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Electrochemical Behavior of Tungsten(VI) Aryloxides and Catecholates

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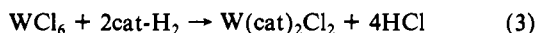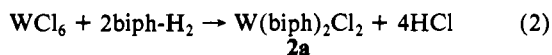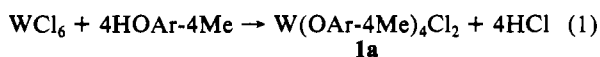The electrochemical behavior of a number of tungsten(VI) aryloxides and catecholates has been investigated. For deep red octahedral $W(OAr-Me)_6$ (OAr-Me = 4-methylphenoxide), two one-electron reduction waves are present in its cyclic voltammogram in THF with 0.2 M n-$Bu_4N^+PF_6^-$ (TBAH) as a supporting electrolyte. The first wave is reversible both chemically and electrochemically while the second electron transfer is totally irreversible. In contrast, the use of chelating aryloxides gives compounds such as $W(biph)_3$ (biph = 2,2'-biphenoxide) and $W(t$-$Bu_2cat)_3$ (t-Bu_2cat = 3,5-di-*tert*-butylcatecholate), which exhibit reversibility for both the first and second electron-transfer steps. With the less bulky catecholates, 4-methyl- and 4-*tert*-butylcatecholate (Mecat and t-Bucat), the electrochemical data are consistent with these complexes existing as dimers in solution, $W_2(Mecat)_6$ and $W_2(t$-$Bucat)_6$. Reduction occurs to generate the mononuclear anions $W(Mecat)_3^-$ and $W(t$-$Bucat)_3^-$, respectively. Although reoxidation of these anions initially produces neutral monomers, they rapidly dimerize to the thermodynamically favored dimers. Relatively stable derivatives of the tungsten(V) monoanions can be obtained with cobaltocene as reducing agent.

Introduction

The homoleptic phenoxides of tungsten(VI), $W(OAr)_6$, were synthesized as early as 1937 by Funk and co-workers.[1,2] Some initial data concerning the electrochemical properties of this compound was described,[3] indicating that two one-electron reductions could be observed by polarography. During our studies of early-transition-metal aryloxide chemistry[4] we have synthesized a number of tungsten(VI) aryloxides and related catecholates. Despite the extensive studies made on catecholate derivatives of more biologically important metals,[5] those of tungsten have only received limited investigation.[6] We wish to report here our studies of the electrochemical behavior of these complexes.

Results and Discussion

Synthetic Aspects. Tungsten hexachloride, WCl_6, will react rapidly with phenolic reagents to evolve HCl and generate mixed chloro–aryloxy compounds. This contrasts with the reaction of WCl_6 with aliphatic alcohols where reduction to W(V) takes place. Hence, addition of 4-methylphenol, biphenol, or a catechol reagent to WCl_6 allows the ready isolation of the corresponding dichlorides (eq 1–3). (biph-H_2 = 2,2'-biphenol; cat = catecholate (complex

$$WCl_6 + 4HOAr-4Me \rightarrow W(OAr-4Me)_4Cl_2 + 4HCl \quad (1)$$
$$\mathbf{1a}$$

$$WCl_6 + 2biph-H_2 \rightarrow W(biph)_2Cl_2 + 4HCl \quad (2)$$
$$\mathbf{2a}$$

$$WCl_6 + 2cat-H_2 \rightarrow W(cat)_2Cl_2 + 4HCl \quad (3)$$
$$\mathbf{3a}$$

3a); 3,5-di-*tert*-butylcatecholate, t-Bu_2cat (complex **4a**); 4-methylcatecholate, Mecat (complex **5a**); 4-*tert*-butylcatecholate, t-Bucat (complex **6a**).

Substitution of the two remaining chloride ligands occurs on heating with excess phenolic reagent in hydrocarbon solvents to give the corresponding homoleptic compounds (**b**).

The dichlorides (**a**) are all intense red-black materials both in the solid and in solution while the homoleptic compounds (**b**) are deep red. In the mass spectrum are seen parent molecular ions along with characteristic fragments. However, in the case of some of the catecholate complexes some W_2-containing species were detected (vide infra).

