

## Preliminary communication

 $\eta^6$ -Hydroquinone and catechol complexes of manganese tricarbonyl.  
 Molecular structure of  $[(\eta^6\text{-hydroquinone})\text{Mn}(\text{CO})_3]_2\text{SiF}_6$ <sup>1</sup>

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## Abstract

The reaction of  $(\eta^6\text{-acenaphthene})\text{Mn}(\text{CO})_3^+$  with hydroquinone and catechol affords the stable  $\pi$ -bonded complexes  $(\eta^6\text{-hydroquinone})\text{Mn}(\text{CO})_3^+$  (**1**) and  $(\eta^6\text{-catechol})\text{Mn}(\text{CO})_3^+$  (**2**). The X-ray structure of  $[\text{1}]_2\text{SiF}_6$  shows an approximately planar arene ligand with the -OH substituents strongly hydrogen bonded to fluorine atoms in the  $\text{SiF}_6^{2-}$  anion. Deprotonation of **1** and **2** by  $\text{NEt}_3$  yields the corresponding  $\pi$ -bonded semiquinone complexes.

**Keywords:** Manganese; Hydroquinone; Catechol; Semiquinone

Complexes containing a transition metal  $\pi$ -bonded in a  $\eta^4$  manner to the diene carbons of a 1,4-quinone have been known for some time [1–9]. In principle, protonation of the oxygen atoms in such complexes should provide a route to  $\pi$ -bonded  $\eta^5$ -semiquinone and  $\eta^6$ -hydroquinone analogues. Although this has been accomplished with several  $\eta^4$ -diquinone complexes [6,7,9], in general the chemistry of  $\pi$ -bonded 1,4-semiquinones and hydroquinones is little developed — a fact most likely due to difficulty in synthesis and/or high reactivity. For example,  $(\eta^6\text{-hydroquinone})\text{Cr}(\text{CO})_3$  is reported to be a heat- and air-sensitive compound that can be characterized in solution, but cannot be isolated as a pure solid [10,11]. Herein we demonstrate that  $(\eta^6\text{-hydroquinone})\text{Mn}(\text{CO})_3^+$  (**1**) can be readily synthesized and isolated as the  $\text{BF}_4^-$  salt.

Many complexes containing 1,2-quinone, 1,2-semiquinone and 1,2-dihydroxybenzene (catechol) ligands are known with the metal coordinated via the oxygen atoms [12]. There are very few reported examples of such ligands being bound to the metal through the carbon–carbon  $\pi$  network [13–16]. As detailed below, we have found that catechol itself is easily coordinated to manganese to afford  $(\eta^6\text{-catechol})\text{Mn}(\text{CO})_3^+$  (**2**).

Both **1** and **2** were synthesized in good yield and high purity by the recently reported [17] method of manganese tricarbonyl transfer from (polyarene) $\text{Mn}(\text{CO})_3^+$  complexes. In this case the polyarene was acenaphthene, which is very easily displaced from the manganese by more strongly donating arenes. Thus, a mixture of 0.25 mmol of hydroquinone (or catechol) and 0.20 mmol of  $[(\eta^6\text{-acenaphthene})\text{Mn}(\text{CO})_3]\text{BF}_4$  in 8 ml of  $\text{CH}_2\text{Cl}_2$  was heated to 70°C for 1 h in a pressure tube. After cooling, the product was precipitated with diethyl ether as the light yellow  $\text{BF}_4^-$  salt [18]. Repeated attempts to grow crystals of  $[\text{1}]\text{BF}_4$  suitable for X-ray study were unsuccessful. However, diethyl ether vapor diffusion at –20°C into an acetone solution of  $[\text{1}]\text{BF}_4$  containing a small amount of  $\text{HBF}_4$  (to suppress  $\text{H}^+$  dissociation, vide infra) led to well-formed crystals of the  $\text{SiF}_6^{2-}$  salt. Presumably, this resulted from the action of  $\text{HBF}_4$  on the walls of the glass container to produce a continuous supply of  $\text{SiF}_6^{2-}$  anions at low concentration. It was found that  $[\text{1}]_2\text{SiF}_6$  is insoluble in acetone, indicating that a very low concentration of  $\text{SiF}_6^{2-}$  was a necessary condition for successful crystal growth.

