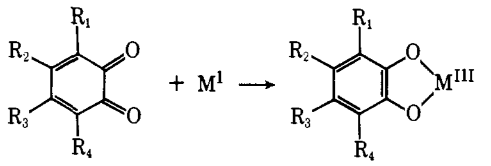
# Oxidative Addition of *o*-Quinones to Complexes of Rhodium(I) and Iridium(I)

**Y. S. Sohn and A. L. Balch***

*Contribution from the Department of Chemistry, University of California, Davis, California 95616.* *Received July 23, 1971*

**Abstract:** Tetrachloro-1,2-benzoquinone adds to the complexes $M(CO)Cl(PR_3)_2$ (M = Rh, Ir; $PR_3$ = $PPh_3$, $PPh_2Me$) to yield the six-coordinate complexes $M(1,2\text{-}O_2C_6Cl_4)(CO)Cl(PR_3)_2$ in a reaction which has been formulated as an oxidative addition to the metal. The stereochemistry of the addition has been investigated by examination of the infrared and pmr spectra of the new complexes. The reactions of a variety of other quinones with $Ir(CO)X(PPh_3)_2$ are described. Tetrachloro-1,2-benzoquinone reacts with $Rh(PPh_3)_3Cl$ to yield the five-coordinate monomer $Rh(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2Cl$ which in turn reacts with bases like carbon monoxide or pyridine to yield the coordinatively saturated species $Rh(1,2\text{-}O_2C_6Cl_4)base(PPh_3)_2Cl$. The cyclooctadiene complexes $[M(1,5\text{-}C_8H_{12})Cl]_2$ (M = Rh, Ir) react with tetrachloro-1,2-benzoquinone to yield complexes of the type $[M(1,2\text{-}O_2C_6Cl_4)(1,5\text{-}C_8H_{12})Cl]_n$.

Considerable attention has been focused recently on oxidative-addition reactions of metal complexes.[1–4] Two classes of these reactions have received study. In one class the reaction results in the cleavage of a $\sigma$ bond of the oxidant and coordination of the two resultant, formally anionic, fragments to the metal. Bonds which may be cleaved in this manner include both homonuclear bonds (*e.g.*, halogen–halogen, hydrogen–hydrogen, carbon–carbon) and heteronuclear bonds (*e.g.*, hydrogen–halogen, metal–halogen, halogen–carbon). The other class involves the addition of a multiple bond, usually one bearing electron-withdrawing substituents (*e.g.*, tetrafluoroethylene, dimethyl acetylenedicarboxylate, dioxygen), to the metal complex. Recent studies in this[5,6] and other[7,8] laboratories have demonstrated that a third class of oxidative-addition reaction must be considered along with the above two. This reaction involves the addition of an *o*-quinone to a metal complex to generate a complex containing an *o*-diolato ligand.



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The reactions of *o*-quinones with metal ions and metal complexes have received relatively little attention. The intensely colored compounds resulting from the addition of phenanthrenequinone or acenaphthenequinone to simple metal salts apparently involve coordination of the metal ion by the ketonic functions of the quinone,[9–12] since the C=O stretching frequency of the quinone undergoes a shift of 40–60 cm$^{-1}$ to lower energies upon complexation. Tetrachloro-1,2-benzoquinone and 3,5-di-*tert*-butyl-1,2-benzoquinone react with nickel carbonyl to yield compounds with the composition Ni(*o*-quinone)$_2$. The paramagnetism and low solubilities of these complexes have led to the suggestion that they consist of a polymeric structure involving octahedrally coordinated Ni(II).[13]

In contrast, several types of interactions between metal complexes and *p*-quinones have been recorded. *p*-Quinones have been shown to function as chelating diolefins in complexes such as $(\pi\text{-}C_5H_5)Rh[1,4\text{-}O_2C_6(CH_3)_4]$[14] and $(1,5\text{-}C_8H_{12})Ni[1,4\text{-}O_2C_6(CH_3)_4]$.[15] No examples of an *o*-quinone bound to a metal in this manner appear to have been reported. Charge-transfer complexes between metal complexes and *p*-quinones have been isolated.[16,17] In these cases the principle charge-transfer interaction involves the quinone $\pi$ orbitals and $\pi$ orbitals on the ligands of the metal complex. The reaction between $[Co(CN)_5]^{3-}$ and *p*-benzoquinone which produces the binuclear complex, $[(NC)_5Co\text{-}OC_6H_4O\text{-}Co(CN)_5]^{6-}$, has been formulated as an example of oxidative addition.[18]

