J. Am. Chem. Soc. **1992,** *114,* 1736–1740

Phenol–Cyclohexadienone Equilibrium for η^2-Coordinated Arenes

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Received August 26, 1991

Abstract: The effect of η^2 coordination on an arene is explored in the context of the phenol–ketodiene equilibrium. Whereas for the free ligand this equilibrium heavily favors the phenol tautomer, we find that for the complexes $[Os(NH_3)_5(2,3\text{-}\eta^2\text{-arene})]^{2+}$ (arene = phenol; 4-, 5-, 6-methylphenol; 4,5-dimethylphenol) the corresponding equilibrium constants approach unity (20 °C). Starting with the phenolic isomer in methanol, conversion to 2,4-cyclohexen-1-one is kinetically favored over the formation of the 2,5-analogue, although the latter is the thermodynamically favored product. All tautomerization processes are stereocontrolled, with protonation and deprotonation occurring selectively at the ring face opposite the metal. Electrochemical studies indicate that the phenol–2,5-dienone equilibrium is not profoundly influenced by complexation of osmium(III). In addition to the mononuclear species, where L = phenol, two binuclear complexes are characterized of the form $[\{Os(NH_3)_5\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-L})]^{4+}$ where L = 2,4- or 2,5-cyclohexadien-1-one.

The reactivity of aromatic molecules can be profoundly affected by their coordination to a transition metal, and a great variety of systems have been investigated in which an arene is coordinated symmetrically (i.e., η^6).[1] Such coordination can activate the arene toward nucleophilic attack or deprotonation, and these processes have found synthetic applications.[2] Although several examples of η^2-arene complexes have been reported,[3] their ligand chemistry remains largely unexplored owing to the tendency of these species to undergo oxidative addition or dissociation. Pentaammineosmium(II) forms η^2-arene complexes which are relatively stable in this regard[4] and, as such, provides the opportunity to explore how η^2 coordination affects the arene reactivity. In contrast to η^6-arene complexes, η^2 coordination partially localizes the ligand π electrons, an outcome which enhances the 1,3-diene nature of arenes.[5] To probe the extent of this dearomatization, we have undertaken an investigation of the phenol–dienone equilibrium for several η^2-phenol complexes of pentaammineosmium(II).

Experimental Section

Infrared spectra were recorded on a Mattson Cygnus 100 FTIR spectrometer as KBr pellets. ^{13}C and ^1H NMR spectra were obtained on a General Electric QE300 (300 MHz), GN300 (300 MHz), or GN500 (500 MHz) spectrometer and are reported vs tetramethylsilane. Electrochemical experiments were performed under nitrogen using a PAR Model 362 potentiostat driven by a PAR Model 175 universal programmer. Cyclic voltammograms (CV) were recorded (Kipp & Zonen X-Y recorder) in a standard three-electrode cell[6] from +1.5 to −1.5 V with a glassy carbon working electrode. All potentials are reported vs NHE and, unless otherwise noted, were determined in acetonitrile (~0.5 M tetrabutylammonium hexafluorophosphate (TBAH)) using ferrocene ($E_{1/2} = 0.55$ V), decamethylferrocene ($E_{1/2} = 0.04$ V), or cobaltocenium hexafluorophosphate ($E_{1/2} = -0.78$ V) in situ as a calibration standard. The peak to peak separation ($E_{p,a} - E_{p,c}$) was between 60 and 80 mV for all reversible couples reported unless otherwise noted. This work was carried out under nitrogen atmosphere in a Vacuum Atmospheres Co. glovebox.

Reagents. $[Os(NH_3)_5(OTf)](OTf)_2$ (OTf = $CF_3SO_3^-$) was synthesized as described by Lay et al.[7] Methanol was dried by distillation over $Mg(OMe)_2$ prepared in situ from Mg^0 and I_2 under nitrogen.[8] 1,2-Dimethoxyethane (DME) was dried over Na^0 and distilled after 48 h. Magnesium powder was activated under nitrogen in a DME solution of iodine for 1 h followed by copious washing with DME and Et_2O. Anhydrous ether was obtained from distillation over sodium metal and benzophenone, and CH_2Cl_2 was distilled from P_2O_5. All other reagents were used as purchased without further purification. All solvents were deoxygenated by purging with nitrogen.

Preparations. Synthesis of $[Os(NH_3)_5(\eta^2\text{-phenol})](OTf)_2$ (1a). $Os(NH_3)_5(OTf)_3$ (515 mg, 0.71 mmol) and phenol (1.03 g, 10.0 mmol) were dissolved in a mixture of DME (8.0 mL) and *N*,*N*-dimethylacetamide (DMA; 2.0 mL). The solution was then treated with 1.10 g of activated magnesium powder and rapidly stirred. After a period of 5 min, the mixture was filtered and the filtrate added to 250 mL of CH_2Cl_2. The resulting orange precipitate was collected, washed with diethyl ether, and dried under vacuum. Yield: 380 mg, 0.56 mmol, 80%. CV (CH_3CN/TBAH/100 mV/s): **1a**, $E_{p,a} = 0.39$ V (NHE). ^{13}C NMR δ 56.3 (CH), 63.7 (CH), 97.2 (CH), 123.0 (CH), 129.9 (CH), 148.2 (CO) (OTf^-, 122, q).

