Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

Oxidative-addition of *o*-quinones to ruthenium complexes

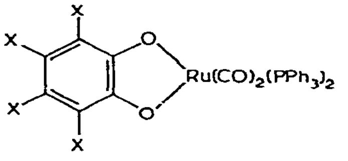
A.L. BALCH and Y.S. SOHN

Department of Chemistry, University of California, Davis, California 95616 (U.S.A.)

(Received April 14th, 1971)

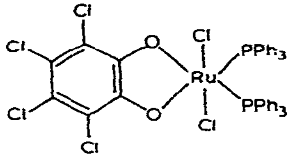
Recently the oxidative-addition of *o*-quinones to low-valent d_{10} and d_8 complexes (*e.g.* $(Ph_3P)_4Pt$, $M(CO)Cl(PPh_3)_2$ (M = Ir, Rh)) have been reported[1–3]. We now report that analogous addition of *o*-quinones to Ru^0 and Ru^{II} complexes occur under mild conditions.

Reaction of tetrachloro-1,2-benzoquinone with *trans*-$Ru(CO)_3(PPh_3)_2$ in dichloromethane solution at 25° yields the orange, crystalline complex $Ru(o\text{-}O_2C_6Cl_4)(CO)_2(PPh_3)_2$ (Ia). A similar reaction occurs with tetrabromo-1,2-benzoquinone to give the golden complex Ib. In both complexes the carbon monoxide ligands are located in *cis* positions since two C≡O stretching frequencies are observed for each in their infrared spectra (2044, 1983 cm^{-1} for both Ia and Ib in dichloromethane solution). The strong carbonyl absorptions of the free quinone are absent in the complexes Ia and Ib; rather, absorptions characteristic of the reduced ligands (at 1500w, 1290s, 790s, and 740 m cm^{-1} for Ia in KBr matrix) are observed. The oxidative nature of the reaction leading to I is confirmed by an alternate preparation of Ia from the Ru^{II} complex, *cis*-$Ru(CO)_2(PPh_3)_2Cl_2$, and tetrachloropyrocatechol in the presence of base.



(Ia, X=Cl ; Ib, X=Br)

Of greater interest are the observations that a variety of *o*-quinones react with the Ru^{II} complex $Ru(PPh_3)_3Cl_2$. Oxidative-addition reactions of d_6 complexes in general have received less attention than is the case for d_{10} and d_8 systems, although oxidative reactions of Mo^0, W^0, and Re^I complexes with halogens have been described[4,5]. Addition of tetrachloro-1,2-benzoquinone to $Ru(PPh_3)_3Cl_2$ leads to the formation of the green, monomeric complex $Ru(o\text{-}O_2C_6Cl_4)(PPh_3)_2Cl_2$ (II). The infrared spectrum of this complex closely resembles that of Ia except for the absence of bands associated with the coordinated carbon monoxide and the presence of a Ru–Cl stretching frequency at 342 cm^{-1} (nujol mull). The observation of a single Ru–Cl stretching frequency, which is in a region consistent with a *trans*-$RuCl_2$ group[6], defines the coordination as diagramed. 1,2-Naphthoquinone, which is a weaker oxidant than tetrachloro-1,2-benzoquinone, also adds to $Ru(PPh_3)_3X_2$ (X = Cl, Br) to yield blue Ru-$(1,2$-$O_2C_{10}H_6)(PPh_3)_2X_2$. Similarly another weakly oxidizing quinone, 9,10-phenanthrenequinone, adds to both $Ru(PPh_3)_3Cl_2$ and $Ru(SbPh_3)_3Cl_2$ to yield Ru-$(9,10$-$O_2C_{14}H_8)(PPh_3)_2Cl_2$ and Ru-$(9,10$-$O_2C_{14}H_8)(SbPh_3)_2Cl_2$, respectively. The infrared spectra of the complexes derived from 1,2-naphthoquinone and 9,10-phenanthrenequinone do not exhibit bands in the region where the carbonyl groups of the parent quinones absorb; rather, bands characteristic of the reduced forms of these ligands are present. These new complexes, which formally contain Ru^{IV}, are electron-deficient in the sense that they do not obey the inert gas rule. Certain six-coordinate Mo^{II} and W^{II} (d_4) complexes react with Lewis bases to form seven-coordinate species[4,7]. However, attempts to add small Lewis bases to the new six-coordinate Ru^{IV} complexes reported here have not as yet been successful.



(II)

ACKNOWLEDGEMENT

The research was supported by grant Am-14946 from the National Institutes of Health.

REFERENCES

1 Y.S. Sohn and A.L. Balch, *J. Amer. Chem. Soc.*, 93 (1971) 1290.
2 J.S. Valentine and D. Valentine, Jr., *J. Amer. Chem. Soc.*, 92 (1970) 5795.
3 D.M. Barlex, R.D.W. Kemmitt and G.W. Littlecott, *Chem. Commun.*, (1971) 199.
4 J.R. Moss and B.L. Shaw, *J. Chem. Soc., A*, (1970) 595 and references therein.
5 W.J. Kirkham, A.G. Osborne, R.S. Nyholm and M.H.B. Stiddard, *J. Chem. Soc., A*, (1965) 550.
6 J.D. Gilbert and G. Wilkinson, *J. Chem. Soc., A*, (1969) 1749.
7 R. Colton, G.R. Scollary and I.B. Tomkins, *Austral. J. Chem.*, 21 (1968) 15.