## Experimental Section

**Preparation of Compounds.** The complexes $M(CO)Cl(PPh_3)_2$ (M = Rh,[19] Ir[20]), $Ir(CO)Cl(PPh_2Me)_2$,[21] $[(1,5\text{-}C_8H_{12})MCl]_2$ (M = Rh,[22] Ir[23]), and $Rh(PPh_3)_3Cl$[24] were prepared by standard procedures. Bromo and iodo complexes were obtained by me-

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tathesis with the appropriate lithium salt. The quinones were commercial samples which were used as received except for 9,10-phenanthrenequinone, which was sublimed twice before use. All operations involving oxygen-sensitive phosphines and metal complexes were performed under prepurified nitrogen. However, the quinone adducts, which are air stable, were purified and handled under normal atmospheric conditions.

**$Ir(1,2\text{-}O_2C_6Cl_4)(CO)Cl[P(C_6H_5)_3]_2\cdot CH_2Cl_2$.** A solution of 0.21 g (0.85 mmol) of tetrachloro-1,2-benzoquinone in 10 ml of dichloromethane was added to a stirred suspension of 0.52 g (0.67 mmol) of $Ir(CO)Cl(PPh_3)_2$ in 30 ml of dichloromethane. The clear orange solution which resulted was filtered, and to it was added 20 ml of cyclohexane. Dichloromethane was distilled from the solution until its volume was reduced to 25 ml. Upon cooling, orange crystals of the product (0.48 g, 70%) were obtained. Purification was achieved by recrystallization from dichloromethane–cyclohexane followed by vacuum drying; mp 210–212°.

*Anal.* Calcd: C, 47.57; H, 2.90; Cl, 22.34. Found: C, 48.11; H, 2.91; Cl, 22.78.

The complex is soluble in polar organic solvents. In freshly prepared *N*,*N*-dimethylformamide solution, the complex is a nonelectrolyte. It is diamagnetic in the solid state. The analogous $Ir(1,2\text{-}O_2C_6Cl_4)(CO)Br(PPh_3)_2$ (decomposes above 215°) was similarly prepared from $Ir(CO)Br(PPh_3)_2$ and characterized by its infrared spectrum.

The following complexes were obtained in a similar fashion.

**$Rh(1,2\text{-}O_2C_6Cl_4)(CO)Cl[P(C_6H_5)_3]_2\cdot 1.5C_6H_{12}$.** The complex was obtained as deep blue crystals; mp 141–143°, with resolidification and melting at 180.5–182°. The complex is a nonelectrolyte in *N*,*N*-dimethylformamide solution. It is diamagnetic in the solid state. The presence of solvent of crystallization was verified by observation of bands at 2920 and 2840 $cm^{-1}$ in the infrared spectrum.

*Anal.* Calcd: C, 58.75; H, 4.55; Cl, 16.67; P, 5.82; mol wt, 937. Found: C, 58.59; H, 4.67; Cl, 16.57; P, 5.87; mol wt, 943.

The bromo complex $Rh(1,2\text{-}O_2C_6Cl_4)(CO)Br(PPh_3)_2$ (mp 171–173° dec) was obtained similarly from $Rh(CO)Br(PPh_3)_2$ and identified by its infrared spectrum.

**$Ir(1,2\text{-}O_2C_6Br_4)(CO)Cl[P(C_6H_5)_3]_2$.** The complex was obtained as orange crystals after recrystallization from dichloromethane; mp 211–214°.

*Anal.* Calcd: C, 42.90; H, 2.51; Br, 26.55; P, 5.15. Found: C, 42.77; H, 2.36; Br, 26.27; P, 5.64.