Synthesis of compounds **2a**–**5a** were accomplished using the procedure outlined above substituting 6-methyl- (**2a**), 5-methyl- (**3a**), and 4-methylphenol (**4a**) or 4,5-dimethylphenol (**5a**) for phenol.[9] CV (CH_3CN/100 mV/s): **2a**, $E_{p,a} = 0.34$ V; **3a**, $E_{p,a} = 0.35$ V; **4a**, $E_{p,a} = 0.34$ V; **5a**, $E_{p,a} = 0.34$ V ($E_\lambda = 0.7$ V, −1.5 V).

The tendency of these η^2-arene complexes to dissociate ($t_{1/2}$ = 4–10 h; 20 °C) hampered our efforts to purify complexes **1a**–**5a** by ion-exchange chromatography or recrystallization. The purity of all compounds prepared was estimated to be >90% on the basis of electrochemical data and ^1H NMR spectra recorded with a known mass of an internal integration standard added to the sample.[10]

Synthesis of Binuclear Cyclohexadienone Complexes. A solution of **1** (112 mg), $Os(NH_3)_5(OTf)_3$ (132 mg, 1.1 equiv), DME (5.0 g), and DMA (1.2 g) is stirred with 50 mg of Mg^0 powder. After 2.5 h, the solution is filtered and the filtrate treated with CH_2Cl_2. The yellow precipitate is filtered, washed with more CH_2Cl_2, and dried under vacuum. Yield of $[\{Os(NH_3)_5\}_2(2,3\text{-}\eta^2\text{:}4,5\text{-}\eta^2\text{-}\mu\text{-}(2,4\text{-cyclohexadien-1-one})](OTf)_4$ (**6c**): 180 mg, 86%. ^1H NMR for **6c** (acetone-d_6): δ 5.32 (m, 1 H), 5.23 (b, 3 H), 4.92 (b, 3 H), 4.68 (d, 1 H), 4.48 (d, 1 H), 3.83

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(9) Synthesis of the phenol complex **1a** was also attempted in methanol using Zn/Hg in place of Mg^0, but with somewhat less success: Significant amounts (10–15%) of the 2,5-dienone tautomer (**1b**) were produced, as well as small amounts (~5%) of another Os(II) species, thought to be the species $[Os(NH_3)_5(2,3\text{-}\eta^2\text{-}2,4\text{-cyclohexadien-1-one})](OTf)_2$ (**1c**) (Table I).

(10) Accurate integrations were obtained by setting a delay of 10 s between pulses. The only unaccounted diamagnetic impurities are attributed to binuclear species as presently described. Longer reduction times result in significant amounts of the ketodiene tautomers and severe darkening of the solution.

0002-7863/92/1514-1736$03.00/0

Table I. ^1H NMR Data for Various Pentaammineosmium(II) Complexes of η^2-Phenols and η^2-Phenol Ethers

ligand	H2	H3	R4	R5	R6	H1	*cis*-NH_3	*trans*-NH_3
anisole	5.06 (d)	5.35 (t)	6.72 (t)	6.48 (t)	5.72 (d)		3.48 (b)	4.72 (b)
phenol (**1a**)	5.03 (d)	5.32 (t)	6.59 (t)	6.36 (t)	5.70 (d)	8.65 (b)	3.45 (b)	4.70 (b)
6-MP (**2a**)[a]	5.08 (d)	5.38 (t)	6.57 (m)	6.34 (d)	2.08 (s)	8.02	3.48 (b)	4.75 (b)
5-MP (**3a**)	4.99 (d)	5.29 (m)	6.37 (d)	2.12 (s)	5.68 (s)	*b*	3.46 (b)	4.70 (b)
4-MP (**4a**)	5.12 (d)	5.38 (d)	2.28 (s)	6.13 (d)	5.52 (d)	9.25 (b)	3.55 (b)	4.72 (b)
4,5-DMP(**5a**)	5.12 (d)	5.40 (d)	2.23 (s)	2.04 (s)	5.60 (s)	8.39 (b)	3.49 (b)	4.64 (b)
phenol (**1b**)	4.37 (d)	4.61 (m)	2.77 (m)	6.89 (m)	5.85 (d)	2.93 (m)	3.71 (b)	4.91 (b)
6-MP (**2b**)	4.27 (d)	4.59 (m)	2.62 (m)	6.65 (m)	1.70 (s)	2.92 (m)	3.66 (b)	4.97 (b)
5-MP (**3b**)	4.22 (d)	4.58 (m)	2.96 (d)	1.95 (s)	5.73 (s)	3.03 (dd)	3.67 (b)	4.99 (b)
phenol (**1c**)	4.6 (d)	~5.1[c]	5.85 (dd)	6.60 (m)	2.2 (dm)	1.46 (dm)	3.78 (b)	5.18 (b)
4,5-DMP (**5c**)	4.52 (d)	5.06 (d)	1.80 (s)	1.95 (s)	~2.1[c]	~1.5[c]	3.77 (b)	5.09 (b)

[a] All values reported in ppm vs TMS at 20 °C. Spectra recorded in acetone-d_6. Recorded at −20 °C. [b] Resonance not observed due to deuterium exchange. [c] Uncertain assignment due to overlap.

