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η^5-Semiquinone and η^4-Quinone Complexes of Manganese Tricarbonyl. Intermolecular Hydrogen Bonding in the Solid State and in Solution

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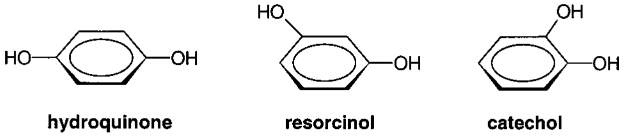
Cationic manganese tricarbonyl complexes containing η^6-hydroquinone (**1a**), η^6-catechol (**2a**), and η^6-resorcinol (**3a**) ligands are readily deprotonated in DMSO with triethylamine or other weak bases to afford stable (η^5-semiquinone)Mn(CO)$_3$ (**1b**−**3b**) and (η^4-quinone)-Mn(CO)$_3^-$ (**1c**−**3c**) complexes. The relative acidity in DMSO follows the qualitative order **2a** > **3a** > **1a**. NMR spectra of the semiquinones **1b**−**3b** indicate dynamic, strong hydrogen bonding in solution. The crystal structures of **1b** and **2b** feature strong intermolecular hydrogen bonding, resulting in polymers with **1b** and dimers with **2b**. Deprotonation of **1a**−**3a** or **1b**−**3b** with sodium acetate in DMSO allowed the isolation and characterization of the η^4-quinone salts Na[**1c**−**3c**]·3H$_2$O. The crystal structure of Na[**2c**]·3H$_2$O shows the sodium cation to be bonded to just one quinone oxygen. IR and crystal structure data of both η^5-semiquinone and η^4-quinone complexes provide clear evidence of significant contributions to the overall structure from more polar η^6-resonance forms.

Introduction

Examples of complexes containing a hydroquinone, catechol, or resorcinol ligand (Chart 1) π-bonded to a transition metal are surprisingly rare. This is due in part to a propensity[1] for such ligands to σ-bond to metals through the oxygen atoms rather than π-bond through the carbocyclic ring. There are, however, some stable multimetallic catechol complexes known in which both σ- and π-modes of bonding occur.[2] Although some simple complexes, such as (η^6-hydroquinone)Cr(CO)$_3$, are thermally and oxidatively unstable,[3] a sufficient number of purely π-bonded hydroquinone complexes have been reported[4−7] to suggest that in general such species are viable and, depending on the particular metal and auxiliary ligands, may possess the stability required for isolation and utilization.

Chart 1



The fundamental importance[8] of substituted hydroquinones in mediating electron and proton transfers in biological systems (Scheme 1) is a good reason for investigating the influence of metal π-coordination on such processes. In particular, one may anticipate that the attachment of a metal fragment to the π-system would facilitate proton and, perhaps, electron transfer. There are a number of examples of tetramethylquinone (duroquinone) π-bonded in an η^4-fashion to a transition metal.[4,9] In the case of (η^4-duroquinone)CoCp*, it was reported[4] that protonation yielded the corresponding η^5-semiduroquinone cation and the η^6-hydroduroquinone dication. In a related manner, it was recently shown[7] that the stable complex (η^6-hydroquinone)Ir(Cp*)$^{2+}$ could be synthesized from hydroquinone as the starting material and that single and double deprotonation occurs easily to afford η^5- and η^4-products. We recently reported[6] the synthesis of (η^6-hydroquinone)Mn(CO)$_3^+$ (**1a**) and (η^6-catechol)Mn(CO)$_3^+$ (**2a**) and provided preliminary evidence that the presence of the Mn(CO)$_3^+$ moiety greatly facilitates (reversible) proton loss. Scheme 2 illustrates the relevant chemistry. Even though the sequences in Scheme 2 can be viewed as simple depro-

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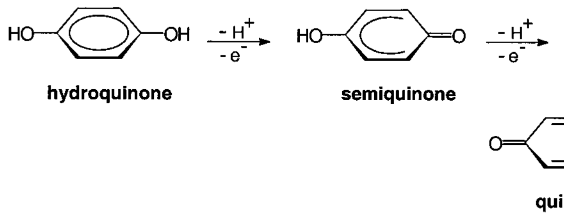
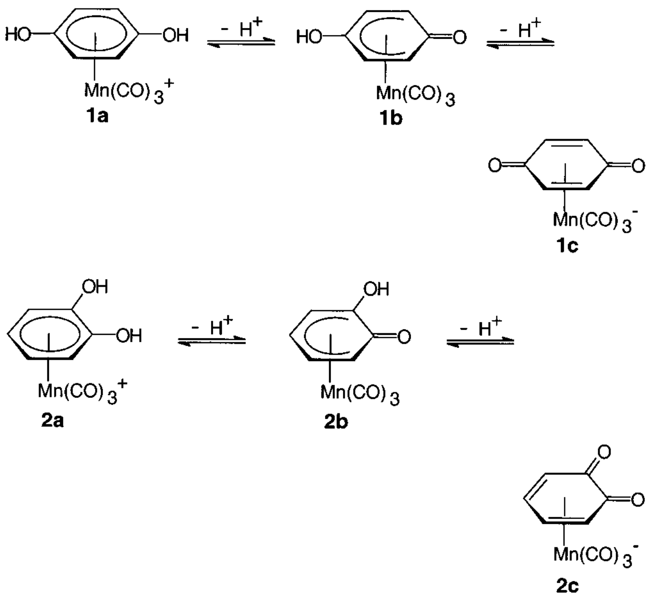
Scheme 1



