fe/Cp$_2$Fe$^+$ couple was measured at +0.47 V consistent to ±10 mV, with a separation between the anodic and cathodic waves of 90 mV.

1. Ti(OAr-*i*-Pr$_2$)$_4$ (1). To a slurry of lithium 2,6-diisopropylphenoxide (20.7g; 0.11 mol) in benzene (200 mL) was slowly added dropwise TiCl$_4$ (5.33g; 0.028 mol) with vigorous stirring. The initially white suspension became red and then light yellow and was allowed to stir overnight. Filtration gave a deep yellow-orange solution from which solvent was removed under vacuum. Recrystallization of the resulting solid from warm hexane gave the pure product as golden-yellow plates in 60% yield. Anal. Calcd for TiC$_{48}$H$_{68}$O$_4$: C, 76.15; H, 9.07. Found: C, 75.97; H, 9.57. ^{1}H NMR (C$_6$D$_6$ 30 °C): δ 1.19 (d, CH*Me*$_2$); 3.64 (septet, CH*Me*$_2$); 6.8–7.4 (m, aromatics).

2. Ti(OAr-Me$_2$)$_4$ (2). To a solution of 2,6-dimethylphenol (33.4 g; 0.27 mol) in hexane (400 mL) was added Ti(O-*i*-Pr)$_4$ (18.9 g; 0.066 mol) in several portions. The initially colorless solution became deep yellow and was stirred overnight. Removal of solvent and generated 2-propanol followed by recrystallization from warm hexane gave the pure product

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(16) Wood, J. S. *Prog. Inorg. Chem.* **1972**, *16*, 227.

as light yellow plates. Yield: 31.3 g (88%). Anal. Calcd for TiC$_{32}$H$_{36}$O$_4$: C, 72.16; H, 6.83. Found: 72.05; H, 7.27. ¹H NMR. (C$_6$D$_6$, 30 °C): δ 2.20 (s, CH$_3$); 6.7–7.2 (m, aromatics).

3. Zr(OAr-*i*-Pr$_2$)$_4$ (3). To a colorless solution of Zr(CH$_2$SiMe$_3$)$_4$ (1.5 g; 3.4 mmol) in hexane (15 mL) was slowly added 2,6-diisopropylphenol (2.7 g; 15.1 mmol). The solution became warm and was allowed to cool down before being reduced in volume by one-half, whereupon white crystals of product began to form. The crystals were removed and washed with a small amount of cold hexane. Yield: 1.0 g (37%). Anal. Calcd for ZrC$_{48}$H$_{68}$O$_4$: C, 72.03; H, 8.58. Found: C, 70.99; H, 8.41. ¹H NMR. (C$_6$D$_6$, 30 °C): δ 1.15 (d, CH*Me*$_2$); 3.60 (septet, C*H*Me$_2$); 6.7–7.2 (m, aromatics).

4. [(thf)$_2$Na·Ti(OAr-*i*-Pr$_2$)$_4$] (4). A yellow-gold solution of (1) (3.0 g, 3.96 mmol) in thf rapidly became deep green on addition of sodium amalgam (1.1 equiv of Na). After the mixture was stirred at room temperature for 2 h, the resulting green solution was decanted from the mercury and the solvent removed to give the crude product. Yield: 3.0 g (96%). Recrystallization can be readily achieved from hot toluene, yielding light blue crystals. Anal. Calcd for TiC$_{56}$H$_{84}$O$_6$Na: C, 72.77; H, 9.18. Found: C, 69.83; H, 8.90.

5. Ti(OAr-*i*-Pr$_2$)$_3$(py)$_2$ (5). To a dark green solution of (4) (0.50 g; 0.54 mmol) in toluene (10 mL) was added pyridine (0.1 mL). The resulting deep green mixture was stripped to dryness and extracted with 160 mL of a 6:1 mixture of hexane/toluene to give 0.32 g of crude product (81%). Recrystallization from toluene gave 0.10 g of deep purple needles. Anal. Calcd for TiC$_{46}$H$_{61}$O$_3$N$_2$: C, 74.86; H, 8.35; N, 3.80. Found: C, 75.59; H, 7.90; N, 3.65.

X-ray Crystallography

General operating procedures have been reported previously.[17]

(17) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.
(18) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III 3 and 13.)

