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Preliminary communication

Pendant-*para*-benzoquinonyl substituted cyclopentadienyl ligands: preparation of 1-*para*-benzoquinonyl-2,3,4,5-tetraphenylcyclopentadienyl (η^5-‡CpQ) ruthenium(II) carbonyl complexes

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Abstract

The preparations of the 2,5-dimethoxyphenyl-, *para*-hydroquinonyl- and *para*-benzoquinonyl-tetraphenylcyclopentadienyl complexes $[(\eta^5\text{-}^{\ddagger}\mathrm{CpQMe_2})\mathrm{Ru(CO)(L)Br}]$ (**2**: L = CO, **5**: L = PPh_3), $[(\eta^5\text{-}^{\ddagger}\mathrm{CpQH_2})\mathrm{Ru(CO)(L)Br}]$ (**3**: L = CO, **6**: L = PPh_3) and $[(\eta^5\text{-}^{\ddagger}\mathrm{CpQ})\mathrm{Ru(CO)(L)Br}]$ (**4**: L = CO, **7**: L = PPh_3) are described. It is demonstrated that the *para*-benzoquinonyl/hydroquinonyl-substituted complexes support substituent-centred electron and proton transfer reactions.

Although cyclopentadienyls can stabilise metals in both high and low oxidation states, they generally are "innocent" ligands and do not take part in the reactivity of a complex [1,2 *]. One way of complementing and perhaps enhancing the reactivity displayed by a particular cyclopentadienyl complex is to add either a chemically active or an electrochemically active pendant substituent to the cyclopentadienyl ligand. *para*-Benzoquinones are universally used as hydrogen acceptors and along with their redox derivatives (*para*-benzosemiquinones and *para*-benzohydroquinones) form perhaps the simplest of organic electron transfer cycles [3]. In this communication we describe the synthesis of a cyclopentadienyl ligand substituted by *para*-benzoquinone, and demonstrate that its ruthenium carbonyl complexes can act as electron and/or hydrogen acceptors.

Scheme 1 summarises our synthetic results [4*]. All compounds are completely characterised by their analytical and spectroscopic data. Ligand **1** was synthesised by simple modification of the established methodology for †CpBr [5,6]—1,4-dimethoxybenzene was directly monolithiated with one equivalent of ^{n}BuLi and tetramethylethylenediamine (TMEDA) in diethylether, the resultant 1-lithio-2,5-dimethoxybenzene treated with tetraphenylcyclopentadienone to give the alcohol ‡CpQMe$_2$OH, and this reacted with 48% HBr to give **1** (‡CpQMe$_2$Br) in 54% overall

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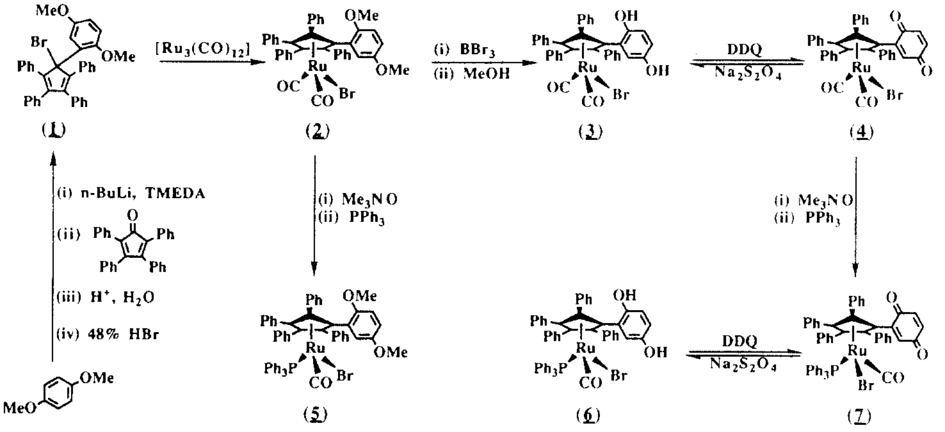
* Reference number with asterisk indicates a note in the list of references.