**$Ir(1,2\text{-}O_2C_6Cl_4)(CO)Cl[P(C_6H_5)_2CH_3]_2\cdot {}^2/_3C_6H_{12}$.** Orange crystals were obtained similarly from $Ir(CO)Cl[P(C_6H_5)_2CH_3]_2$; mp 190–191°. The presence of solvent of crystallization was verified by observation of a nmr resonance in deuteriochloroform at $\tau$ 8.58 due to cyclohexane.

*Anal.* Calcd: C, 46.38; H, 3.57; Cl, 18.50. Found: C, 46.55; H, 3.68; Cl, 18.28.

**$Ir(9,10\text{-}O_2C_{14}H_8)(CO)I[P(C_6H_5)_3]_2$.** The complex was obtained in 70% yield as black crystals after recrystallization from dichloromethane–*n*-hexane; mp 195–200°.

*Anal.* Calcd: C, 56.72; H, 3.55; I, 11.75. Found: C, 57.14; H, 3.53; I, 12.00.

**$Rh(CO)Cl[P(C_6H_5)_2CH_3]_2$.** A solution of 0.5 ml of methyldiphenylphosphine in 20 ml of *n*-heptane was added to a solution of 0.20 g of $[Rh(CO)_2Cl]_2$ in 100 ml of *n*-heptane, and the mixture was refluxed for 10 min. Upon slow cooling yellow needles of the product were obtained; mp 127–129°. The complex is the trans isomer, as indicated by the presence of a methyl triplet at $\tau$ 7.83 (3.5-Hz splitting) in the pmr spectrum in deuteriochloroform solution.

*Anal.* Calcd: C, 57.21; H, 4.62. Found: C, 57.49; H, 4.66.

**$Rh(1,2\text{-}O_2C_6Cl_4)(CO)Cl[P(C_6H_5)_2CH_3]_2$.** A solution of 0.12 g (0.50 mmol) of tetrachloro-1,2-benzoquinone in 15 ml of *n*-heptane was added to a solution of 0.71 g (1.25 mmol) of $Rh(CO)Cl(PPh_2Me)_2$ dissolved in a minimum volume of boiling *n*-heptane. Upon cooling the product separated as deep blue crystals; mp 192–195°.

*Anal.* Calcd: C, 48.77; H, 3.22; Cl, 21.81. Found: C, 48.95; H, 3.28; Cl, 22.26.

**$[Rh(1,2\text{-}O_2C_6Cl_4)(1,5\text{-}C_8H_{12})Cl]_n$.** A solution of 0.44 g (1.8 mmol) of tetrachloro-1,2-benzoquinone in 10 ml of dichloromethane was added dropwise with stirring to a solution of 0.43 g (0.90 mmol) of $[Rh(1,5\text{-}C_8H_{12})Cl]_2$ in 35 ml of dichloromethane. The fine, black, crystalline solid (0.70 g, 84%) which formed rapidly was collected by filtration and washed with dichloromethane and vacuum dried.

*Anal.* Calcd: C, 34.15; H, 2.46; Cl, 36.00. Found: C, 33.82; H, 2.84; Cl, 36.02.

**$[Ir(1,2\text{-}O_2C_6Cl_4)(1,5\text{-}C_8H_{12})Cl\cdot CH_2Cl_2]_n$.** The black crystalline complex was obtained in the manner used for the rhodium analog; mp 181–182°.

*Anal.* Calcd: C, 27.02; H, 2.12; Cl, 37.23. Found: C, 27.04; H, 2.33; Cl, 36.97.

**$Rh(1,2\text{-}O_2C_6Cl_4)[P(C_6H_5)_3]_2Cl\cdot 0.5C_6H_{12}$. 1.** A solution of 0.16 g of tetrachloro-1,2-benzoquinone in 10 ml of dichloromethane was added to a stirred slurry of 0.53 g of $Rh(PPh_3)_3Cl$ in 15 ml of dichloromethane. Cyclohexane (25 ml) was added to the green solution and the solvent was distilled off until a dark oil separated. The mixture was allowed to stand until the oil crystallized. The product was collected by filtration and purified by recrystallization from dichloromethane–cyclohexane, mp 188–191°. The product was obtained as violet crystals which dissolve in noncoordinating solvents (*e.g.*, dichloromethane, chloroform, benzene) to give deep green solutions. The complex is diamagnetic as a solid and a nonelectrolyte in *N*,*N*-dimethylformamide. The presence of solvent of crystallization was indicated by infrared absorptions at 2920 and 2840 $cm^{-1}$.