Ti(OAr-*i*-Pr$_2$)$_4$ (1). A systematic search of a limited hemisphere revealed a set of diffraction maxima with monoclinic symmetry. An initial assignment of P2$_1$/a was discovered to be incorrect after data collection had been in progress for some time, as body centering was present. The correct space group was then identified as I2/a, and no attempt was made to convert it to the standard setting (C2/c).

The structure was solved by direct methods and Fourier techniques and refined by full-matrix least squares. All hydrogen atoms were located and refined isotropically (anisotropic refinement for Ti, C, and O). A final difference Fourier was featureless, the largest peak being 0.32 e/Å³. No attempt was made to correct the data for absorption.

[Ti(OAr-*i*-Pr$_2$)$_4$·Na(thf)$_2$] (4). Crystals of this complex diffracted only weakly. Hence, the results obtained, although not as accurate as one expects, represent the best we have been able to achieve. A small well-formed crystal was selected and transferred to the diffractometer, where it was cooled to −159 °C and characterized in the usual manner. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited orthorhombic symmetry. The systematic extinctions of *h*00 for *h* odd, 0*k*0 for *k* odd, and 00*l*, for l odd identified the space group as P2$_1$2$_1$2$_1$.

The structure was solved by a combination of direct methods and heavy-atom techniques. The Ti and Na atoms were located by direct methods, and the remaining atoms were located by successive difference Fourier maps. The structure was refined by full-matrix least squares. Ti, Na, and O atoms were assigned anisotropic thermal parameters. Hydrogen atoms were not located but were introduced in calculated fixed positions. The refinements were carried out by using only 1810 reflections having $F > 2.33\sigma(F)$. The number of unique reflections was 3911.

The enantiomer shown in this report was selected from refinements of both enantiomers; however, the difference in *R* was quite small.

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Structural Variations Induced by Changes in Oxidation State and Their Role in Electron Transfer. Crystal and Molecular Structures of *cis*-[Ru(bpy)$_2$Cl$_2$]·3.5H$_2$O and *cis*-[Ru(bpy)$_2$Cl$_2$]Cl·2H$_2$O

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The results of an X-ray crystallographic study are reported on the hydrates *cis*-[Ru^{II}(bpy)$_2$Cl$_2$]·3.5H$_2$O and *cis*-[Ru^{III}-(bpy)$_2$Cl$_2$]Cl·2H$_2$O (bpy is 2,2′-bipyridine, C$_{10}$H$_8$N$_2$). The Ru(II) complex crystallizes in the monoclinic space group C2/c with four molecules in a cell of dimensions *a* = 18.248 (14) Å, *b* = 13.146 (5) Å, *c* = 10.792 (4) Å, and β = 119.49 (5)° and was refined to a final value of the weighted *R* factor of 0.031 based on 1912 independent observations. The Ru(III) complex crystallizes in the triclinic space group P$\overline{1}$ with two molecules in a cell of dimensions *a* = 7.042 (3) Å, *b* = 13.000 (5) Å, *c* = 12.321 (3) Å, α = 89.93 (2)°, β = 100.62 (2)°, and γ = 92.23 (3)° and was refined to a weighted *R* factor of 0.033 based on 2104 independent observations. In terms of intramolecular structure, there is a significant shortening (0.10 Å) of the Ru−Cl bond upon oxidation and a slighter *increase* (0.04 Å) in the Ru−N distances trans to the Ru−Cl bonds. An analysis of the contribution of intramolecular vibrations to the vibrational barrier to electron transfer for the [Ru(bpy)$_2$Cl$_2$]$^{+/0}$ couple is presented based on the structures and available vibrational information. The lattice structure of the hydrate [Ru(bpy)$_2$Cl$_2$]·3.5H$_2$O is notable both for the appearance of bpy-based stacking interactions between neighboring molecules and for the existence of an infinite chain of H-bonded water molecules. The latter exists as an aqueous channel within the crystal, individual water molecules of which are H-bonded to bound Cl⁻.

Introduction

Complexes of Ru(II) and Ru(III) have played an important role in the study of optical and thermal electron transfer because of coordinative stability in both oxidation states.[1,2] From current

theory, the activation energy to electron transfer is a function of the energy required to modify the solvent structure around the reactants, the electrostatic energy of interaction between the reactants, and the inner-sphere reorganization energy. The in-

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(2) Richardson, D. E.; Walker, D. D.; Sutton, J. E.; Hodgson, K. O.; Taube, H. *Inorg. Chem.* **1979**, *18*, 2216.