Scheme 1.

yield. The ^{1}H and ^{13}C{^{1}H}-NMR data for **1** revealed that it was isolated as the mixture of isomers arising from bromine substitution at the three inequivalent cyclopentadienyl ring positions [7*]. Reaction of three equivalents of **1** with $[Ru_3(CO)_{12}]$ in toluene heated at reflux gave $[(\eta^5\text{-}^{\ddagger}CpQMe_2)Ru(CO)_2Br]$, **2**, in 67% yield (Scheme 1). A variable temperature ^{1}H-NMR study of **2** (Fig. 1) clearly demonstrates that the 2,5-dimethoxyphenyl substituent rotates on the NMR time-scale (models show that the *ortho*-methoxy group can point either away from or towards the ruthenium atom) [7*]. Two pairs of methoxy peaks (at δ 3.63, 3.07 ppm and δ 3.24, 3.15 ppm with ~ 4 : 1 integrated intensity ratio) were found in the static limiting spectrum obtained below 260 K. These peaks broadened on warming until coalescence was observed at 340 K. Accompanying changes were also observed in the phenyl region of the ^{1}H-NMR spectra. The molecular structure of **2** has been determined by an X-ray crystal structure analysis [8*]. It confirms that **2** crystallises with the *ortho*-methoxy groups orientated away from the ruthenium atom in the solid state (Fig. 2). The dihedral angles between the cyclopentadienyl ring and the phenyl substituents (clockwise in Fig. 2a from the 2,5-dimethoxyphenyl substituent) are 43.5°, 59.8°, 48.0° compared to a dihedral angle of 74.9° between the 2,5-dimethoxyphenyl substituent and the cyclopentadienyl ring.

"Deprotection" of the methoxy groups in **2** was readily effected by BBr_3 in dichloromethane to give the hydroquinonyl-substituted complex $[(\eta^5\text{-}^{\ddagger}CpQH_2)Ru(CO)_2Br]$, **3**, in 78% yield [7*]. The hydroquinonyl complex **3** was sparingly soluble in CH_2Cl_2 but very soluble in MeOH whereas **2** was insoluble in MeOH and very soluble in CH_2Cl_2. In infrared spectra of **3** ν(CO) bands were observed at 2054 and 2006 cm^{-1} and ν(OH) bands were found at 3422 and 3295 cm^{-1}. Interestingly, interconversion between the two rotamers arising from the two possible orientations of the hydroquinonyl ring (ie. with the *ortho*-OH group either oriented away or towards the ruthenium atom) was not observed in the ^{1}H-NMR spectrum of **3**. Apart from the phenyl multiplets, peaks were found for the hydroquinonyl ring protons of both rotamers in the region δ 6.75–6.17 ppm as well as four distinct but broader hydroquinonyl OH proton resonances at δ 5.50, 4.98, 4.24 and 4.08 ppm [9*].