Scheme 2



tonations, the analogy to the proton *and electron* transfers in Scheme 1 is evident if it is considered that each proton loss is accompanied by electron transfer to the metal.

Herein we fully document these deprotonation reactions and report the crystal structures of complexes **1b**, **2b**, and **2c**. With **1b** and **2b**, it is demonstrated that intermolecular hydrogen bonding is prominent in both the solid state and solution, resulting in polymers with **1b** and dimers with **2b**. Also presented are the related deprotonation reactions of (η^6-resorcinol)$Mn(CO)_3^+$ (**3a**).

Results and Discussion

We previously reported the synthesis and characterization of the cationic hydroquinone and catechol complexes **1a** and **2a**.[6] The resorcinol analogue, **3a**, was easily made as the BF_4^- salt by reaction of resorcinol with the manganese tricarbonyl transfer reagent [(η^6-acenaphthene)$Mn(CO)_3$]BF_4.[10] When complexes **1a**–**3a** are dissolved in DMSO solvent, IR spectra indicate that they undergo spontaneous proton dissociation to give a mixture of **1a**–**3a** and the corresponding semiquinone species **1b**–**3b**, as shown in Schemes 2 and 3. The IR spectra showed that the relative acidities of **1a**–**3a** are in the qualitative order **2a** > **3a** > **1a**. It was found that both single and double deprotonation of **1a**–**3a** could be conveniently and reversibly effected by the addition of the weak base NEt_3. A typical experiment is illustrated in Figure 1 for complex **1a**. Spectrum a indicates that **1a** is ca. 50% dissociated to **1b** in pure DMSO. Spectrum b shows that several equivalents of NEt_3 transforms **1a** to the quinone complex **1c**, which can be cleanly reprotonated to **1b** with 1 equiv of $HBF_4 \cdot Et_2O$ (spectrum c). Additional $HBF_4 \cdot Et_2O$ converts **1b** to **1a**, as shown in spectrum d. The deprotonation process can be repeated by the addition of NEt_3 (spectrum e). All three neutral semiquinone complexes **1b**–**3b** were found to be stable in solution and in the solid state. The anionic quinone complexes **1c**–**3c**, which are stable in solution, could not be isolated as the $HNEt_3^+$ salts. However, deprotonation of **1a**–**3a** with sodium acetate led to the isolation of **1c**–**3c** as stable sodium salts (vide infra).

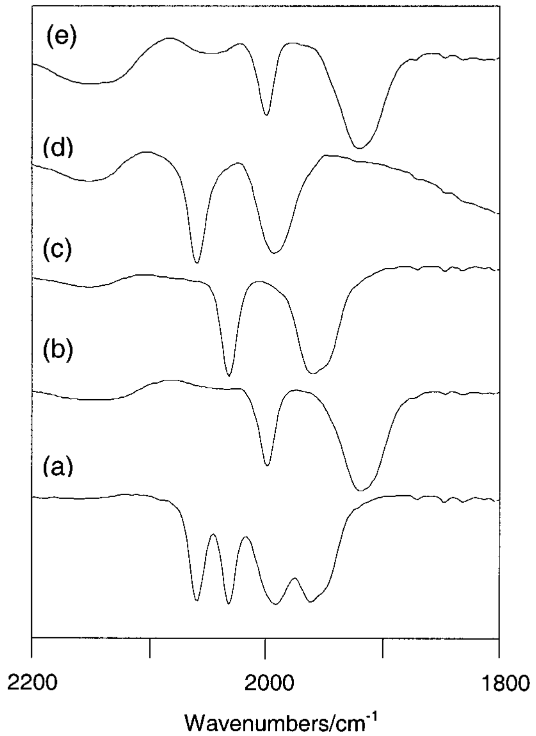
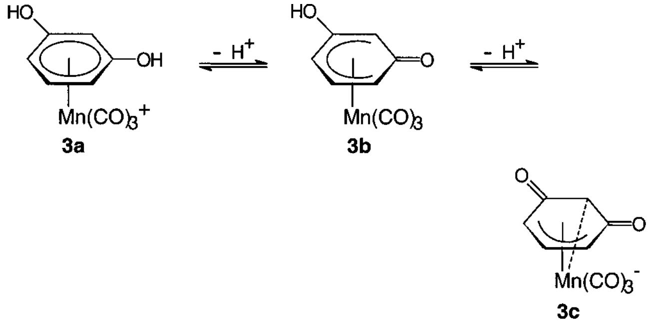