*Anal.* Calcd: C, 56.84; H, 3.82; Cl, 18.64; mol wt, 909. Found: C, 57.02; H, 4.00; Cl, 18.50; mol wt, 957.

**2.** A solution of 0.42 g (1.6 mmol) of triphenylphosphine in 30 ml of dichloromethane was added to 0.24 g (0.49 mmol) of $[Rh(1,2\text{-}O_2C_6Cl_4)(1,5\text{-}C_8H_{12})Cl]$. The solution was heated under reflux for 15 min and filtered. Cyclohexane (25 ml) was added and the solvent was distilled off until its volume reached 25 ml. Upon cooling, the product separated as violet, oily crystals. These (0.24 g, 54%) were purified by recrystallization from dichloromethane–cyclohexane and shown to be identical with the material prepared by method 1 by melting point, behavior on thin layer chromatography, and infrared spectrum.

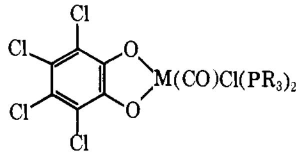
**$Rh(1,2\text{-}O_2C_6Cl_4)[P(C_6H_5)_3]_2[C_5H_5N]Cl$.** Two drops of pyridine were added to a solution of 1.20 g of $Rh(1,2\text{-}O_2C_6Cl_4)[P(C_6H_5)_3]_2Cl$ in 30 ml of dichloromethane. The volume of the resulting violet solution was reduced to 20 ml after addition of 15 ml of 2-propanol. The rose crystals which separated were collected by filtration and recrystallized from dichloromethane-2-propanol; mp 190–193°.

*Anal.* Calcd: C, 57.14; H, 3.57; Cl, 17.94. Found: C, 56.80; H, 3.56; Cl, 18.42.

**Physical Measurements.** Infrared spectra were recorded on a Beckman IR-12 spectrometer. A Varian A-60 spectrometer was used for pmr measurements. Conductivities were determined by use of a Serfass conductivity bridge. The diamagnetism of selected complexes as solids was determined by the Faraday technique. Molecular weights were measured at 37° by a Mechrolab vapor pressure osmometer using chloroform as solvent and triphenylphosphine as the standard.

## Results and Discussion

Tetrachloro-1,2-benzoquinone reacts with the square-planar complex $M(CO)Cl(PPh_3)_2$ (M = Rh, Ir) to yield the six-coordinate adducts **1** and **2** which were obtained respectively as blue and orange crystals. In solution the adducts are monomeric nonelectrolytes. The infrared spectra (Table I) of the adducts are similar. Whereas the parent quinone shows intense carbonyl absorption at 1711 and 1692 $cm^{-1}$, there are no strong absorptions in the 1800–1500-$cm^{-1}$ region for the adducts except for a weak band at *ca.* 1530 $cm^{-1}$. Since a similar weak band also is found in the infrared spectrum of the complex $Ni(o\text{-}O_2C_6Cl_4)_2^{2-}$ and of tetrachloropyrocatechol, it must be character-



1, M = Rh, $PR_3 = PPh_3$
**2**, M = Ir, $PR_3 = PPh_3$
**3**, M = Rh, $PR_3 = PPh_2Me$
**4**, M = Ir, $PR_3 = PPh_2Me$

