Contrasting Pathways for the Reactions of the Electron-acceptor Ligands Tetrachloro-1,2- and -1,4-benzoquinone with the Diruthenium Diphosphazane-bridged Derivatives $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i)

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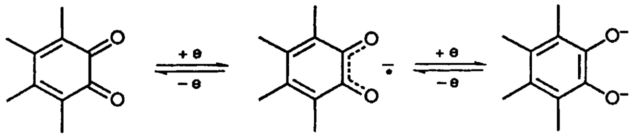
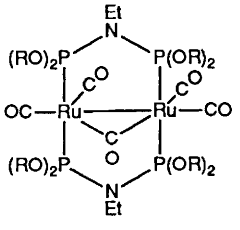
Treatment of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) with *o*-chloranil leads to electron transfer and the fission of one of the diphosphazane ligands to form $[Ru_2\{\mu\text{-}(RO)_2PN(Et)C(O)\}\{(RO)_2POC_6Cl_4O\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}]$, characterized by X-ray crystallography for R = Me, and found to contain a chelating $(MeO)_2POC_6Cl_4O$ group and a novel bridging ligand derived by the coupling of a $(RO)_2PN(Et)$ fragment to a co-ordinated carbonyl group; in contrast, reaction with *p*-chloranil gives the radical anion salt $[Ru_2Cl(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2][p\text{-}OC_6Cl_4O]$ resulting from the *p*-chloranil functioning as a chlorinating agent as well as an electron acceptor.

o- and *p*-Quinones and their substituted derivatives readily function as electron-acceptor ligands on reaction with metal complexes, with *o*-quinones for instance tending to co-ordinate as either the semiquinone (**B**) or as the catecholate (**C**), depending on the electron richness of the metal complex and the electron withdrawing properties of the substituents on the benzene ring. However, while the co-ordination chemistry of quinones is extensive,[1–7] reported examples of radical anion salts derived from quinones are rare.[8]



A **B** **C**



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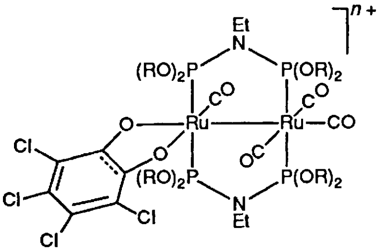

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We have shown previously that the electron-rich diruthenium diphosphazane-bridged derivatives $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **1** (R = Me or Pr^i) react with a wide range of electrophiles and in all cases the $Ru_2\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2$ unit remains intact.[9,10] On the basis of the oxidation potentials for these dinuclear compounds[11] and the nature of the products from their reactions with the electron-acceptor ligand 7,7,8,8-tetracyanoquinodimethane,[12] it was anticipated that their treatment with *o*-chloranil (tetrachloro-1,2-benzoquinone) would lead to the eventual formation of $[Ru_2(o\text{-}O_2C_6Cl_4)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{n+}$ **2**, either ionic (n = 1, $o\text{-}OC_6Cl_4O^-$ salt) or neutral (n = 0) in which the co-ordinated *o*-chloranil is chelated to a single ruthenium atom as either a semiquinone or as a catecholate respectively. Reaction between this quinone and these diruthenium species was observed to take place readily on treatment of the latter with an equimolar amount of the quinone in tetrahydrofuran at room temperature but the $^{31}P\text{-}\{^1H\}$ NMR spectra of the products, formed in near quantitative yield, were indicative of their being very different to that expected. A single-crystal structure determination on the tetramethoxydiphosphazane derivative revealed that its dinuclearity had been retained but that a most unusual rearrangement had taken place resulting from the fission of a phosphorus–nitrogen bond of one of the diphosphazane ligands. Coupling of the $(MeO)_2PN(Et)$ moiety with a co-ordinated carbonyl group and of the $(MeO)_2P$ fragment with the quinone ligand was found to have occurred leading to $(MeO)_2PN(Et)C(O)$ and $(MeO)_2POC_6Cl_4O$ groups respectively with the former co-ordinating in the bridging and the latter in the chelating co-ordination mode.

The molecular stereochemistry of this compound is illustrated in Fig. 1.* Two further salient features with respect to the structure are as follows: (*i*) one of the phosphorus atoms is co-ordinated axially, in contrast to that found for the parent compound, resulting from the effective interchange of co-ordination sites of a $P(OMe)_2$ moiety and a carbonyl group; (*ii*) the two ruthenium atoms which are separated by a distance of 2.882(1) Å, corresponding to a formal ruthenium–ruthenium bond, are best described in terms of one having a formal oxidation state of zero and the other +2.