Figure 1. IR spectra in DMSO showing reversible deprotonation/protonation of complex **1a** according to Scheme 2: (a) complex **1a** dissolved in DMSO, showing dissociation into an equilibrium mixture of **1a** and **1b**; (b) addition of NEt_3, generating **1c**; (c) addition of $HBF_4 \cdot Et_2O$ to (b), protonating **1c** to form **1b**; (d) addition of more $HBF_4 \cdot Et_2O$, protonating **1b** to form **1a**; (e) addition of NEt_3 to (d), regenerating the quinone complex **1c**.

Scheme 3



The NMR and IR spectra in DMSO of the semiquinone complex **1b** proved to be quite interesting and informative. The ν_{CO} bands of **1b** are ca. 20 cm^{-1} higher

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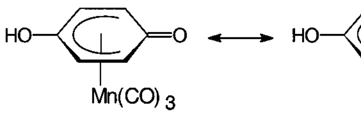
Table 1. Crystallographic Data for 1b, 2b, and Na[2c]

	1b	**2b**	Na[**2c**]·3H_2O
formula	$C_9H_5MnO_5$	$C_9H_5MnO_5$	$C_9H_{10}MnNaO_8$
fw	248.07	248.07	324.10
temp, K	298	298	298
wavelength, Å	0.710 73	0.710 73	0.710 73
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	6.3941(19)	6.8655(6)	6.3066(8)
b, Å	6.5547(19)	6.9081(6)	6.6858(8)
c, Å	12.346(3)	10.3711(9)	15.437(2)
α, deg	92.175(6)	91.617(2)	78.345(2)
β, deg	95.337(6)	94.366(2)	80.699(2)
γ, deg	115.953(4)	110.734(2)	80.650(2)
V, Å^3	461.4(2)	457.88(7)	623.39(14)
Z	2	2	2
d_{calcd}, g cm^{-3}	1.785	1.799	1.727
μ, mm^{-1}	1.426	1.437	1.125
F(000)	248	248	328
cryst dimens, mm	0.20 × 0.19 × 0.12	0.42 × 0.24 × 0.08	0.36 × 0.32 × 0.18
θ range, deg	1.66−28.29	1.97−26.36	2.72−26.41
no. of rflns collected	6555	4202	4862
no. of indep rflns	6555 (R_{int} = 0.000)	1840 (R_{int} = 0.0236)	2520 (R_{int} = 0.0163)
no. of data/ restraints/ params	6555/0/163	1840/4/156	2520/0/207
GOF on F^2	1.065	1.070	1.090
R1, wR2 ($I > 2\sigma(I)$)	0.0544, 0.1478	0.0257, 0.0712	0.0339, 0.0895
R1, wR2 (all data)	0.0628, 0.1544	0.0281, 0.0727	0.0363, 0.0906

than those normally found for (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes, a fact that we ascribe to a significant contribution from the η^6-resonance form **1b′**. The ^{1}H NMR of **1b** shows only one aromatic C−H signal, and the ^{13}C NMR shows only two aromatic carbon signals. This behavior suggests dynamic strong hydrogen-bonding interactions that have the effect of equilibrating the two aromatic C−O linkages. The crystal structure of **1b**, which appears to be the first one of a simple η^5-semiquinone to be reported, supports the interpretation of the IR and NMR spectra given above. Relevant crystal data are given in Table 1. As Figure 2 shows, the structure consists of linear chains of strongly hydrogen-bonded semiquinone molecules extending through the crystal in the [110] direction. The hydrogen-bonded O(2)- - -O(1) donor−acceptor distance is remarkably short at 2.47 Å and can be compared to the O- - -O distance of 2.74 Å reported[11] for the hydrogen-bonded dimer consisting of hydroquinone and quinone (quinhydrone). This interaction has the effect of “mixing” the C−OH and the C═O ends of the molecule with the consequence that both bend or “envelope” out of the plane defined by C(2)−C(3)−C(5)−C(6). Thus, C(3)−C(4)−C(5) is bent up by 6.7° and C(2)−C(1)−C(6) by 11.3°. The latter interplanar angle is much less than those seen in typical (cyclohexadienyl)Mn(CO)$_3$ complexes[12] as well as those found in (η^5-pentamethylbenzyl)Mn(CO)$_3$[13] and (η^5-oxocyclohexadienyl)Mn(CO)$_3$.[14] In concert with this, the Mn−C(1) distance of 2.342(2) Å in **1b** is short enough to indicate some bonding interaction at the C═O link, although less than that which occurs at the C−OH end of the ring: Mn−C(4) = 2.259(2) Å.