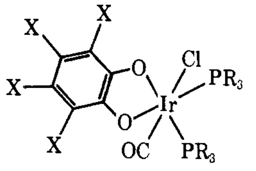
Table I. Selected Infrared Absorptions

| Complex | $\nu$-(C≡O)[a] | $\delta$-(C≡O)[b] | $\nu$-(M—X)[b] | Bands characteristic of the *o*-diolato ligands | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $Rh(CO)Cl(PPh_3)_2$ | 1968 | 576 | 313[c] | | | | | | | |
| $Rh(1,2\text{-}O_2C_6Cl_4)(CO)Cl(PPh_3)_2$ | 2072 | 580 | 338[c] | 1529 | 1256 | 969 | 808 | | | |
| $Ir(CO)Cl(PPh_3)_2$ | 1954 | 605 | 317[c] | | | | | | | |
| $Ir(1,2\text{-}O_2C_6Cl_4)(CO)Cl(PPh_3)_2$ | 2066 | 575 | 311[c] | 1529 | 1258 | 970 | 808 | 794 | | |
| $Rh(CO)Cl(PPh_2Me)_2$ | 1968 | 569 | 311 | | | | | | | |
| $Rh(1,2\text{-}O_2C_6Cl_4)(CO)Cl(PPh_2Me)_2$ | 2084 | 578 | 338 | 1527 | 1258 | 965 | 812 | 795 | | |
| $Ir(CO)Cl(PPh_2Me)_2$ | 1958 | 597 | 315 | | | | | | | |
| $Ir(1,2\text{-}O_2C_6Cl_4)(CO)Cl(PPh_2Me)_2$ | 2061 | 581 | 315 | 1528 | 1263 | 971 | 807 | 792 | | |
| $Rh(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2Cl$ | | | 336 | 1528 | 1265 | 969 | 808 | 795 | | |
| $Rh(1,2\text{-}O_2C_6Cl_4)(py)(PPh_3)_2Cl$ | | | 342 | 1521 | 1260 | 970 | 808 | 793 | | |
| $[Rh(1,2\text{-}O_2C_6Cl_4)(1,5C_8H_{12})Cl]_n$ | | | 308, 265[d] | 1538 | 1262 | 970 | 812 | | | |
| $[Ir(1,2\text{-}O_2C_6Cl_4)(1,5C_8H_{12})Cl]_n$ | | | 308, 271[d] | 1538 | 1257 | 972 | 812 | 800 | | |
| $Ir(1,2\text{-}O_2C_6Br_4)(CO)Cl(PPh_3)_2$ | 2072 | 572 | 314 | 1501 | 1260 | 1236 | 928 | 919 | | |
| $Ir(9,10\text{-}O_2C_{14}H_8)(CO)I(PPh_3)_2$ | 2026 | | | 1608 | 1589 | 1339 | 1051 | 1029 | 938 | 789 |

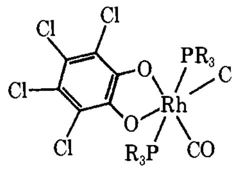
[a] $CH_2Cl_2$ solution. [b] Nujol mull. [c] The spectra of the analogous bromo complexes do not have an absorption in this region. [d] Assignment as $\nu$(M—X) uncertain.

istic of the reduced form of the ligand. Other new bands in the adduct at *ca.* 1260, 810, and 795 cm$^{-1}$ are easily correlated with infrared absorptions found for the free quinone itself and are diagnostic for the formation of an adduct. The lower energy bands at *ca.* 810 and 795 cm$^{-1}$ are carbon–chlorine stretching frequencies. Another infrared absorption which is characteristic of adduct formation is found at *ca.* 970 cm$^{-1}$ in **1**–**4**. The frequency of this band and the fact that there are no bands in this region in the spectrum of the free quinone suggest that this band may be largely due to a carbon–oxygen stretching motion. The $\nu$(C≡O) absorptions in the parent complexes are shifted by *ca.* 100 cm$^{-1}$ to higher energy upon adduct formation. Such shifts are characteristic of oxidative-addition reactions and are caused by the reduced metal to carbon monoxide donation due to the higher metal oxidation level present in the adducts. Analogous adducts with similar infrared spectral characteristics have been prepared from $M(CO)Cl(PPh_2Me)_2$ (M = Rh, Ir).