The molecular structure of  $[\text{1}]_2\text{SiF}_6$  is shown in Fig. 1 [19]. Selected bond lengths and angles are given in Table 1. An examination of the structural details shows that the hydroquinone ligand is fairly planar (mean deviation 0.032 Å). There is, however, a small distortion in the sense that C(1) and C(4) are displaced by

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<sup>1</sup> Dedicated to Professor Marvin Rausch on the occasion of his 65th birthday.



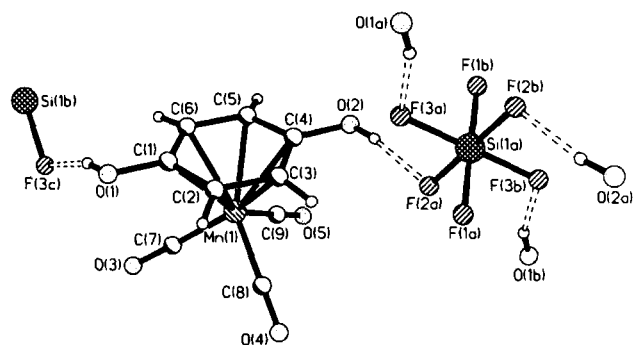
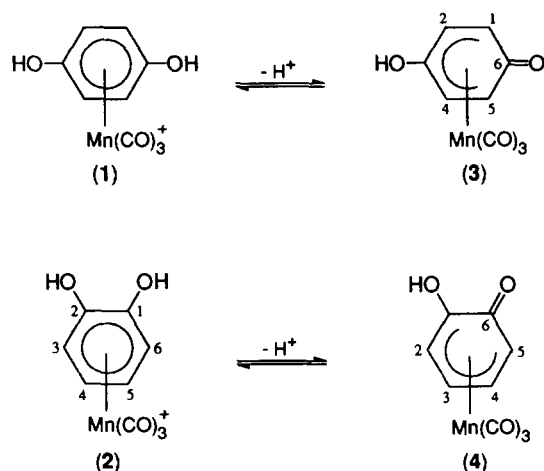


Fig. 1. Molecular structure of  $[(\eta^6\text{-hydroquinone})\text{Mn}(\text{CO})_3]_2\text{SiF}_6$  (1). Also shown is the strong hydrogen bonding interaction between each -OH substituent and a fluorine atom on the anion. Atom labels that include letters are derived from those without letters by symmetry operations of the space group.

0.05 Å from the plane defined by C(2), C(3), C(5), and C(6). As a consequence, the planes C(2), C(1), C(6), O(1) and C(3), C(4), C(5), O(2) form angles of 2.6° and 1.6°, respectively, with the aforementioned plane. This causes the hydroquinone ligand to be folded by ca. 6° with respect to the C(1)⋯C(4) vector. The most interesting structural feature of  $[\text{1}]_2\text{SiF}_6$  is the strong hydrogen bonding between each -OH substituent and a fluorine atom in the  $\text{SiF}_6^{2-}$  anion. Four of the six F atoms in each  $\text{SiF}_6^{2-}$  are hydrogen bonded: F(2) and F(3) and equivalents. F(1) and its equivalent do not participate in hydrogen bonding because there are not enough donors, accounting for the shorter Si–F(1) distance in comparison with Si–F(2) and Si–F(3) (Table 1). The strong hydrogen bonds in  $[\text{1}]_2\text{SiF}_6$  account for its insolubility in acetone (the  $\text{BF}_4^-$  salt is quite soluble). Pertinent data documenting the hydrogen bonding are: O(1)⋯F(3) distance, 2.656(2) Å; O(2)⋯F(2) distance, 2.599(2) Å; O(1)–H(1)⋯F(3) angle, 162.7(1)°; O(2)–H(2)⋯F(2) angle, 167.9(1)°.