1b **1b'**

The catechol semiquinone complex **2b** also gave NMR spectra that indicate the existence of dynamic, strong hydrogen bonding in DMSO solution. Thus, only two aromatic proton and three aromatic carbon signals appear in the ^{1}H and ^{13}C spectra, respectively. The crystal structure of **2b** is shown in Figure 3, and crystal data given in Table 1. The structure consists of hydrogen-bonded dimers with an intermolecular hydrogen bond donor−acceptor distance O(2)- - -O(1A) of 2.63 Å. As with **1b**, the IR spectrum and crystal structure of **2b** suggest some contribution from an η^6-resonance form akin to that shown for **1b′** (Mn−C(1) = 2.469(2) Å in **2b**). Because of this, and the hydrogen-bonding interactions, the observed fold angle between the C(2)−C(1)−C(6) plane and the dienyl plane C(2)−C(3)−C(4)−C(5)−C(6) is quite small at 11.3°.

NMR spectra in DMSO of the resorcinol semiquinone complex **3b** indicates, as with **1b** and **2b**, that the aromatic C−OH and C═O groups rapidly interchange via hydrogen bonding. As a result, **3b** displays only three aromatic proton and four aromatic carbon NMR signals.

Deprotonation of the semiquinone complexes **1b**−**3b** was found to be facile in DMSO using NEt_3 as the base (see Figure 1). Isolation of the product quinone salts **1c**−**3c** proved to be difficult with $HNEt_3^+$ as the counterion, but deprotonation with sodium acetate led to stable sodium salts. As in the case of the semiquinones, IR spectra of **1c**−**3c** show ν_{CO} bands at wavenumbers considerably higher than those reported for other anionic (η^4-diene)Mn(CO)$_3^-$ complexes: e.g., (η^4-naphthalene)Mn(CO)$_3^-$ and (η^4-xylylene)Mn(CO)$_3^-$.[15] In the case of **2c**, for example, we interpret this to mean that resonance forms **2c′** and **2c″** shown in Scheme 4 make a nontrivial contribution. The crystal structure of the sodium salt of **2c** is shown in Figure 4. The molecule is essentially η^4-bonded, with the average Mn−C diene distance being 2.16 Å. The other aromatic carbon atoms, C(1) and C(2), are at much greater distances from the manganese (2.47 and 2.48 Å) but are close enough to indicate some interaction, as depicted in **2c′** and **2c″**. The interplanar angle between the diene, C(3)−C(4)−C(5)−C(6), and the dioxo part of the carbocyclic ring, C(3)−C(2)−C(1)−C(6), is only 8.3°. This value is much less than the 37° found[15a] in (η^4-naphthalene)Mn(CO)$_3^-$ and again points to a contribution from **2c′** and **2c″**.