The quinone promoted cleavage and rearrangement of a phosphorus ligand is novel and, as far as we are aware,

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* *Crystal data:* $C_{23}H_{34}Cl_4N_2O_{15}P_4Ru_2$, M = 1046.33, monoclinic, space group $P2_1/n$, a = 15.412(6), b = 11.678(4), c = 20.874(8) Å, β = 90.33(2)°, U = 3756.9 Å^3, D_c = 1.849 g cm^{-3}, Z = 4, $F(000)$ = 2088, λ(Mo-Kα) = 0.710 69 Å, μ(Mo-Kα) = 7.04 cm^{-1}. 7418 Reflection intensities were measured on a Nonius CAD-4 diffractometer using the ω–2θ scan mode in the range $3 < \theta < 27°$, 6044 of which were classed as observed [$I > 3\sigma(I)$]. These data were corrected for Lorentz and polarisation effects and for absorption using the empirical method. The structure was solved by standard Patterson and Fourier techniques and refined (SHELX 76[13]) by full-matrix least-squares methods to R = 0.061 {R' = 0.084, $w = 2.11/[\sigma^2(F) + 0.04F^2]$} with anisotropic thermal parameters assigned to the Ru, P and Cl atoms and isotropic thermal parameters to the remaining atoms. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

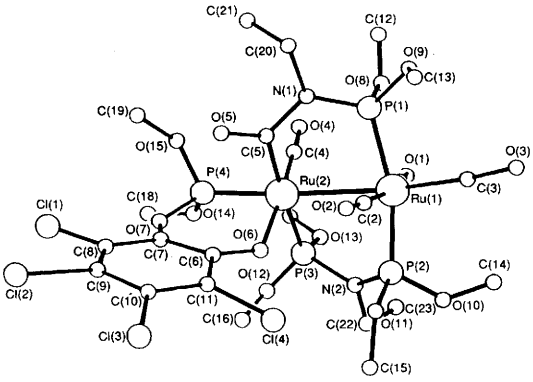
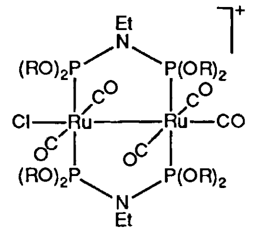


Fig. 1 Molecular stereochemistry of $[Ru_2\{\mu\text{-}(MeO)_2PN(Et)C(O)\}\{(MeO)_2POC_6Cl_4O\}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}]$. Selected bond distances (Å): Ru(1)–Ru(2) 2.882(1), Ru(1)–P(1) 2.312(2), Ru(1)–P(2) 2.320(2), Ru(2)–P(3) 2.353(2), Ru(2)–P(4) 2.208(2), Ru(2)–C(5) 2.111(7), Ru(2)–O(6) 2.170(5), C(5)–O(5) 1.195(9)



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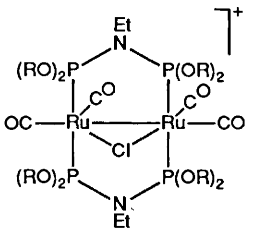

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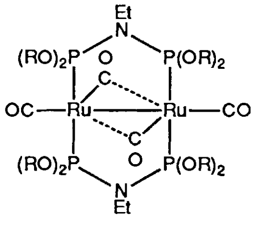

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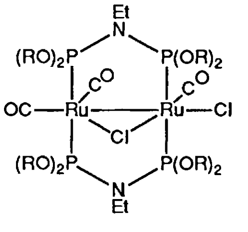

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unprecedented although Connelly *et al.*[14] have established that reaction of *o*-chloranil with $[Rh(\eta\text{-}C_5R_5)(CO)L]$ ($R = H$ or Me, $L = CO$ or PPh_3) affords $[Rh(\eta\text{-}C_5R_5)\{o\text{-}C(O)OC_6Cl_4O\}L]$ in which an *o*-$C(O)OC_6Cl_4O$ ligand has resulted from the linking of catecholate and carbonyl ligands.

A different reactivity pattern was observed for *p*-chloranil (tetrachloro-1,4-benzoquinone). In particular treatment of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **1** with a twice molar amount of this electron acceptor in toluene at room temperature was found to lead to the separation from solution of brown microcrystalline products, identified both microanalytically (C, H, N, Cl) and spectroscopically as $[Ru_2Cl(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{+\bullet}$ salts.* These brown species proved to be unstable in solution, slowly decarbonylating to products which afforded $^{31}P\text{-}\{^1H\}$ NMR and IR spectra in the C–O stretching region identical with those for $[Ru_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ **4**, previously shown to be decarbonylation products of $[Ru_2Cl(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$.[9] The semiquinone radical anion salts of these chloro-bridged cationic species were more readily obtained however by reaction of the formally unsaturated compounds $[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **5**[15] with a twice molar amount of *p*-chloranil in toluene, the brown microcrystalline materials which separated from solution being formulated as salts of $[Ru_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ **4*** on the basis of the microanalytical results.† Significantly, irradiation of mixtures of $[Ru_2Cl(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2][p\text{-}OC_6Cl_4O]$ and $[Ru_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2][p\text{-}OC_6Cl_4O]$ in acetone with ultraviolet light was shown to produce the previously synthesized neutral dichlorotricarbonyl derivatives $[Ru_2(\mu\text{-}Cl)Cl(CO)_3\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **6**.[9]