Oxidation of **3** with dichlorodicyanoparabenzoquinone (DDQ) cleanly gave the

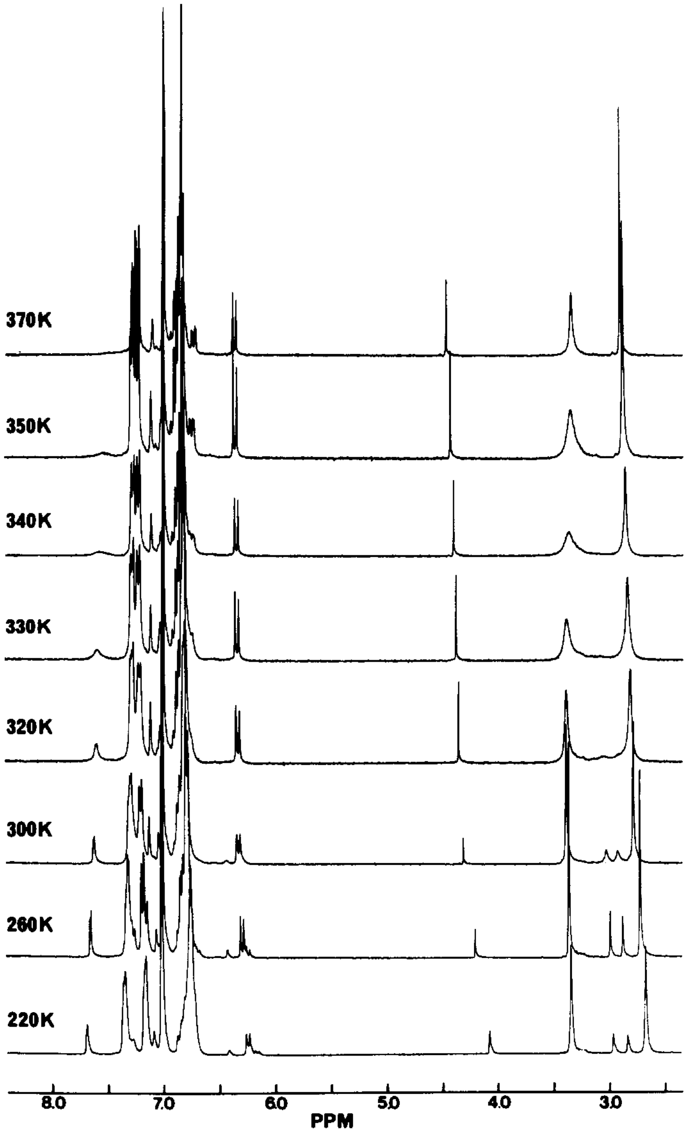


Fig. 1. Variable temperature ^{1}H-NMR spectra of [(η^5-‡CpQMe$_2$)Ru(CO)$_2$Br] (2) in toluene-d_8 (300 MHz, the signals at δ 7.0 and ~ 4.3 ppm are due to protic impurities in the toluene-d_8 solvent and to CH_2Cl_2 of crystallisation, respectively).

para-benzoquinonyl-substituted complex [(η^5-‡CpQ)Ru(CO)$_2$Br], **4** [7*]. At ambient temperature, the high temperature average ^{1}H-NMR spectrum of the two rotamers of **4** is obtained. Comparison of the ^{1}H-NMR data for **2**–**4** suggest that rates of rotation of the cyclopentadienyl substituents increase in the order: **4** < **2** < **3**. The solution infrared spectrum of **4** showed ν(CO) bands at 2057, 2009 cm^{-1} (carbonyl ligands) and a third band at 1669 cm^{-1} (quinonyl C=O stretch). The minor perturbation in ν(CO) frequencies for the carbonyl ligands (~ 3 cm^{-1}) on going from " electron-rich" hydroquinonyl-substituted **3** to "electron-poor" *para*-