Table II. ^{13}C NMR Data for Selected Pentaammineosmium(II) Complexes of η^2-Phenols and η^2-Phenol Ethers[a]

ligand	C1	C2	C3	C4	C5	C6	other
anisole	169.6	56.7	62.6	125.2	122.1	93.6	55.4
phenol (**1a**)	148.2	56.3	63.7	129.9	123.0	97.2	
4,5-DMP (**5a**)	163.3	55.4	67.3	128.4	126.1	100.8	20.3, 18.1
6-MP (**2b**)	200.4	51.6	53.1	29.6	142.6	136.3	15.3
5-MP (**3b**)	200.2	50.3	51.5	33.9	160.0	126.5	22.4
4,5-DMP (**5c**)	213.2	51.1	57.5	129.3	122.6	44.7	19.4, 17.7

[a] All values reported in ppm vs TMS at 20 °C.

(m, 1 H), 3.92 (b, 12 H), 3.74 (b, 12 H), 2.13 (b, 2 H). ^{13}C NMR (CD_3CN): δ 210.8 (CO), 57.5 (CH), 52.4 (CH), 48.9 (CH), 41.5 (CH), 37.9 (CH_2) (OTf^-, 121, q). IR (KBr) for **6c**-d_{30}: 1616 cm^{-1}. The ammine hydrogens were exchanged in slightly basic CD_3OD in order not to obscure the CO stretch in the infrared absorption spectrum.

The reaction product **6c** was eluted with 1.0 M NaCl down a column of Sephadex SP C-25 and precipitated with $NaBPh_4$. The solid recovered was found to contain approximately 30% of the new tautomer [$\{Os(NH_3)_5\}_2(2,3\text{-}\eta^2{:}5,6\text{-}\eta^2\text{-}\mu\text{-}(2,5\text{-cyclohexadien-1-one}))](BPh_4)_4$ (**6b**). A similar result was obtained by allowing the product **6c** to stand in acidic methanol for 24 h. Following the tautomerization in methanol-d_4 by ^1H NMR reveals an equilibrium ratio of **6b** to **6c** of 3:1. Anal. ($C_{102}H_{116}Os_2ON_{10}B_4$)·$4H_2O$ (a mixture of **6b** and **6c** as tetraphenylborate salts) H, N; C: calcd 61.45; found, 60.82. Partial characterization of **6b** follows. ^1H NMR (acetone-d_6): δ 5.21 (b, 6 H), 3.95 (d, 2 H), 3.85 (b, 24 H), 4.20 (m, 2 H), 2.9 (2 H, obscured by HOD).

Results

The reduction of $Os(NH_3)_5(OTf)_3$ in the presence of various alkylated phenols results in a series of complexes, **1a–5a**, of the form $[Os(NH_3)_5(2,3\text{-}\eta^2\text{-phenol})]^{2+}$. ^1H NMR spectral data for these compounds are reported in Table I, where the previously reported anisole derivative[4a] is included for comparison. With the exception of **2a**, all compounds show quadrupole broadened ammine resonances and resolved arene signals from 5 to 7 ppm, indicative of η^2 coordination.[4a] ^1H NMR signals for the 6-methylphenol-derived complex (**2a**) are somewhat broadened at room temperature owing to a 2,3 ↔ 3,4 η^2 tautomerization process.[4a] Data for this compound entered in Table I were recorded at −20 °C. Judging from homonuclear decoupling studies, in all cases the metal is η^2 coordinated through C2 and C3. Although ^1H NMR data indicate the presence of a phenolic proton, infrared data are inconclusive as the O–H stretch appears to be concealed by the ν(NH) region of 3100–3400 cm^{-1}. In order to confirm our assignment of **1a** as an η^2-phenol complex, a ^{13}C NMR spectrum was recorded which shows excellent correlation with that of the anisole derivative. Most notably, the two ring carbons bound to the metal are shifted upfield to 56.3 and 63.7 ppm. Cyclic voltammetric data for **1a–5a** are also consistent with the formation of η^2-bound arene complexes of pentaammineosmium(II), revealing a chemically irreversible oxidation wave at 100 mV/s near 0.35 V, a value similar to that reported for L = benzene.[11]

Formation and Characterization of 2,5-Dienone Tautomers 2b and 3b. Fresh samples of the phenolic complexes **1a–4a** were dissolved in acidic CH_3CN (0.03 M HOTf), and after 5 min, a mixture of salts was precipitated from solution with excess Et_2O and collected. The 6-methyl- (**2b**) and 5-methylphenol (**3b**) products were found to contain greater than 90% of the 2,5-cyclohexadien-1-one tautomer and were chosen for more detailed characterization as is subsequently described. The 4-methylphenol and phenol products from this procedure contained mostly the phenolic tautomer (**4a**, **1a**), although significant amounts (15–30%) of the 2,5-diene-1-one species (**1b**) were also present in the latter sample.[12] In no case was the metal found in a position other than C2 and C3.