Table 1  
Selected bond lengths (Å) and angles (deg) for  $[(\eta^6\text{-hydroquinone})\text{Mn}(\text{CO})_3]_2\text{SiF}_6$  (1)

Bond lengths			
Mn–C(1)	2.252(2)	Mn–C(2)	2.189(2)
Mn–C(3)	2.188(2)	Mn–C(4)	2.239(2)
Mn–C(5)	2.191(2)	Mn–C(6)	2.202(2)
Mn–C(7)	1.820(2)	Mn–C(8)	1.813(3)
Mn–C(9)	1.809(2)	C(7)–O(3)	1.135(3)
C(8)–O(4)	1.132(3)	C(9)–O(5)	1.143(3)
C(1)–O(1)	1.337(3)	C(4)–O(2)	1.336(3)
C(1)–C(6)	1.414(3)	Si–F(1)	1.650(2)
Si–F(2)	1.697(1)	Si–F(3)	1.675(2)
Bond angles			
Mn–C(1)–O(1)	130.7(2)	Mn–C(4)–O(2)	129.3(2)
Mn–C(7)–O(3)	177.0(2)	Mn–C(8)–O(4)	179.1(2)
Mn–C(9)–O(5)	178.1(2)	C(2)–C(1)–O(1)	117.8(2)
C(6)–C(1)–O(1)	123.4(2)	C(3)–C(4)–O(2)	124.1(2)
C(5)–C(4)–O(2)	117.3(2)	C(2)–C(1)–C(6)	118.8(2)
C(3)–C(4)–C(5)	118.5(2)	C(1)–C(2)–C(3)	120.6(2)



Scheme 1.

Preliminary experiments indicate that **1** is readily deprotonated by an equivalent of  $\text{NEt}_3$  in THF to give the neutral semiquinone complex **3** according to Scheme 1 [21]. Similarly, the catechol complex **2** is deprotonated to **4**, but excess  $\text{NEt}_3$  is required, i.e. **1** is a stronger acid than is **2** [21]. This acidity difference is thermodynamic rather than kinetic since the results did not depend on time. It has been shown previously that the arene -OH in the complex  $(\text{phenol})\text{Mn}(\text{CO})_3^+$  is readily deprotonated by  $\text{Bu}^t\text{OK}$  [22].

We have shown that stable hydroquinone and catechol complexes of  $\text{Mn}(\text{CO})_3^+$  are easily synthesized. They can be deprotonated to afford semiquinone (and quinone) analogs. A detailed study of the deprotonation, redox, and electrophilic chemistry of these complexes is underway.

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## References and notes

- [1] G.G. Aleksandrov and Y.T. Struchkov, *Zh. Strukt. Khim.*, 12 (1971) 1037.
- [2] V.A. Uchtman and L.F. Dahl, *J. Organomet. Chem.*, 40 (1972) 403.
- [3] G.G. Aleksandrov and Y.T. Struchkov, *Zh. Strukt. Khim.*, 14 (1973) 1067.
- [4] N.A. Bailey and H. Adams, *Cryst. Struct. Commun.*, 9 (1980) 120.
- [5] M. Valderrama, M. Scotti, R. Ganz, L.A. Oro, F.J. Lahoz, C. Foces-Foces and F.H. Cano, *J. Organomet. Chem.*, 288 (1985) 97.