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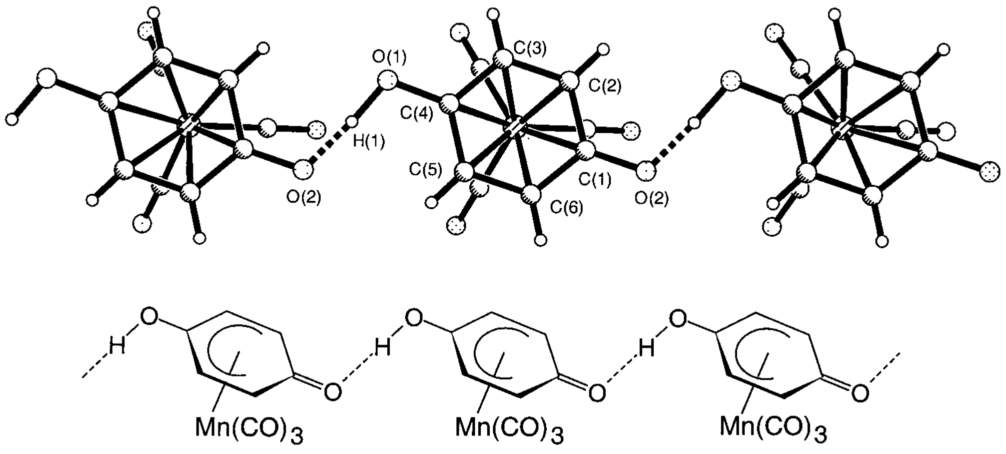
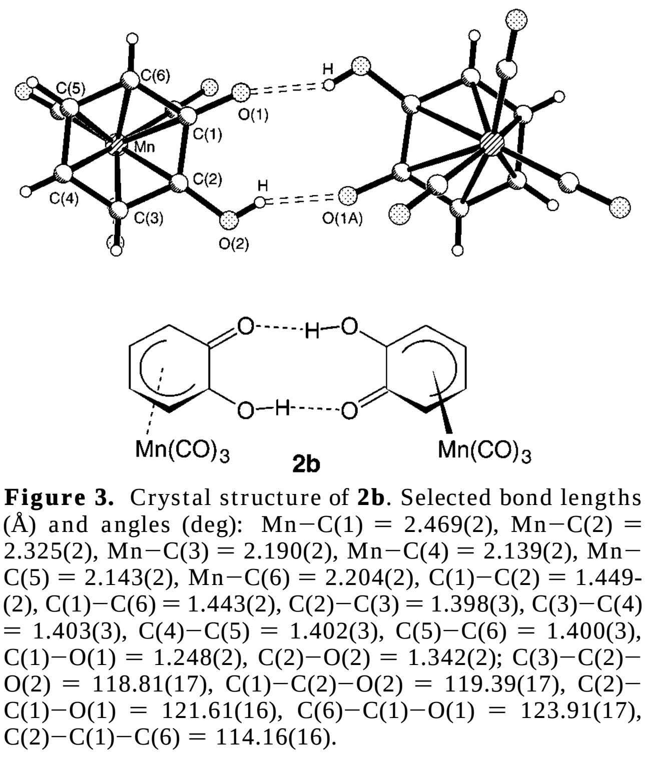


1b

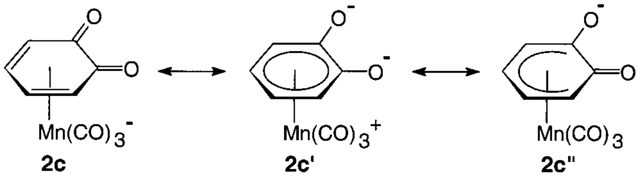
Figure 2. Crystal structure of **1b**. Selected bond lengths (Å) and angles (deg): Mn−C(1) = 2.342(2), Mn−C(2) = 2.188(2), Mn−C(3) = 2.183(2), Mn−C(4) = 2.259(2), Mn−C(5) = 2.164(2), Mn−C(6) = 2.180(2), C(1)−C(2) = 1.440(3), C(1)−C(6) = 1.416(3), C(2)−C(3) = 1.398(3), C(3)−C(4) = 1.412(3), C(4)−C(5) = 1.407(3), C(5)−C(6) = 1.412(3), C(1)−O(2) = 1.287(2), C(4)−O(1) = 1.327(2); C(4)−O(1)−H(1) = 109.4(17), C(2)−C(1)−C(6) = 115.14(17), C(2)−C(1)−O(2) = 122.39(18), C(6)−C(1)−O(2) 122.13(18), C(3)−C(4)−O(1) = 118.99(17), C(5)−C(4)−O(1) = 123.62(18).



2b

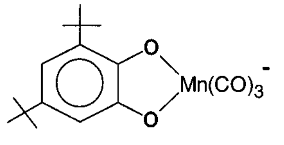
Figure 3. Crystal structure of **2b**. Selected bond lengths (Å) and angles (deg): Mn−C(1) = 2.469(2), Mn−C(2) = 2.325(2), Mn−C(3) = 2.190(2), Mn−C(4) = 2.139(2), Mn−C(5) = 2.143(2), Mn−C(6) = 2.204(2), C(1)−C(2) = 1.449(2), C(1)−C(6) = 1.443(2), C(2)−C(3) = 1.398(3), C(3)−C(4) = 1.403(3), C(4)−C(5) = 1.402(3), C(5)−C(6) = 1.400(3), C(1)−O(1) = 1.248(2), C(2)−O(2) = 1.342(2); C(3)−C(2)−O(2) = 118.81(17), C(1)−C(2)−O(2) = 119.39(17), C(2)−C(1)−O(1) = 121.61(16), C(6)−C(1)−O(1) = 123.91(17), C(2)−C(1)−C(6) = 114.16(16).