Electrochemical Behavior. We have investigated the electrochemical behavior (cyclic voltammetry, coulometry, and prepa-

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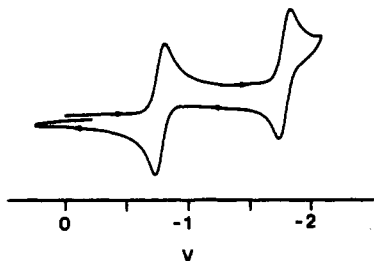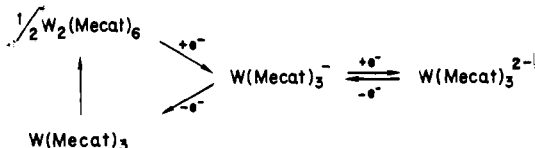(6) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45.

Table I. Electrochemical Data (V vs. Ag Pseudoreference Electrode)

compd	$E°$(THF)	$E°$(CH_2Cl_2)
$W(OAr-4Me)_6$ (**1b**)	-0.71	-0.78
	-1.80[a]	-1.78
$W(biph)_3$ (**2b**)	-0.50	-0.56
	-1.47	-1.56
$W(t$-$Bu_2cat)_2Cl_2$ (**4a**)	+0.16	+0.09
	-1.31	-1.30
$W(t$-$Bu_2cat)_3$ (**4b**)	-0.19	-0.28
	-2.06	[c]
$W_2(Mecat)_6$ (**5b**)	-0.50[a]	-0.50[a]
	-1.72	[c]
	+0.03[b]	+0.0
$W_2(t$-$Bucat)_6$ (**6b**)	-0.56[a]	-0.56[a]
	-1.72	-1.72
	+0.01[b]	+0.00[b]

[a] Irreversible $E_{p,c}$ quoted. [b] Irreversible $E_{p,a}$ quoted. [c] Not observed due to solvent limit.

rative electrolysis) of these complexes at a platinum-disk electrode in the two solvents tetrahydrofuran (THF) and methylene chloride. Tetrabutylammonium hexafluorophosphate (TBAH; 0.2 M) was used as supporting electrolyte (Table I). In the case of the dichlorides, broad, irreversible waves were typically given in the cyclic voltammogram. However, the homoleptic compounds show cyclic voltammograms from which considerable chemical information can be obtained.

Deep red THF/TBAH solutions of the hexakis(aryloxide) $W(OAr-4Me)_6$ (**1b**) show two one-electron reduction waves. The first, reversible wave at -0.78 V vs. the Ag quasi-reference electrode represents the reaction shown in eq 4.

$$W(OAr-4Me)_6 + e^- \rightleftarrows W(OAr-4Me)_6^- \quad (4)$$
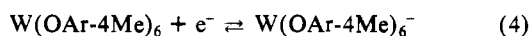
The reversibility of the electron transfer was judged by the ratio $i_{p,c}/i_{p,a} = 1$ for scan rates between 20 and 800 mV/s with the peak spread of the wave being similar to that of the Cp_2Fe^+/Cp_2Fe couple under identical conditions. Controlled-potential reduction at -0.8 V produces, after the passage of one electron/W, a yellow solution whose CV is identical with that of **1a** except that now the wave at -0.78 V is an oxidation. This solution, therefore, contains the tungsten(V) anion $W(OAr-4Me)_6^-$ although EPR measurements failed to show any sharp signals due to this d^1 complex. The second reduction wave at -1.78 V is totally irreversible, as indicated by the lack of any corresponding oxidation wave on reversing the CV scan. It hence appears that the product of the second electron transfer, $W(OAr-4Me)_6^{2-}$, is unstable presumably due to aryloxide dissociation. A broad oxidation wave at +0.7 V corresponding to the oxidation of phenoxide was also present. In $CH_2Cl/TBAH$, however, both reduction waves appear to be electrochemically reversible (Figure 1). The greater stability of the dianion in CH_2Cl_2 may reflect the poorer coordinating properties of this solvent.

Figure 1. Cyclic voltammogram of $W(OAr-4Me)_6$ (**1b**) in $CH_2Cl_2/0.2$ M TBAH. The scan rate is 25 mV/s, and the potential is vs. an Ag pseudoreference electrode.

Scheme I

With the chelating ligand 2,2′-biphenol (biph-H_2) similar behavior is found for W(biph)₃ (**2b**) except that now the two reduction waves are reversible in THF. Complex **2b** is slightly easier to reduce than the hexakis(aryloxide) by about 200–300 mV in THF/TBAH (Table I).