For both the 6-methyl- (**2b**) and 5-methylphenol (**3b**) tautomers, $^1H,^1H$-COSY spectra are consistent with the formation of a pentaammineosmium(II) complex of 2,5-cyclohexadien-1-one in which 2,3-η^2-coordination of the organic ring is maintained. For each complex, strongly coupled ($J \cong 24$ Hz) diastereotopic methylene resonances appear near 3 ppm (Table I). ^{13}C and DEPT spectra reveal one carbonyl and one sp^3 carbon in the ring of each compound, and infrared data[13] show ν(C=O) absorptions shifted about 25 cm^{-1} lower in energy than expected for the free ligand (1670 cm^{-1}).[14] A similar shift is observed for the 2-cyclohexen-1-one analogue $[Os(NH_3)_5(C_6H_8O)](OTf)_2$ (**7**), prepared for purposes of comparison,[15] and is indicative of substantial donation of electron density into the LUMO of the organic ligand.[16] Electrochemical data further support the assignment of **2b** and **3b** as dienone species: reversible oxidations occur for both species with $E_{1/2}$ = 0.92 V (NHE), a value similar to that obtained for the cyclohexenone species **7** (0.88 V) and more than 0.5 V positive of the corresponding value for the arene precursors.[17]

Equilibrium Studies (1–4). A sample of **1a** (25 mg, 37 μmol) in CD_3OD (1.0 mL) containing 0.03 M DOTf (<1 equiv) is monitored by ^1H NMR over a period of 3 h.[18] Within 5 min spectra reveal the equilibrium formation of a new pentaammineosmium(II) species in solution, **1b**, the 2,5-cyclohexadien-1-one tautomer of **1a**. The phenolic species is found to be thermodynamically favored by a ratio of 5:1. In contrast, when this experiment is repeated with the 6-methyl- (**2a**) and 5-methylphenol (**3a**) derivatives, the suspected 2,5-dien-1-one isomers **2b** and **3b** are formed as major products (K_{eq} = 3 ± 0.5). The

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[11] For the complex $[Os(NH_3)_5(\eta^2\text{-benzene})]^{2+}$ in CH_3CN, $E_{1/2}$ = 0.31 V, NHE (200 mV/s). Harman, W. D. Ph.D. Dissertation, Stanford University, 1987.

[12] The phenol sample **1** also contains trace amounts of species **1c**, the 2,4-ketodiene tautomer.

[13] Infrared data (KBr): **2b**, 1647 cm^{-1}; **3b**, 1641 cm^{-1}.

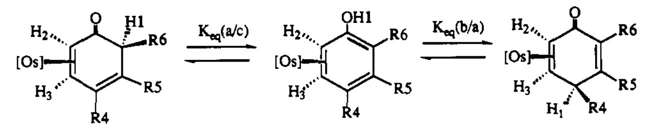
[14] Lasne, M. C.; Ripoll, J. L. *Tetrahedron Lett.* **1980**, *21*, 463.

[15] ν(CO) for $[Os(ND_3)_5(\text{cyclohexenone})](OTf)_2$ 1628 cm^{-1}. The ammine hydrogens were exchanged in slightly basic CD_3OD in order not to obscure the CO stretch in the infrared absorption spectrum. For the synthesis of the ^1H analogue, see: Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2682.

[16] See, for example: Rickard, C. E. F.; Roper, W. R.; Wright, L. J.; Young, L. *J. Organomet. Chem.* **1989**, *364*, 391.

[17] For $[Os(NH_3)_5(\eta^2\text{-benzene})]^{2+}$ $E_{1/2}$ differs from $E_{p,a}$ by less than 50 mV. See ref 4a. We assume that substitution rates on osmium(III) are comparable for the case of L = benzene and L = phenol and, hence, that $E_{1/2}$ lies in the range of $E_{p,a}$ ± 100 mV for **1a–4a**. For **1b**, $E_{1/2}$ = 0.95 V, NHE.

[18] DOTf was generated in situ from the reaction of CD_3OD (4.08 g) and CH_3OTf (20 mg).



(1-5)c (1-5)a (1-5)b

Figure 1. Stereospecific tautomerizations of osmium(II) η^2-phenols (R = CH_3, H).

4-methylphenol derivative fails to yield detectable amounts of any dienone species under these conditions. When this series of experiments is repeated using a separate batch of arene complex and a 0.02 M HOTf solution, similar equilibrium constants are obtained. Using a methanol solution containing 0.02 M diisopropylethylamine, equilibrium constants also are obtained consistent with those found in acid for **1**–**4**. Finally, a sample of **1** containing 30% of the 2,5-dienone tautomer **1b** is dissolved in acidic methanol and allowed to reach equilibrium at which point a value of K_{eq} is obtained consistent with previous experiments. The phenol–dienone equilibrium for **1** is not altered when acidic acetonitrile (~0.02 M HOTf) was substituted as the solvent.