Scheme 4



It was originally anticipated that the sodium counterion in **2c** would bridge the two quinone oxygen atoms in a bidentate manner. However, as illustrated in Figure 4, the sodium cation is bonded to only one quinone oxygen, with the rest of its coordination sphere being occupied by water. The water likely originated from the NaOAc·3H$_2$O reagent used in the synthesis.

A compound that is effectively isomeric with **2c** was reported previously by Pierpont and co-workers.[16] They synthesized the disubstituted catecholate complex **4**, in



4

which the Mn(CO)$_3$ moiety is σ-bonded to the oxygens rather than π-bonded to the carbocyclic ring as in **2c**. The reported crystal structure showed clearly that the best representation of **4** is that of a coordinated aromatic catecholate dianion, as shown. In contrast, the structure of **2c** indicates that the major resonance form is that of a coordinated *o*-benzoquinone, in agreement with the suggestion (Scheme 2) that the Mn(CO)$_3$ moiety π-bonded to the carbocyclic ring in catechol acts as an electron sink when the −OH groups are deprotonated. In other words, deprotonation of **2a** can be viewed as involving simultaneous reduction of the metal and oxidation of the catechol, first to the semiquinone (**2b**) and then to the quinone (**2c**).

It can be imagined that the η^4-π-bonded quinone complexes would interact with a wide variety of metal ions by σ-bonding through the oxygen atoms. Preliminary work indicates that this type of reaction occurs readily with **1c**−**3c**. For example, it has recently been shown[17] that transition metals σ-bonding through the oxygens in **1c** generate polymeric networks that are propagated in one, two, or three dimensions in a manner that depends on the preferred geometry of the metal ion and the presence of "spacer" molecules. Quinoid polymers derived from **2c** and **3c** may also be accessible, and work in this area is in progress.

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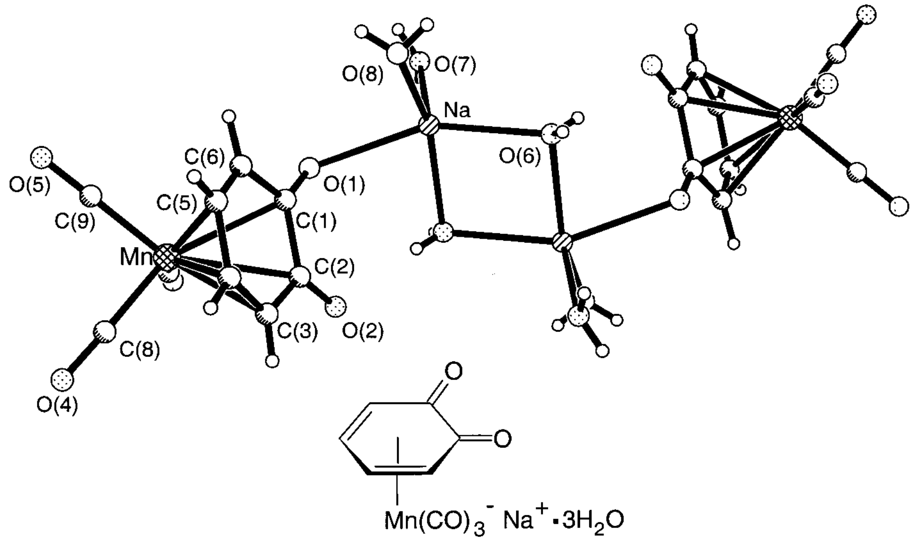

2c

Figure 4. Crystal structure of Na[**2c**]·3H$_2$O. Selected bond lengths (Å) and angles (deg): Mn−C(1) = 2.468(2), Mn−C(2) = 2.483(2), Mn−C(3) = 2.203(2), Mn−C(4) = 2.123(3), Mn−C(5) = 2.122(3), Mn−C(6) = 2.200(2), C(1)−C(2) = 1.480(3), C(1)−C(6) = 1.424(3), C(2)−C(3) = 1.419(3), C(3)−C(4) = 1.416(4), C(4)−C(5) = 1.385(4), C(5)−C(6) = 1.412(4), C(1)−O(1) = 1.273(3), C(2)−O(2) = 1.267(3), Na−O(1) = 2.448(2), Na−O(6) = 2.394(2), Na−O(7) = 2.317(2), Na−O(8) = 2.328(2); C(2)−C(1)−O(1) = 119.9(2), C(6)−C(1)−O(1) = 123.1(2), C(1)−C(2)−O(2) = 119.7(2), C(3)−C(2)−O(2) = 123.3(2), C(1)−O(1)−Na = 116.1(1).