The stereochemistry of the addition products has been determined through the examination of their pmr and far-infrared spectra. The iridium–chlorine stretching vibrations in the adducts **2** and **4** occur at frequencies very similar to those found for the parent planar complexes. Since these values are within the range observed for an iridium–halogen bond trans to a carbon monoxide ligand,[25] it appears that the trans arrangement of the Ir–Cl and Ir–CO units is maintained upon addition. In contrast, the rhodium–chlorine stretching frequencies in **1** and **3** occur at higher energies than the corresponding vibrations of their planar precursors. Since rhodium–chlorine stretching vibrations with chlorine trans to a carbon monoxide or a phosphine generally occur at frequencies lower than 315 cm$^{-1}$,[26] the chloride must be situated trans to one of the oxygen atoms of the added ligand. The pmr spectra of the methyldiphenylphosphine complexes **3** and **4** confirm the fact that the addition reaction has taken different courses depending on the central metal. The pmr spectrum of **4** exhibits a methyl doublet at $\tau$ 7.77 ($J_{P-H}$ 12.0 Hz). The spectroscopic equivalence of both phosphine methyl groups, the lack of virtual coupling,[27] and the infrared results indicate that **4** and probably **2** as well have been isolated as isomer **5**. The pmr spectrum of **3** exhibits a pseudo triplet at $\tau$ 7.82 (splitting of 4.3 Hz), which is indicative of virtually coupled phosphine ligands in a trans arrangement. Consequently, the geometry of **3** and probably of **1** as well is that depicted in **6**. It is difficult to understand why the stereochemistry of addition takes two different courses depending upon the central metal. No evidence of the formation of other isomers has been found. Both metals have the same electronic configuration and, owing to the lanthanide contraction, are of similar size. However, the rhodium complex is more labile and therefore possibly has undergone isomerization after initial formation. This lability is demonstrated in the observation that attempts to recrystallize the rhodium complex **1** from dichloromethane–methanol mixtures led to the recovery of $Rh(CO)Cl(PPh_3)_2$, whereas the iridium analog **2** was stable under these conditions.



**5**



**6**

The reaction of a variety of quinones with $Ir(CO)Cl(PPh_3)_2$ has been examined. It is to be anticipated that the addition of a quinone to this substrate may be effected by the oxidizing nature of the quinone. In order to gauge the oxidizing ability of the quinones, polarographic half-wave potentials for the reduction of some pertinent quinones to their corresponding semiquinone radical anions are given in Table II. This information is presented solely to allow a ranking of quinones as oxidizing agents; no implication about the intermediacy of semiquinone radicals in the reaction path is intended. Indeed, the semiquinones are probably not involved in the mechanism of addition. *p*-Quinones, including the strong oxidant tetrachloro-1,4-benzoquinone, do not react with $Ir(CO)Cl(PPh_3)_2$ or its rhodium analog. Tetrabromo-1,2-benzoquinone adds readily to $Ir(CO)Cl(PPh_3)_2$ to yield the orange

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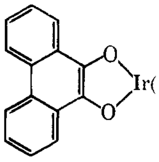
**Table II.** Polarographic Half-Wave Potentials for the Reduction of Quinones to Semiquinone Radicals

| Quinone | $E_{1/2}$, V[a] |
|---|---|
| Tetrachloro-1,2-benzoquinone | +0.14[c] |
| Tetrachloro-1,4-benzoquinone | +0.01[e] |
| 1,4-Benzoquinone | −0.51[e] (−0.38)[b,f] |
| 9,10-Phenanthrenequinone | −0.66[e] (−0.55)[b,f] |
| Acenaphthenequinone | (−0.81)[b,f] |
| Benzil | −1.18[d] |

[a] Measured in acetonitrile solution. [b] Measured in *N*,*N*-dimethylformamide solution. [c] Data from ref 13. [d] This work. [e] M. E. Peover, *J. Chem. Soc.*, 4540 (1962). [f] S. F. Nelson, B. M. Trost, and D. H. Evans, *J. Amer. Chem. Soc.*, **89**, 3034 (1967).