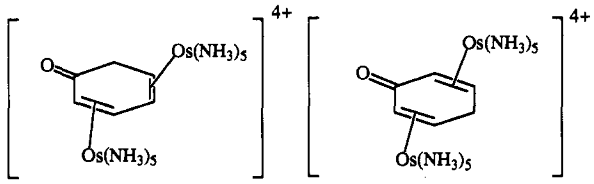
Deuterium Exchange. In CD_3OD (20 °C) under either acidic or basic conditions, all the monomeric arene and ketodiene complexes show extensive deuterium exchange at the ortho (H2, H6) and para (R4) positions of the ring, as well as at the ammines. Predictably, ^1H NMR resonances corresponding to meta protons (H3, H5) show no signs of decay over a 24-h period.

For the symmetrical ligands phenol (**1**) and 4-methylphenol (**4**), in which the arene tautomer dominates, the complete exchange of ortho and para protons occurs in less than 20 min under the basic conditions reported. Under acidic conditions, exchange of these protons is markedly slower: After 20 min, **1a** (L = phenol) shows virtually no exchange of ring protons. After 15 h, **1a** (L = phenol) and **4a** (L = 4-methylphenol) show ~90% exchange of H2 and H6, but for the phenol complex, the para proton (H4) remains largely intact. For these complexes, the metal spends an equal share of time coordinating 2,3-η^2 and 5,6-η^2, and as a consequence, proton signal intensities for H2 and H6 remain equal over time. For **1a** in acid, the relative rate of exchange for the ring protons decreases as follows: H2, H6 (ortho) > H4 (para) ≫ H3, H5 (meta).

For the 2,5-dienone tautomers derived from 6-methyl- (**2b**) and 5-methylphenol (**3b**), deuterium exchange is also markedly slower in acidic CD_3OD than for the basic conditions reported. In acid after 12 h, virtually no deuterium exchange of the para proton (H4) occurs for **2b** *even though this species is in dynamic equilibrium with its arene tautomer.* for **3b**, exchange of this proton is somewhat faster ($t_{1/2} \sim 10$ h) but is at least 2 orders of magnitude slower than the rate of arene–dienone tautomerization for **3**. No scrambling is observed between H1 and H4 for either **2b** or **3b** over the course of 15 h, the signal for H4 appearing as a slightly broadened singlet in both cases. Coupling is undetected between H4 and H3 in either case, an observation which suggests that H4 is syn to the osmium as depicted in Figure 1 (see Discussion). The ortho protons of **3b** (H2 and H6) exchange at different rates as a result of the methyl group (R5) destabilizing the 5,6-η^2 configuration relative to that of 2,3-η^2. The relative rate of exchange for the ring protons for **3b** in base or in acid is as follows: H6 > H4 > H2 ≫ H3.

After a 24-h period, ^1H NMR spectra for **1**–**4** show significant amounts of uncoordinated arene with deuterium exchange patterns which are consistent with those reported for the complexes **1a**, **2b**, **3b**, and **4a**.

Formation and Characterization of 2,4-Dienone Tautomer 5c. In contrast to compounds **1**–**4**, the 4,5-dimethylphenol product **5** was isolated as a 1:1 mixture of two mononuclear species. The ^1H NMR signals for one species are readily interpreted as belonging to the phenolic ligand (**5a**) and agree well with what is reported for **1a**–**4a**. The second product is inconsistent with a 2,5-dienone complex in that both methyl groups show singlet resonances and there are only two olefinic protons. Yet, ^{13}C spectrum recorded in acetonitrile at −30 °C reveals a carbonyl resonance at 213.2 ppm and other requisite signals, supporting the notion of a dienone species which is similar to that recorded for **2b** and **3b**. Together, these observations argue for a 2,4-cyclohexadienone species **5c** as shown in Figure 1.



6c **6b**

Figure 2. Binuclear pentaamminceosmium(II) complexes of cyclohexadienone.

Binuclear Formation. When the phenol complex **1a** is treated with a second equivalent of $[Os(NH_3)_5]^{2+}$, a new species is formed (**6c**) which on the basis of ^1H NMR contains two inequivalent pentaammineosmium(II) units per phenol. ^1H COSY and DEPT data are consistent with a species in which the metals are bridged by the 2,4-cyclohexadien-1-one tautomer of phenol. A ^{13}C resonance at 210.8 ppm and a ν(CO) at 1616 cm^{-1} indicate the presence of a conjugated carbonyl group. When **6c** is allowed to stand in acidic methanol or in water for extended periods of time, this species equilibrates with its tautomer $[\{Os(NH_3)_5\}_2$-(2,3-η^2:5,6-η^2-μ-(2,5-cyclohexadien-1-one)$]^{4+}$ (**6b**), the former species being favored by about 3:1. The NMR spectrum of **6b** reveals a single set of cis and trans ammines and three ring protons, indicating the formation of the symmetrical binuclear species shown in Figure 2.