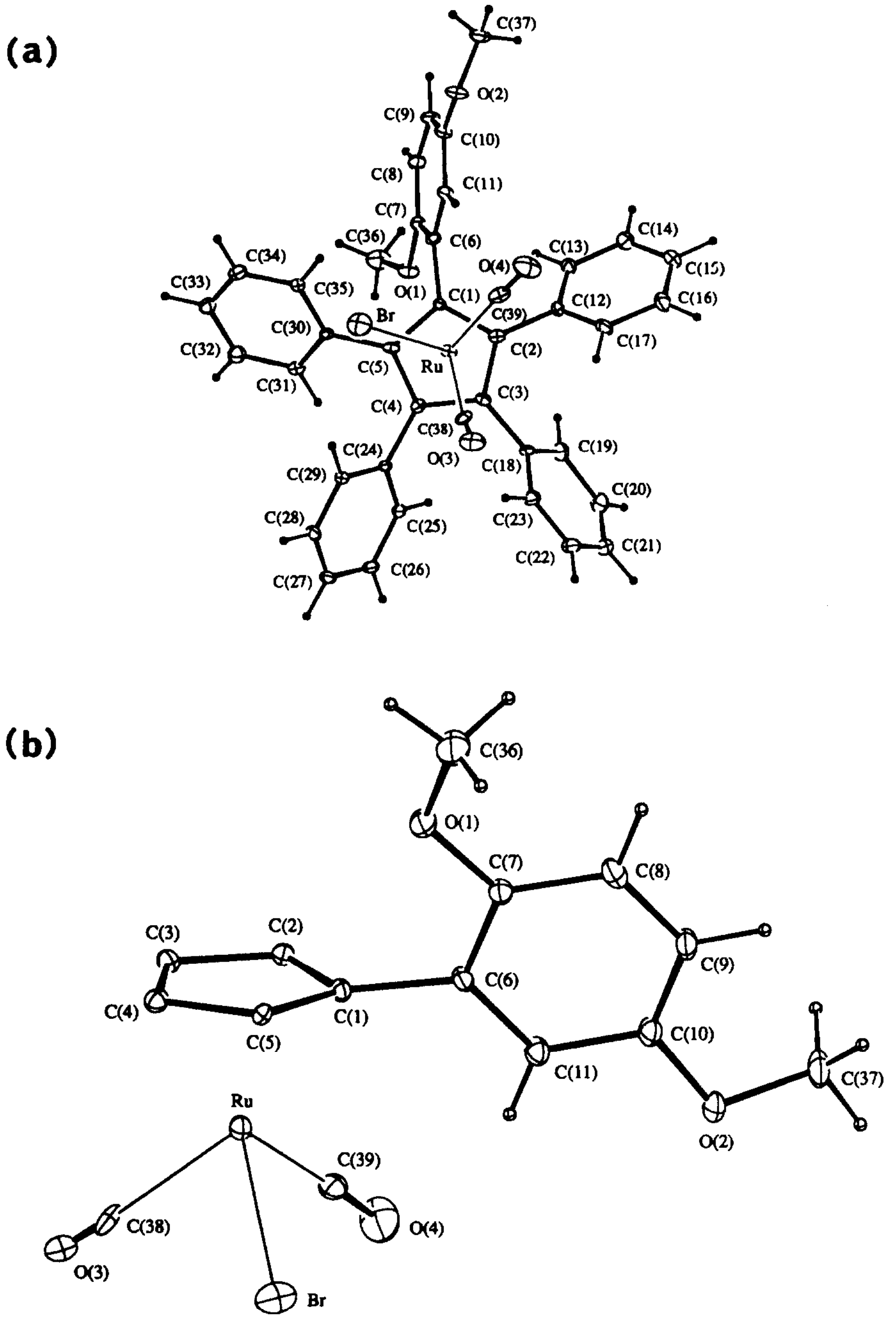


Fig. 2. (a) The molecular structure of [(η^5-‡CpQMe$_2$)Ru(CO)$_2$Br] (**2**) with atom labelling. (b) View of **2** emphasising the orientation of the 2,5-dimethoxyphenyl substituent with respect to the cyclopentadienyl ring (phenyl groups deleted for clarity). Selected bond distances (Å) and angles (°): Ru–Br 2.531(2), Ru–C(1) 2.234(10), Ru–C(2) 2.228(10), Ru–C(3) 2.228(10), Ru–C(4) 2.253(10), Ru–C(5) 2.222(10), Ru–C(38) 2.095(14), Ru–C(39) 1.966(15); Br–Ru–C(1) 110.0(2), Br–Ru–C(38) 82.8(2), Br–Ru–C(39) 89.7(4), C(1)–Ru–C(39) 103.2(4), C(38)–Ru–C(39) 89.1(7), C(5)–C(1)–C(2) 109.4(8), C(2)–C(1)–C(6) 123.9(8), C(5)–C(1)–C(6) 125.3(9).

benzo-quinonyl-substituted **4** suggests that there is little electronic delocalisation between the cyclopentadienyl and quinonyl/hydroquinonyl moieties and is consistent with each molecule having orthogonal redox centres (ie. the quinonyl/hydroquinonyl substituent is perpendicular to the cyclopentadienyl ring) [10*]. Shaking a dichloromethane solution of **4** with aqueous sodium dithionite gave back **3** in almost quantitative yield. Cyclic voltammograms of **4** in 1,2-dichloroethane (0.2 *M* $^{n}Bu_4NPF_6$) showed a fully reversible one-electron reduction at −0.36 V (vs. Ag/AgCl) [11*], which may be confidently assigned to the one-electron reduction of the pendant quinonyl moiety to its semiquinone. (For comparison, the corresponding benzoquinone/benzosemiquinonyl radical anion couple measured under the same conditions was −0.53 V. Also, **2** is electrochemically inactive between +1.42 V and −1.37 V [7*,12].) Thus, both a chemically reversible $2e^-$, $2H^+$ reduction to the hydroquinone and an electrochemically reversible one-electron reduction to the semiquinonyl radical anion can be effected in the pendant quinone substituent.