Conclusions

It has been shown that η^6-hydroquinone, catechol, and resorcinol complexes of manganese tricarbonyl are rapidly and reversibly deprotonated by triethylamine to afford the corresponding η^5-semiquinone and η^4-quinone complexes. The semiquinone complexes derived from hydroquinone and catechol participate in strong intermolecular hydrogen bonding that persists in solution as well as in the solid state.[18] The anionic η^4-quinone complexes can be isolated as stable sodium salts. In the metal-mediated deprotonation sequence hydroquinone → semiquinone → quinone reported herein, the metal moiety acts as an electron sink and is related to coupled proton and electron tranfers that occur in biological quinoid systems.[19] Application of this deprotonation strategy to (η^6-cresol)Mn(CO)$_3^+$ complexes may allow access to coordinated quinone methides, which as free molecules are unstable transients of great significance in biological transformations.[20]

Experimental Section

General Considerations. Standard materials were purchased from commercial sources and used without further purification. Acetone and dichloromethane solvents were HPLC grade and opened under nitrogen. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 300 and 400 MHz instruments.

Hydroquinone Complexes 1a−3a. Literature methods were used to synthesize [(η^6-hydroquinone)Mn(CO)$_3$]BF$_4$ (**1a**) and [(η^6-catechol)Mn(CO)$_3$]BF$_4$ (**2a**).[6] Some updated characterization data are as follows for [**1a**]BF$_4$: IR (DMSO) ν_{CO} 2059 (s), 1991 (s, br) cm^{-1}; IR (CH$_3$CN) ν_{CO} 2070 (s), 2009 (s, br) cm^{-1}; ^{1}H NMR (d_6-DMSO) δ 9.37 (OH), 6.01 (s, 4H); ^{1}H NMR (CD$_3$CN) δ 8.67 (OH), 6.08 (s, 4H); ^{13}C NMR (CD$_3$CN) δ 218.4 (Mn−CO), 139.0, 88.5. Characterization data for [**2a**]BF$_4$: IR (DMSO) ν_{CO} 2059 (s), 1988 (s, br) cm^{-1}; IR (CH$_3$CN) ν_{CO} 2069 (s), 2006 (s, br) cm^{-1}; ^{1}H NMR (d_6-DMSO) δ 10.30 (OH), 5.75 (br, 2H), 5.67 (br, 2H); ^{1}H NMR (CD$_3$CN) δ 6.21 (br, 2H), 5.91 (br, 2H); ^{13}C NMR (CD$_3$CN) δ 218.0 (Mn−CO), 143.5, 93.3, 90.5. [(η^6-resorcinol)Mn(CO)$_3$]BF$_4$ (**3a**) was synthesized by treating the manganese tricarbonyl transfer reagent [(η^6-acenaphthene)Mn(CO)$_3$]BF$_4$ with resorcinol according to a published procedure.[6,10] Characterization data for [**3a**]BF$_4$: yield 90%; IR (DMSO) ν_{CO} 2056 (s), 1985 (s, br) cm^{-1}; IR (CH$_3$CN) ν_{CO} 2071 (s), 2008 (s, br) cm^{-1}; ^{1}H NMR (d_6-DMSO) δ 6.57 (br, 1H), 5.31 (br, 2H), 5.12 (s, 1H); ^{1}H NMR (CD$_3$CN) δ 6.63 (t, J = 6.9 Hz, 1H), 5.63 (s, 1H), 5.50 (d, J = 6.9 Hz, 2H); ^{13}C NMR (CD$_3$CN) δ 217.6 (Mn−CO), 150.9, 105.2, 76.6, 74.7.

Semiquinone Complexes 1b−3b. Triethylamine (0.33 mmol) was added to a solution of [**1a**]BF$_4$ (100 mg, 0.30 mmol) in acetone (10 mL) under nitrogen at room temperature. Within a few minutes a pale yellow precipitate of **1b** formed, which was filtered and washed three times with acetone. Characterization data for **1b**: yield 90%; IR (DMSO) ν_{CO} 2031 (s), 1958 (s, br) cm^{-1}; ^{1}H NMR (d_6-DMSO) δ 10.55 (br, OH), 5.37 (br, 4H); ^{13}C NMR (d_6-DMSO) δ 223.4 (Mn−CO), 149.7, 86.1. Anal. Calcd for C$_9$H$_5$MnO$_5$: C, 43.57; H, 2.03. Found: C, 43.33; H, 2.09. Yellow crystals suitable for X-ray analysis were formed by slow cooling of a DMSO solution from 70 °C to room temperature. To synthesize complexes **2b** and **3b**, the same procedure used for the synthesis of **1b** was followed, except that the products **2b** and **3b** did not spontaneously precipitate. For **2b**, the acetone solvent was removed and the product taken up in dichloromethane and precipitated with diethyl ether. For **3b**, diethyl ether (30 mL) was added to the reaction mixture to induce precipitation. For **2b**: yield 78%; IR (DMSO)

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(18) The self-recognition inherent in intermolecular hydrogen bonding in organometallic systems may be useful in the construction of supramolecular compounds and molecular networks. See, for example: Braga, D.; Maini, L.; Grepioni, F.; Elschenbroich, C.; Paganelli, F.; Schiemann, O. *Organometallics* **2001**, *20*, 1875 and references therein.