Discussion

Although a variety of η^6-arene and η^5-ketodienide complexes have been characterized originating from phenol,[19] **1a** appears to be the first η^2-phenol complex reported. Cyclohexadienone complexes such as $Fe(CO)_3(\eta^4$-2,4-cyclohexadien-1-one) are well established,[20] but the observance of η^2-bound cyclohexadienone species is unprecedented. The pentaammineosmium(II) system has been widely studied by Taube and co-workers,[21] with interest stemming largely from the tendency of this metal to form π complexes with unsaturated ligands. The strong interaction of metal d_π orbitals with ligand π^* orbitals has been considered the primary source of stabilization for these species, as is the case in the current study.

Owing to the instability of 2,5- and 2,4-cyclohexadien-1-one, their equilibrium with phenol has not been determined in solution. However, these dienones have been generated by vacuum pyrolysis and partially characterized.[22] More recently, Shiner et al.[23] have determined the gas-phase heats of formation for 2,5- or 2,4-cyclohexadien-1-one as $\Delta H_{298} = -13 \pm 3$ and -17 ± 3 kcal/mol, respectively. Compared to the corresponding value for phenol (−23.04 kcal/mol), ΔH for the tautomerization of phenol to the 2,4-dienone is 6 kcal/mol, and for the 2,5-tautomer, phenol is favored by about 10 kcal/mol. Assuming that $T\Delta S$ has relatively little contribution to ΔG at 20 °C in the case of $K_{eq}(b/a)$,[24] ΔH for the conversion of phenol to 2,5-cyclohexadien-1-one on osmium(II) approaches zero. Thus, such coordination reduces ΔH of tautomerization for **1a** by about 10 kcal/mol relative to the free ligand.

In the limit of formalism, osmium rehybridizes C2 and C3 forming a metallocyclopropane. This effectively removes much of the resonance energy which stabilizes the enolic form of the free ligand. It is useful to consider as a model for the phenol

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[19] See, for example: Vichard, D.; Gruselle, M.; Amouri, H. E.; Jaouen, G. *J. Chem. Soc., Chem. Commun.* **1991**, 46 and references therein.

[20] Birch, A. J.; Chamberlain, K. B. *Org. Synth.* **1977**, *57*, 107–112.

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[22] Lasne, M. C.; Ripoll, J. L. *Tetrahedron Lett.* **1980**, *21*, 463.

[23] Shiner, C. S.; Vorndam, P. E.; Kass, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 5699.

[24] Typical values for $T\Delta S$ for enolizations are less than 1 kcal/mol at 20 °C. See: Rappoport, Z. *The Chemistry of Enols*; Wiley: Chichester, 1990; p 341.

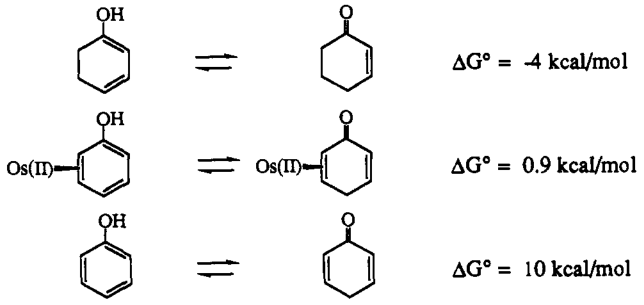

Figure 3. Free energy of ketonization (25 °C) for the η^2-phenol complex as compared to phenol and 1,3-cyclohexadienol.

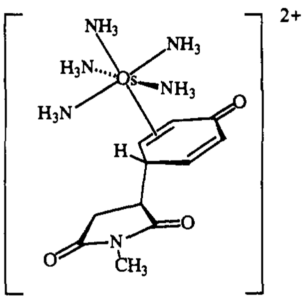

Figure 4. Reaction product of **1a** with *N*-methylmaleimide.

complex **1a** the compound 1,3-cyclohexadienol, where C–H bonds have replaced those to osmium (Figure 3). Although thermodynamic data for enolization equilibria are scarce for dienol systems, ΔH for the ketonization of (*E*)-1,3-butadien-1-ol has been determined in the gas phase to be −2.4 kcal/mol (298 K).[25] Taking the isomerization energy of 3-buten-1-one to 2-butenone as −6 kcal/mol,[26] ΔH for the enolization of 1,3-dien-1-ols to 2-en-1-ones may be approximated as ~3–4 kcal/mol. Finally, noting that gas-phase values of $\Delta H°$ and those of $\Delta G°_{H_2O}$ for enolizations vary by only a few kilocalories per mole,[24] we conclude that the osmium significantly reduces the aromatic character of phenol but does not destroy it.