Connelly and Manners recently reported that in the $^{\dagger}Cp$ analogue of **2**–**4** (i.e. $[(\eta^5\text{-}^{\dagger}Cp)Ru(CO)_2Br]$) carbonyl substitution by phosphines stabilises the Ru^{III}/Ru^{II} couple [12]. Therefore, the triphenylphosphine derivatives of **2**–**4** were also prepared in order to probe for intramolecular interactions between ruthenium and pendant redox centres. No reaction occurred when **2** was heated with excess triphenylphosphine in toluene at reflux [13*]. However, the phosphine-substituted complex $[(\eta^5\text{-}^{\ddagger}CpQMe_2)Ru(CO)(PPh_3)Br]$, **5**, was readily obtained by treating **2** in dry dichloromethane with an equivalent of anhydrous Me_3NO followed by an equivalent of triphenylphosphine (Scheme 1). The analogous reaction of **4** gave a surprisingly good yield (76%) of the phosphine-substituted quinonyl complex $[(\eta^5\text{-}^{\ddagger}CpQ)Ru(CO)(PPh_3)Br]$, **7** (Scheme 1). None of the products expected from complications such as nucleophilic attack on the pendant quinone by triphenylphosphine or released trimethylamine were observed [14*]. The phosphine-substituted hydroquinonyl complex $[(\eta^5\text{-}^{\ddagger}CpQH_2)Ru(CO)(PPh_3)Br]$, **6**, was obtained in near quantitative yield by shaking a solution of **7** in dichloromethane with aqueous sodium dithionite (Scheme 1). Fluxional behaviour arising from equilibration of rotamers on the NMR timescale was also observed in the respective ^1H-NMR spectra of **5** and **7** [7*]. Cyclic voltammograms of **5** in 1,2-dichloroethane (0.2 *M* $^{n}Bu_4NPF_6$) revealed the expected metal-centred, reversible one-electron oxidation at +1.03 V (vs. Ag/AgCl) [13*]. The cyclic voltammograms of **7** were characterised by two reversible one-electron processes at +1.19 V and −0.50 V, which correspond to oxidation of the ruthenium centre and to reduction of the quinonyl moiety, respectively. The shifts in the Ru^{III}/Ru^{II} couple of **7** to more positive potential than that of **5** and in the benzoquinone/semiquinone couple of **7** to more negative potential than that of **4** are consistent with the mutual perturbation of the linked "electron-rich" ruthenium and "electron-poor" quinonyl centres in **7** on each other. Another interesting and immediately obvious property of **7** is the intense, almost black colour of its crystals and solutions (**2**–**6** are all pale orange-yellow). In visible spectra recorded in dichloromethane solution intense bands were observed at 480 and 560 nm for **7** whereas **2**–**6** remained transparent over this region. These visible absorptions in **7** are most readily ascribed as charge transfer bands arising from electron transfer from the oxidisable ruthenium centre to the reducible quinonyl centre.

In conclusion, we have shown that organoruthenium complexes with a *para*-benzoquinonyl-substituted cyclopentadienyl ligand, η^5-‡CpQ, can be readily synthesised and that the redox chemistries of these complexes are enhanced by the quinonyl substituent. Currently, we are extending the coordination chemistry of ‡CpQ to other transition metals and are investigating intramolecular oxidations of coordinated substrates by the pendant quinone in selected examples of these η^5-‡CpQ complexes.

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References and notes

1 See any general organometallic textbook, for example: Ch. Elschenbroich and A. Salzer, Organometallics: A Concise Introduction, VCH, Weinheim, 1989; R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, Wiley, New York, 1988; J.P. Collman, L.S. Hegedus, J.R. Norton and R.J. Finke, Principles and Applications of Organotransition Metal Chemistry, second ed., University Science Books, Mill Valley, CA, 1987;

2 There are obvious exceptions to this generalization, for example, cyclopentadienyl ring slippage reactions and organic reactions on the coordinated cyclopentadienyl ligand [1].