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ν_{CO} 2030 (s), 1949 (s, br) cm^{-1}; ^1H NMR (d_6-DMSO) δ 5.64 (m, $J = 4.4$ Hz, 2H), 5.43 (m, $J = 4.4$ Hz, 2H); ^{13}C NMR (d_6-DMSO) δ 222.6 (Mn−CO), 154.6, 86.3, 81.2. Anal. Calcd for $C_9H_5MnO_5$: C, 43.57; H, 2.03. Found: C, 43.14; H, 2.18. Characterization data for **3b**: yield 88%; IR (DMSO) ν_{CO} 2035 (s), 1957 (s, br) cm^{-1}; ^1H NMR (d_6-DMSO) δ 11.28 (br, OH), 6.24 (br, 1H), 4.93 (br, 2H), 4,57 (s, 1H); ^{13}C NMR (d_6-DMSO) δ 222.4 (Mn−CO), 164,7, 102.8, 75.6, 72.4. Anal. Calcd for $C_9H_5MnO_5$: C, 43.57; H, 2.03. Found: C, 43.05; H, 2.08.

Quinone Complexes 1c−3c. To a solution of **1b** (100 mg, 0.40 mmol) in DMSO (10 mL) was added $NaOAc\cdot 3H_2O$ (60 mg, 0.44 mmol) under nitrogen at room temperature. After 20 min, the pale yellow product Na[**1c**] was precipitated by the addition of acetone (20 mL). The product was washed three times with acetone. Characterization data for Na[**1c**]$\cdot 3H_2O$: yield 85%; IR (DMSO) ν_{CO} 1998 (s), 1916 (s, br) cm^{-1}; ^1H NMR (d_6-DMSO) δ 4.55 (br, 4H); ^{13}C NMR (d_6-DMSO) δ 226.7 (Mn−CO), 158.9, 85.4. Anal. Calcd for $C_9H_4MnO_5Na\cdot 3H_2O$: C, 33.35; H, 3.11. Found: C, 32.92; H, 3.15. Complex Na[**2c**] was synthesized by adding $NaOAc\cdot 3H_2O$ (60 mg) to **2b** (100 mg) in acetone (10 mL) under nitrogen. After 10 min the product was precipitated with diethyl ether. Characterization data for Na[**2c**]$\cdot 3H_2O$: yield 78%; IR (DMSO) ν_{CO} 1999 (s), 1906 (s, br) cm^{-1}; ^1H NMR (d_6-DMSO) δ 5.26 (br, 2H), 4.28 (br, 2H); ^{13}C NMR (d_6-DMSO) δ 225.6 (Mn−CO), 170.8, 83.9, 75.1. Anal. Calcd for $C_9H_4MnO_5Na\cdot 3H_2O$: C, 33.35; H, 3.11. Found: C, 33.02; H, 3.17. Crystals suitable for X-ray analysis were grown by diethyl ether diffusion into an acetone solution. Complex Na[**3c**] was synthesized by adding $NaOAc\cdot 3H_2O$ (60 mg) to **3b** (100 mg) in acetone (10 mL) under nitrogen. After 20 min the product was precipitated with diethyl ether. Characterization data for Na[**3c**]$\cdot 3H_2O$: yield 80%; IR (DMSO) ν_{CO} 2008 (s), 1924 (s, br) cm^{-1}; ^1H NMR (d_6-DMSO) δ 5.78 (t, 1H), 4.33 (d, $J = 6.6$ Hz, 2H), 3.78 (s, 1H); ^{13}C NMR (d_6-DMSO) δ 223.8 (Mn−CO), 168.6, 102.0, 76.3, 72.3.

Crystal Structures. The X-ray structure determinations for **1b**, **2b**, and Na[**2c**] were performed conventionally (see the Supporting Information). It is worth noting explicitly, however, that for all three structures, all hydrogen atoms appeared in the difference maps and were refined isotropically without constraints (i.e., they were not inserted in idealized positions).

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Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **1b**, **2b**, and Na[**2c**]. This material is available free of charge via the Internet at http://pubs.acs.org.

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