product $Ir(1,2\text{-}O_2C_6Br_4)(CO)Cl(PPh_3)_2$ (**7**). The spectroscopic properties of this complex are similar to those of **2**. The observation of an iridium–chlorine stretching vibration at 316 cm$^{-1}$ indicates a trans arrangement of the chloro and carbon monoxide ligands; the stereochemistry of this complex consequently must be as depicted in **5**. Under the mild conditions utilized for the addition of the halogenated *o*-quinones, the weaker oxidants 1,2-naphthoquinone, 9,10-phenanthrenequinone, acenaphthenequinone, and benzil do not react with $Ir(CO)Cl(PPh_3)_2$. However, it has been reported that 1,2-naphthoquinone and 9,10-phenanthrenequinone will add to this substrate under photoactivation; also, at 80° the thermal addition of 9,10-phenanthrenequinone to $Ir(CO)Cl(PPh_3)_2$ may be effected.[7] Consequently, it appears that the kinetics of addition are strongly affected by the oxidizing ability of the quinone. Similarly, the nature of the complex itself alters the ease of addition. The iodo-substituted complex $Ir(CO)I(PPh_3)_2$, which is known to be more susceptible to oxidative addition than its chloro-substituted analog, reacts readily at 25° with 9,10-phenanthrenequinone to form the black crystalline adduct **8b**. The reduced electron-withdrawing ability of the ligand derived from phenanthrenequinone relative to those from halogenated *o*-quinones is reflected in the low frequencies for the $\nu(C{\equiv}O)$ bands in the infrared spectra of **8a** (2024 cm$^{-1}$)[7] and **8b** (2028 cm$^{-1}$); in contrast, $\nu(C{\equiv}O)$ for **2** and also for **7** occurs at 2068 cm$^{-1}$.

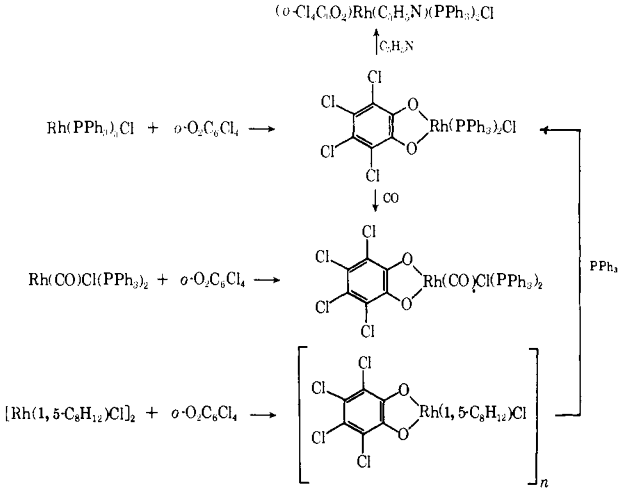


**8a**, X = Cl
**b**, X = I

Addition of tetrachloro-1,2-benzoquinone to $Rh(PPh_3)_3Cl$ produces the crystalline adduct $Rh(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2Cl$, **9**. In solution **9** behaves as a monomeric nonelectrolyte; consequently, it is probably five-coordinate. Oxidative additions to $Rh(PPh_3)_3Cl$ generally produce bisphosphine complexes because of the steric difficulties that would accompany the presence of a third phosphine ligand,[28–32] and a number of these bisphosphine complexes are five-coordinate. The infrared spectrum of **9** closely resembles that of **1** except that the absorptions due to the carbon monoxide ligand in **1** are absent from the spectrum of **9**. Solutions of **9** in noncoordinating solvents are green. In solvents such as *N*,*N*-dimethylformamide, pyridine (py), and acetonitrile, **9** is violet. This color change is undoubtedly due to solvent coordination to give six-coordinate species, and it has been possible to isolate violet, crystalline $Rh(1,2\text{-}O_2C_6Cl_4)(py)(PPh_3)_2Cl$ (**10**) from pyridine-containing solutions of **9**. Similarly, bubbling carbon monoxide through a refluxing chloroform solution of **9** results in addition of CO to form **1**. The complex obtained in this manner has the same stereochemistry as the one formed by addition of tetrachloro-1,2-benzoquinone to $Rh(CO)Cl(PPh_3)_2$.