It is thus apparent that both *o*- and *p*-chloranil readily effect the oxidation of **1** producing semiquinone intermediates, but while the *o*-chloranil radical anion promotes the cleavage of a phosphorus–nitrogen bond of one of the diphosphazane ligands resulting in the formation of neutral $[Ru_2\{\mu\text{-}(RO)_2PN(Et)C(O)\}\{(RO)_2POC_6Cl_4O\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}]$, the *p*-chloranil radical anion functions as a chlorinating agent leading to the formation of the *p*-OC_6Cl_4O radical anion salts of $[Ru_2Cl(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ **3** and their decarbonylation products $[Ru_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ **4**.

Acknowledgements

The authors express their sincere thanks to the Foundation for Research Development and the University of Natal for financial support, Johnson Matthey plc for the loan of ruthenium salts, and Dr. P. H. van Rooyen of the National Chemical Research Laboratory, Council for Scientific and Industrial Research, Pretoria for the intensity data collection.

References

1 A. L. Balch, V. J. Catalano and M. M. Olmstead, *Inorg. Chem.*, 1990, **29**, 1638.
2 S. Bhattacharya and C. G. Pierpont, *Inorg. Chem.*, 1991, **30**, 1511.
3 M. Haga, K. Isobe, E. R. Boone and C. G. Pierpont, *Inorg. Chem.*, 1990, **29**, 3795 and refs. therein.
4 T. P. Blatchford, M. H. Chisholm and J. C. Huffman, *Inorg. Chem.*, 1988, **27**, 2059 and refs. therein.
5 M. Hanaya and M. Iwaizumi, *J. Organomet. Chem.*, 1991, **401**, 31 and refs. therein.
6 W. Kaim, *Coord. Chem. Rev.*, 1987, **76**, 187.
7 C. G. Pierpont and R. M. Buchanan, *Coord. Chem. Rev.*, 1981, **38**, 45.
8 J. B. Torrance, J. J. Mayerle, V. Y. Lee and K. Bechgaard, *J. Am. Chem. Soc.*, 1979, **101**, 4747.
9 J. S. Field, R. J. Haines, E. Minshall, C. N. Sampson, J. Sundermeyer, S. F. Woollam, C. C. Allen and J. C. A. Boeyens, *J. Chem. Soc., Dalton Trans.*, 1991, 2761 and refs. therein.
10 J. S. Field, R. J. Haines, E. Minshall, C. N. Sampson, J. Sundermeyer and S. F. Woollam, *J. Chem. Soc., Dalton Trans.*, 1992, 2629, and refs. therein.
11 J. S. Field, A. M. A. Francis, R. J. Haines and S. F. Woollam, *J. Organomet. Chem.*, 1991, **412**, 383.
12 S. A. Bell, J. S. Field, R. J. Haines, M. Moscherosch, W. Matheis and W. Kaim, *Inorg. Chem.*, 1992, **31**, 3269.
13 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.
14 N. G. Connelly, M. J. Freeman, I. Manners and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1984, 2703.
15 J. S. Field, R. J. Haines, J. Sundermeyer and S. F. Woollam, *J. Chem. Soc., Chem. Commun.*, 1991, 1382.

Received 2nd June 1992; Communication 2/02890E

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* The UV/VIS spectra of these compounds showed peaks at 445 and 480 nm readily assigned to transitions associated with the radical anion $p\text{-}OC_6Cl_4O^{\bullet-}$ while their IR spectra in the C–O stretching region as well as their $^{31}P\text{-}\{^1H\}$ NMR spectra were identical with those previously reported for $[Ru_2Cl(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ **3**.[10] Microanalysis was consistent with two OC_6Cl_4O in the outer coordination sphere, but without crystal structures it was not possible to establish whether **3** and **4** separated as salts of the dimeric anion $(p\text{-}OC_6Cl_4O)_2^-$ or if $p\text{-}OC_6Cl_4O^-$ cocrystallized with neutral *p*-OC_6Cl_4O.

† Confirmation of this formulation was achieved by conversion of these benzosemiquinone salts to the corresponding readily characterized tetraphenylborates $[Ru_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]BPh_4$.[9]