Conjugation. Significantly, the preferred dienone tautomer for **1** is 2,5-cyclohexadien-1-one, the *less stable tautomer* for the uncoordinated ligand. By again approximating the 2,4- (**1c**) and 2,5-dienone tautomers (**1b**) as 2-cyclohexen-1-one and 3-cyclohexen-1-one, respectively, the enhanced stability for the former becomes apparent as a result of conjugation (~2–5 kcal/mol). The implication is that suitable reactions of **1** with electrophiles are likely to occur with increased para/ortho selectivity, relative to the uncoordinated arene. Preliminary results show that this is indeed the case: **1a** reacts with acetonitrilium ion, maleic anhydride, and various maleimides at 20 °C to yield para-substituted products, exclusively.[27] Recently, the reaction product of **1** with *N*-methylmaleimide has been isolated in its 2,5-ketodiene-1-one form as shown in Figure 4.[28] Even in the case of the 4-methylphenol complex (**4a**), where the para position is blocked by a methyl group, electrophilic addition with *N*-phenyl- or *N*-methylmaleimide occurs predominantly at C4 to give stable 4,4-disubstituted 2,5-cyclohexadien-1-ones.

Alkyl Substitution. The addition of a methyl substituent to phenol (i.e., **2**–**4**) causes a shift in the 2,5-dienone–enol equilibrium depending on position. In the case of 4-methylphenol, the methyl group resides on an sp^2 carbon in the enol form but on an sp^3 carbon in the 2,5-dienone tautomer (**4b**). The stabilizing effect of alkyl substitution on olefins apparently is responsible for a shift in the equilibrium to the point where the 2,5-dienone tautomer of 4-methylphenol is no longer detectable. In contrast, methyl substitution at either C6 (**2**) or C5 (**3**) causes an equilibrium shift toward the 2,5-dienone form (**2b**, **3b**). Although the effect of an alkyl substituent on a dienol–enone equilibrium is so minor as to be beyond the accuracy of computational methods,[29] it is noteworthy that thermodynamic group additivities[30] predict that substitution at the 4-position of a 1,3-dienol moiety stabilizes the dienol tautomer compared to the 2-en-1-one moiety. Further, alkyl substitution at the 2- or 3-position slightly destablizes a 1,3-dienol system with respect to a 2-en-1-cne tautomer. Parallel to this, the 2,5-dienone tautomer of the η^2-phenolic systems investigated shows a clear preference for methyl substitution on the olefinic bond, although the stabilization appears to be less than 1 kcal/mol. In order to test this hypothesis, we included in our study the 2,3-η^2-(4,5-dimethylphenol) complex (**5a**) in which both alkyl substituents are expected to stabilize the 2,4-dien-1-one tautomer. Given that alkylation effects are minor in these systems, the direct observance of the **5c**–**5a** equilibrium (1:1) assures that the three tautomeric forms characterized in this investigation (**a**–**c**) lie within 1–2 kcal/mol of each other.

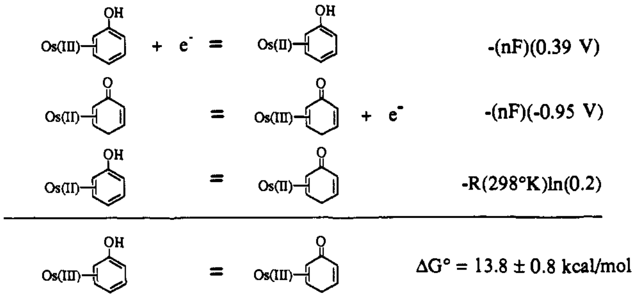

Figure 5. Determination of the free energy of ketonization for phenol on Os(III).

Determination of a Phenol–Ketodiene Equilibrium on Osmium(III). Cyclic voltammetric data indicate that the Os(III)/Os(II) reduction potential is highly dependent on the tautomeric form of the phenol-derived ligand. Though an exact value for compounds **1a**–**5a** was not determined, an earlier study found typical isomerization or substitution rates for pentaammineosmium(III) complexes of η^2-arene complexes to lie from 10^1 to 10^3 s^{-1}.[4,11] Treating the oxidation of the compounds **1a**–**5a** as an E_rC_i process with $k = 10^1$–10^3 s^{-1},[6] a value for $\epsilon°$ can safely be assigned to that of $E_{p,a} \pm 100$ mV. Taking the phenol complex as a model, this puts the reduction potential for the arene form (**1a**) about 600 mV lower than that of the 2,5-dienone tautomer (**1b**). With these two half-reactions in hand, knowledge of the keto–enol equilibrium constant for Os(II) allows for the determination of the corresponding value for Os(III) (Figure 5).

Thus, the phenol complex is 13.8 ± 0.8 kcal/mol more stable than its 2,5-ketodien-1-one isomer at 25 °C. Remarkably, this value represents the same aromatic stabilization as reported for phenol in the gas phase, within experimental error, and indicates that the more electron-deficient Os(III) is completely ineffective in stabilizing the dienone tautomer compared to the arene.

Kinetic Considerations. The complete exchange of ortho and para protons occurs in less than 20 min for compounds **1**–**4** in methanol under the basic conditions reported. Significantly, complete exchange has occurred at the ortho positions of the phenol complex **1a** *before* the phenol–2,5-dienone equilibrium has been established. For the 5-methylphenol analogue (**3a**), this effect is even more pronounced: H/D exchange at R6 is complete in 10 min, whereas the equilibrium for **3a** and **3b** is not reached for several hours. Given that exchange at the ortho positions of **1a** occurs through a 2,4-dienone intermediate (i.e., **1c** or **3c**), protonation of a hypothetical phenolate intermediate is kinetically

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(26) Streitwieser, A.; Heathcock, C. H. *Introduction to Organic Chemistry*; Macmillan: New York, 1976; p 550.