With the sterically quite demanding 3,5-di-*tert*-butylcatecholate (*t*-Bu₂cat) both $WCl_2(t-Bu_2cat)_2$ (**4a**) and $W(t-Bu_2cat)_3$ (**4b**) again show two electrochemically reversible, one-electron reduction waves. In the case of the dichloride both reductions are more accessible than for W(*t*-Bu₂cat)₃ (Table I). The replacement of chloride by aryloxide ligands has been shown to make electrochemical reduction more difficult to other early-transition-metal systems.[4c] Both steps in the reduction of **3b** were shown to be chemically reversible by preparative electrolysis. Hence, controlled-potential reduction at the two values of $E_{p,c}$ produce yellow and orange solutions, respectively. Both solutions exhibited identical CV's to that of **4b**, except that either one or both of the waves are now oxidations. Hence, the two electrochemical waves represent reactions 5 and 6. EPR measurements on yellow

$$W(t-Bu_2cat)_3 + e^- \rightleftharpoons W(t-Bu_2cat)_3^- \qquad (5)$$

$$W(t-Bu_2cat)_3^- + e^- \rightleftharpoons W(t-Bu_2cat)_3^{2-} \qquad (6)$$
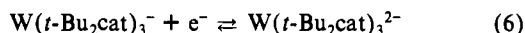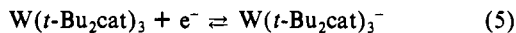
solutions of $W(t-Bu_2cat)_3^-$ in THF showed a broad band at $g = 1.886$, presumably due to this d^1 complex.

With the less bulky catechols Mecat-H_2 and *t*-Bucat-H_2, the tris(catecholates) **5b** and **6b** exhibit quite different electrochemical behavior to that found for W(*t*-Bu₂cat)₃ (**4b**). These compounds were characterized by a totally irreversible one-electron (per W) reduction wave with $E_{p,c}$ between –0.5 and –0.6 V in THF/TBAH. On scanning to more negative potentials we observed a second, this time reversible, wave at –1.72 V. A new oxidation wave at 0.0 V could then be seen on the reverse scan (Figure 2). This oxidation wave at 0.0 V was absent in fresh solutions of **5b** and **6b** and only appeared on scanning past the first reduction wave. Carrying out a bulk reduction at –0.7 V results in a yellow solution whose CV contains two waves, one a reversible reduction at –1.72 V and the other a partly reversible wave at 0.0 V. Further reduction at $E_{p,c}$ of the second wave gave an orange solution that had a CV identical with that of the yellow solution except that now both waves are oxidations (Figure 2). Reoxidation of either of these solutions at + 0.1 V generated deep red solutions exhibiting a CV identical with that of **5b** and **6b**. This data we interpret as shown (Scheme I). Compounds **5b** and **6b** we believe are dimeric both in the solid state and in solution. It has been shown by Pierpont et al. that the related complexes $M(O_2C_6Cl_4)_3$ (M = Mo, W) are also dimeric in the solid state with two pseudooctahedral metal atoms bridged by two catecholate ligands.[7,8]
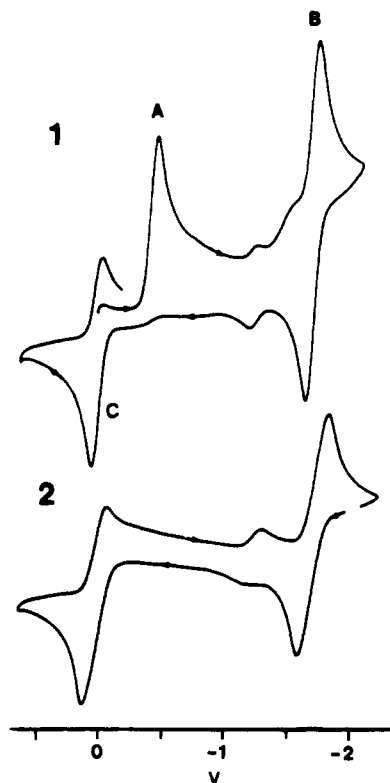
Figure 2. Cyclic voltammograms of THF/TBAH solutions of $W_2(Mecat)_6$ (scan 1) and $W(Mecat)_3^{2-}$ (scan 2). Wave A represents the formation of $W(Mecat)_3^-$ while wave B represents the couple ($W(Mecat)_3^- + e^- \rightleftharpoons W(Mecat)_3^{2-}$. Oxidation wave, C represents the formation of the neutral monomer $W(Mecat)_3$, which dimerizes causing a value of $i_a/i_c > 1$. Scan rates are 50 mV/s.