3 (a) Z. Rappoport and S. Pataï (Eds.), The Chemistry of the Quinonoid Compounds, Vol. 2, Parts 1 and 2, Wiley, New York, 1988; (b) S. Pataï (Ed.) The Chemistry of the Quinoid Compounds, Vol. 1, Parts 1 and 2, Wiley, New York, 1974.

4 An analogous chemistry exists for Mo and W carbonyl complexes: S.B. Colbran, D.C. Craig and C. Saadeh, work in progress.

5 Symbols: $^{\dagger}\mathrm{Cp} = \eta^5\text{-}\mathrm{C_5Ph_5}$, $^{\star}\mathrm{Cp} = \eta^5\text{-}\mathrm{C_5Me_5}$, $^{\ddagger}\mathrm{Cp} = \eta^5\text{-}\mathrm{C_5Ph_4R}$ (2,5-dimethoxyphenyl, R = $\mathrm{QMe_2}$; *para*-hydroquinonyl, R = $\mathrm{QH_2}$; *para*-benzoquinonyl, R = Q).

6 C. Janiak, H. Schumann, C. Stader, B. Wrackmeyer and J.J. Zuckermann, Chem. Ber., 121 (1988) 1745; H. Schumann, C. Janiak and J.J. Zuckerman, ibid., 121 (1988) 207.

7 All new compounds gave satisfactory analyses and the ^{1}H, ^{13}C, ^{31}P NMR and infrared spectra were as expected. Complete data and description will be given in the full paper on this work: S.B. Colbran, D.C. Craig, W.M. Harrison, A.E. Grimley and C. Saadeh, Organometallics, in preparation.

8 Crystal data for $\mathrm{C_{39}H_{29}O_4BrRu}$: M 742.6, monoclinic, space group $P2_1,c$, a 8.393(2), b 17.119(4), c 22.698(6) Å, β 91.14(1)°, V 3261(1) Å^3, $Z = 4$, $2\theta_{\max}$ 45°. Diffraction data were recorded on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromatised Mo-K_α radiation (λ 0.71069 Å). 2184 reflections with $I > 3\sigma$ were considered observed out of 4240 unique data collected. The structure was solved by direct phasing and Fourier methods, and refined using full matrix least squares. Reflection weights used were $1/\sigma^2(F_o)$, with $\sigma(F)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$. Current final residuals are $R = 0.047$, $R_w = 0.054$. Full lists of atomic parameters, thermal parameters, and observed and calculated structure factors are available from D.C.C.

9 The four hydroquinonyl OH resonances shifted slightly from sample to sample and are lost on shaking with $\mathrm{D_2O}$.

10 Larger ν(CO) shifts would be expected if there were significant electronic interactions between the metal and pendant redox centres: S.B. Colbran, B.H. Robinson and J. Simpson, Organometallics, 2 (1983) 943; T.M. Miller, K.J. Ahmed and M.S. Wrighton, Inorg. Chem., 28 (1989) 2347 and references therein.

11 Quoted potentials are from cyclic voltammograms run at a Pt disk electrode (1 mm^2) in the potential range −2.0 V to +2.0 V (vs. Ag/AgCl) with scan rate 100 mV s^{-1} and compound concentration ~10^{-3} *M*. Ferrocene was always added as an internal standard and its potential occurred at 0.46 V (vs. Ag/AgCl).

12 N.G. Connelly and I. Manners, J. Chem. Soc., Dalton Trans., (1989) 283.

13 The complexes [CpRu(CO)$_2$Br] and [*CpRu(CO)$_2$Br] are also inert to phosphine substitution: M.O. Albers, D.J. Robinson and E. Singleton, Coord. Chem. Rev., 79 (1987) 1; although [‡CpRu(CO)$_2$Br] was originally found to be inert to direct phosphine substitution [12], very recent work shows that it is substituted in refluxing xylenes: H. Adams, N.A. Bailey, A.F. Browning, J.A. Ramsden and C. White, J. Organomet. Chem., 387 (1990) 305.

14 Quinones undergo facile Michael addition reactions with phosphines or amines: T.K. Finley, ref. 3a, Ch. 11, p. 537.