(27) Kopach, M. E.; Harman, W. D. Manuscript in preparation.

(28) The reaction of **1a** with *N*-methylmaleimide was carried out in acetonitrile at 20 °C with a catalytic amount of an amine base.

(29) Experimentally, simple enols are stabilized by alkyl substituents at the β-position, but the corresponding differences in energy ($\Delta\Delta H \sim$ 1–2 kcal/mol) are typically beyond experimental error. See ref 24, p 19–21.

(30) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

favored at the ortho position compared to the para. This observation is consistent with what is known for enolates formed from α,β-unsaturated ketones, where the kinetic product of protonation at C is the α-position.[31]

Stereospecific Tautomerizations. The rate of deuterium exchange for 5-methylphenol (**3b**) in acidic methanol-d_4 of either the available (H6) or para position (H4) is orders of magnitude *slower* than that of tautomerization. Yet, the diastereotopic methylene proton H1 readily exchanges. Together, these observations indicate that the tautomerization process is highly stereoselective at C4, and quite probably at C6 as well, provided that the phenol/2,4-dienone tautomerization in acid is as facile as the 2,5-dienone process for **3**. For the 2,5-dienone species **2b** or **3b**, the lack of significant coupling between R4 and the stable meta proton (H3) suggests a dihedral angle of 80–90°.[32] Consideration of molecular models indicates that H4 is the proton syn to the osmium as shown in Figure 1 and that the additional proton enters from the face of the ring anti to the metal. Supporting this conclusion is an earlier study which indicates that hydrogenation of η^2-anisole or η^2-dimethoxybenzene occurs exclusively anti to pentaammineosmium(II).

Conclusions

Osmium(II) coordination stabilizes 2,5-cyclohexadien-1-one to the degree that it reaches an equilibrium with its aromatic tautomer phenol in methanol at a ratio of 1:5; this represents approximately 10 kcal/mol stabilization in the free energy of ketonization, relative to the uncoordinated ligands. The addition of a methyl substituent accounts for 1–2-kcal variation in this free energy depending on position; by proper adjustment of alkyl substituents, the 2,4-dienone tautomer may also be observed as a major product. Starting with the phenolic isomer in basic methanol, conversion to 2,4-cyclohexen-1-one is kinetically favored over the formation of the 2,5 analogue, although the latter is the thermodynamically favored product. All tautomerization processes are stereoselective, with protonation and deprotonation occurring preferentially at the ring face opposite the metal. Preliminary results suggest that electrophiles react with phenol selectively at the para position, paralleling the thermodynamic product of ketonization. Electrochemical studies indicate that the phenol–2,5-dienone equilibrium shows little deviation from that of the free ligand on osmium(III).

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the University of Virginia, the Thomas F. and Kate Miller Jeffress Memorial Trust (J-206), and Catalytica (Mountain View, CA) for their generous support of this work.

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4,6-Dinitrobenzofuroxan: A Stronger Electrophile than the *p*-Nitrobenzenediazonium and H^+ Cations

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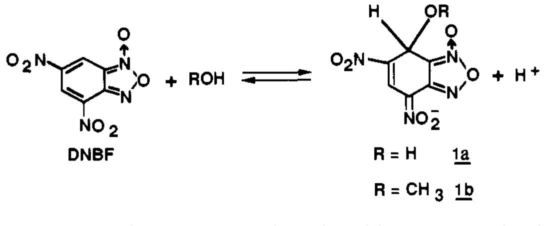
Received July 25, 1991.
Revised Manuscript Received October 16, 1991

Abstract: It is shown by means of a kinetic study of the reactions of 4,6-dinitrobenzofuroxan (DNBF) with the π-excessive heteroaromatics indole, 2-methylindole, and 1,2,5-trimethylpyrrole, producing the corresponding σ-adducts, that DNBF is a more powerful electrophile than the *p*-nitrobenzenediazonium cation and also a much stronger electrophile than the proton.

Much evidence has been recently accumulated that 4,6-dinitrobenzofuroxan (DNBF) is a neutral 10-π-electron heteroaromatic substrate which in many processes exhibits an extremely high electrophilic character. Thus, whereas the common reference electrophile, 1,3,5-trinitrobenzene (TNB), only reacts with the strong oxygen bases hydroxide and methoxide ions, DNBF undergoes facile addition of water or methanol according to eq 1



(1)

to give the hydroxide or methoxide adducts (**1a**, **1b**) which are 10^{10} times thermodynamically more stable than the analogous TNB adducts.[1–6] More importantly, DNBF reacts quantitatively at room temperature with such weak carbon nucleophiles as 1,3,5-trimethoxybenzene (pK_a = −5.7)[7,8] or aniline[9,10] to afford stable anionic C-bonded σ-adducts which are formally the products of S_EAr substitution of the benzene ring.[11] Similar substitutions readily occur with π-excessive heteroaromatics like pyrrole,

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