Furthermore, the mass spectra of **5b** and **6b** show W_2-containing species.

The reduction wave at –0.5 V, therefore, represents both an electron transfer and the breaking apart of these dimers into the octahedral, monomeric anions $W(Mecat)_3^-$ and $W(t-Bucat)_3^-$. A second, reversible reduction then takes place to the tungsten(IV) dianions. Yellow, electrochemically generated solutions of $W(Mecat)_3^-$ show an EPR signal at $g = 1.739$. The final electrochemical process observed at 0.0 V represents the oxidation of the monoanions to the neutral monomers $W(Mecat)_3$ and $W(t-Bucat)_3$. However, the reversibility of this step is scan rate dependent due to a competing recombination of monomers back to the initial dimeric material. This latter process is of interest as it shows that the dimeric starting materials are not kinetically controlled products but clearly are thermodynamically more stable than the simple tris chelates. However, steric bulk on the catechol, as in the case of $W(t-Bu_2cat)_3$ (**4b**), will inhibit dimer formation. The quantitative appearance of the CV of **5b** showed little change on cooling THF/TBAH solutions.

The chemical reduction of these complexes with metallic reagents such as sodium amalgam is not an easy process. However, use of the milder reducing agent cobaltocene[9] ($CoCp_2$, $E_{1/2} = -0.95$ V, in THF/TBAH) allows the one-electron reduction of all of the homoleptic species in THF/TBAH. Hence, addition of $CoCp_2$ to deep red solutions of $W(t-Bu_2cat)_3$ (**4b**) produces an immediate yellow color and a CV identical with that of electrochemically generated $W(t-Bu_2cat)_3^-$ along with waves characteristic of $CoCp_2^+$.

$$CoCp_2 + W(t-Bu_2cat)_3 \rightarrow [CoCp][W(t-Bu_2cat)_3]$$
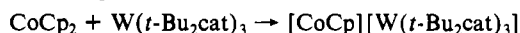
Similarly, the dimer $W_2(Mecat)_6$ reacts to give yellow $[CoCp_2][W(Mecat)_3]$. Carrying out these reactions in hydrocarbon solvents such as benzene or hexane produces brown,

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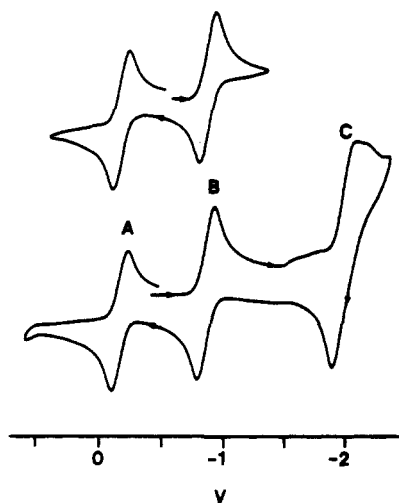
Figure 3. Cyclic voltammograms of [CoCp$_2$][W(t-Bu$_2$cat)$_3$] in THF/TBAH scanned between −1.5 and +0.5 V or between −2.5 and +0.5 V beginning at −0.5 V in both cases. Peak A represents the couple W(t-Bu$_2$cat)$_3$$^-$ ⇌ W(t-Bu$_2$cat)$_3$ + e$^-$ while peak B represents the couple CoCp$_2$$^+$ + e$^-$ ⇌ CoCp$_2$. Wave C is a composite of the two couples W(t-Bu$_2$cat)$_3$$^-$ + e$^-$ ⇌ W(t-Bu$_2$cat)$_3$$^{2-}$ and CoCp$_2$ + e$^-$ ⇌ CoCp$_2$$^-$. Scan rates are 50 mV/s.

sometimes oily products whose CV's are consistent with the above formulations (Figure 3). Unfortunately, these yellow cobaltocenium derivatives do not readily crystallize and are difficult to purify.