- [6] G.M. Bodner and T.R. Englemann, *J. Organomet. Chem.*, **88** (1975) 391.
- [7] G. Fairhurst and C. White, *J. Organomet. Chem.*, **160** (1978) C17.
- [8] S.H. Cho, R. Wirtz and L.S. Liebeskind, *Organometallics*, **9** (1990) 3067.
- [9] U. Koelle, C. Weißschädel and U. Englert, *J. Organomet. Chem.*, **490** (1995) 101.
- [10] M.E. Wright, *J. Organomet. Chem.*, **376** (1989) 353.
- [11] H. Schumann, A.M. Arif and T.G. Richmond, *Polyhedron*, **9** (1990) 1677.
- [12] G.A. Fox and C.G. Pierpont, *Inorg. Chem.*, **31** (1992) 3718; C.G. Pierpont and C.W. Langi, *Prog. Inorg. Chem.*, **41** (1994) 331.
- [13] D.S. Bohle and P.A. Goodson, *J. Chem. Soc., Chem. Commun.*, (1992) 1205; D.S. Bohle, K.T. Carron, A.N. Christensen, P.A. Goodson and A.K. Powell, *Organometallics*, **13** (1994) 1355.
- [14] F. Hartl and A. Vlcek, *Inorg. Chem.*, **31** (1992) 2869.
- [15] W. Paw, J.B. Keister, C.H. Lake and M.R. Churchill, *Organometallics*, **14** (1995) 767.
- [16] S.A. Westcott, N.J. Taylor, T.B. Marder, R.T. Baker, N.J. Jones and J.C. Calabrese, *J. Chem. Soc., Chem. Commun.*, (1991) 304.
- [17] S. Sun, L.K. Yeung, D.A. Sweigart, T.-Y. Lee, S.S. Lee, Y.K. Chung, S.R. Switzer and R.D. Pike, *Organometallics*, **14** (1995) 2613.
- [18] For [1]BF<sub>4</sub>: yield 85%; IR (THF): 2060, 1993 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ 6.48 (s, Ar-H), 3.40 (br, O-H). Anal. for [1]<sub>2</sub>SiF<sub>6</sub>. Found: C, 33.60; H, 1.95; Si, 5.15%. Calc.: C, 33.75; H, 1.88; Si, 4.38%. For [2]BF<sub>4</sub>: yield 70%, IR (THF): 2058, 1990 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ 6.28 (m, H(4,5)), 6.03 (m, H(3,6)).
- [19] X-Ray data collection was carried out on a crystal of dimensions 0.38 × 0.43 × 0.64 mm using a Siemens P4 diffractometer controlled by XSCANS version 2.1 software. Crystal data for [1][SiF<sub>6</sub>]<sub>1/2</sub>: monoclinic, space group *P*2<sub>1</sub>/*c*, with *a* = 6.5298(8) Å, *b* = 15.421(2) Å, *c* = 11.459(2) Å, β = 105.441(10)°, *V* = 1099.2(2) Å<sup>3</sup>, *Z* = 4, *D*<sub>calc</sub> = 1.934 g cm<sup>-3</sup>, data collected at 25°C with Mo Kα radiation, μ = 1.310 mm<sup>-1</sup>, θ range 2.28°–26.00°, 169 variables refined with 2154 independent reflections to *R* = 0.0305, *wR*<sub>2</sub> = 0.0803 (*I* > 2σ(*I*)), and GOF = 1.038. The structure was solved by Patterson and difference map methods. All hydrogen atoms appeared in a difference map, and each was placed in an ideal position, riding on the atom to which it is bonded; each was refined with an isotropic temperature factor 20% greater than that of the ridden atom. All other atoms were refined with anisotropic thermal parameters. Final refinement based on *F*<sup>2</sup>, was carried out using SHELXL 93 [20]. Tables of atom coordinates, thermal parameters, bond lengths, and bond angles have been deposited with the Cambridge Crystallographic Data Centre.
- [20] G.M. Sheldrick, 1993.
- [21] For complex 3: IR (THF): 2033, 1960, 1630 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ 6.07 (d, H(2,4)), 4.77 (d, H(1,5)). For complex 4: IR (THF): 2031, 1948, 1605 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ 6.15 (m, H(4)), 5.88 (d, H(2)), 5.42 (m, H(3)), 5.01 (d, H(5)). Initial results suggest that the use of the stronger base Bu<sup>t</sup>OK leads to double deprotonation to afford the corresponding quinone complexes.
- [22] S.-G. Lee, J.-A. Kim, Y.K. Chung, T.-S. Yoon, N. Kim, W. Shin, J. Kim and K. Kim, *Organometallics*, **14** (1995) 1023.