Experimental Section

Electrochemical Measurements. Cyclic voltammograms were obtained with 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 -gauze working electrode, a Pt-wire auxiliary electrode and a Ag/AgCl pseudoreference electrode[4c] 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 in THF/TBAH and +0.38 V in CH$_2$Cl$_2$/TBAH, consistent to ±10 mV with a separation between the anodic and cathodic waves of 90 mV.

Synthesis of Compounds. Because of the similarity of the methods used, a general procedure for synthesis of the two types of complexes in this study is given.

(a) Dichlorides. Tungsten hexachloride and the solid phenolic reagent (4 equiv for 4-methylphenol, 2 equiv for biphenol and catechols) were mixed in a round-bottom flask under nitrogen. Benzene was then added to the mixture to initiate reaction. Copious amounts of HCl were given off and vented to a fume hood. The black-purple solution was then stirred for 8–12 h before the solvent was removed under vacuum. The resulting glassy red-black solid was purified by heating under vacuum at 80–90 °C to remove any excess phenol or catechol. Anal. Calcd for WCl$_2$O$_4$C$_{28}$H$_{28}$ (**1a**): C, 49.22; H, 4.13; Cl, 10.38. Found: C, 48.19; H, 4.77; Cl, 10.92. Calcd for WCl$_2$O$_4$C$_{12}$H$_8$ (**3a**): C, 30.60; H, 1.72; Cl, 15.05. Found: C, 29.63; H, 1.76; Cl, 15.57. Calcd for WCl$_2$O$_4$-C$_{14}$H$_{12}$ (**5a**): C, 33.83; H, 2.03; Cl, 14.27. Found: C, 34.35; H, 2.86; Cl, 14.92.

(b) Homoleptic Complexes. The dichlorides prepared in (a) were mixed with a slight excess of 4-methylphenol or catechol in benzene, and the mixture was refluxed for 12 h. Removal of solvent yielded a deep red impure product that was heated under vacuum at 80–90 °C to remove excess phenolic reagents. Anal. Calcd for WO$_6$C$_{36}$H$_{24}$ (**2b**): C, 58.72; H, 3.28. Found: C, 58.48; H, 3.92. Calcd for WO$_6$C$_{18}$H$_{12}$ (**3b**): C, 42.55; H, 2.39. Found: C, 42.43; H, 2.17. Calcd for WO$_6$C$_{42}$H$_{60}$ (**4b**): C, 59.71; H, 7.17. Found: C, 60.83; H, 7.62.

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Volumes of Activation for Electron Exchange by Mn(CNR)$_6$$^{+/2+}$ Complexes in Acetonitrile

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The volumes of activation for the electron-self-exchange reaction between manganese(I) and manganese(II) hexakis(alkyl isocyanide) complexes have been measured by ^{55}Mn NMR for acetonitrile solutions at ca. 0.1 M total reactant concentration and 5 °C. The values for ΔV^* in cm^3/mol, with a typical precision of ±1 cm^3/mol, as a function of the alkyl group, are as follows: methyl, −2.4; ethyl, −5.5; *tert*-butyl, −10.2; cyclohexyl, −17.4; *n*-butyl, −19.7. These results are discussed within two models for predicting ΔV^*, both of which are found to be inadequate, given the current knowledge of the relevant parameters. It is concluded that the flexibility of the ligands and not their size contributes most to the observed trends.

Introduction

The study of the kinetics of electron-transfer reactions of transition-metal complexes has long been a major field of research. In recent years, theory and experiment have developed rapidly and cooperatively, to the point that increasingly sophisticated theoretical treatments are being applied to what are superficially rather simple reactions.[1–3] It is our goal to provide experimental data to test these theories and better establish the detailed characteristics of electron-transfer kinetics. To this end, we have been investigating the electron-self-exchange reactivity of manganese(I) and manganese(II) hexakis(alkyl isocyanide) complexes.

These complexes were chosen for several reasons. They are quite symmetric, the alkyl group can be varied over a wide range, and they are soluble in a variety of solvents. Both oxidation states of the complexes are substitution inert, thus they must react by an outer-sphere mechanism, and the electron-self-exchange process can be followed directly by ^{55}Mn NMR line broadening. Previous studies have concerned the physical properties of the complexes,[4–6] and the effect of changing the alkyl group, temperature, added electrolyte,[7] and the solvent[8] on the electron-transfer reactivity. Thus, this series of complexes is rapidly becoming one of the best characterized systems available.

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