Tetrachloro-1,2-benzoquinone reacts with the cyclooctadiene complex $[(1,5\text{-}C_8H_{12})RhCl]_2$ to yield $[Rh(1,2\text{-}O_2C_6Cl_4)(1,5\text{-}C_8H_{12})Cl]_n$, **11**, as a black, microcrystalline solid. The infrared spectrum of **11** exhibits bands due to the coordinated, reduced form of the quinone and to the chelating diolefin. Because of its low solubility in noncoordinating solvents, it has not been possible to measure the molecular weight of **11** and consequently it has not been possible to ascertain whether **11** is a five-coordinate monomer like **9** or a halogen-bridged dimer. Reaction of **11** with an excess of triphenylphosphine leads to the formation of **9**. Chart I summarizes the various interrelationships of the rhodium complexes. An iridium complex, $[Ir(1,2\text{-}O_2C_6Cl_4)(1,5\text{-}C_8H_{12})Cl]_n$ (**12**), analogous to **11**, has been obtained from the reaction of tetrachloro-1,2-benzoquinone with $[(1,5\text{-}C_8H_{12})IrCl]_2$. As was the case with **11**, the low solubility of **12** precluded a molecular weight determination. The electronic spectra of some representative adducts are set out in Table III.

**Chart I.** Interrelationships of Rhodium Complexes



Although addition of *o*-quinones, particularly tetrachloro-1,2-benzoquinone, appears to be a general reaction for Rh(I) and Ir(I) complexes, other less easily oxidized d$^8$ complexes do not readily react with these quinones. No reaction occurs between tetra-

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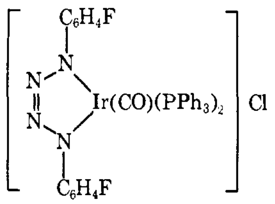
Table III. Electronic Spectra of Some Representative Complexes

| Compound | $\lambda_{max}$, nm ($\epsilon$)[a] |
|---|---|
| $Ir(1,2-O_2C_6Cl_4)(CO)Cl(PPh_3)_2$ | 460 (770), 318 (6500 sh), 310 (32,000) (sh) |
| $Ir(1,2-O_2C_6Cl_4)(CO)Br(PPh_3)_2$ | 480 (890), 320 (5800) (sh), 265 (29,000) (sh) |
| $Ir(1,2-O_2C_6Br_4)(CO)Cl(PPh_3)_2$ | 370 (1300) (sh), 310 (13,000) |
| $Rh(1,2-O_2C_6Cl_4)(CO)Cl(PPh_3)_2$ | 533 (1600), 323 (32,000) |
| $Rh(1,2-O_2C_6Cl_4)(C_6H_6N)Cl(PPh_3)_2$ | 721 (640), 504 (840), 330 (9800) (sh), 265 (37,000) |
| $Rh(1,2-O_2C_6Cl_4)(PPh_3)_2Cl$ | 725 (3600), 490 (1600), 390 (1200) (sh), 330 (13,000) (sh), 260 (28,000) (sh) |

[a] Measured in dichloromethane solution.

chloro-1,2-benzoquinone and $Pt(PPh_3)_2Cl_2$ or $Pd(py)_2Cl_2$. Prolonged refluxing of a chloroform solution containing this quinone and $Pd(PPh_3)_2Cl_2$ leads to the eventual precipitation of red, crystalline $[Pd(PPh_3)Cl_2]_2$[33] but no addition of the *o*-quinone occurs.

Attempts to extend this class of reaction to the addition of analogous nitrogen donors has been unsuccessful. The isolation of **13**[34] suggests that $\alpha$-diimines may add to $Ir(CO)Cl(PPh_3)_2$, although **13** was formed *via* a quite different route. However, attempts to add the $\alpha$-diimine biacetylbisanil[35] to $Ir(CO)Cl(PPh_3)_2$ with either thermal or photochemical activation have led only to the recovery of starting material.



**13**

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# Solvation of Ions. XVI.[1] Solvent Activity Coefficients of Single Ions. A Recommended Extrathermodynamic Assumption

**R. Alexander, A. J. Parker,*[2] J. H. Sharp, and W. E. Waghorne**

*Contribution from the Research School of Chemistry,*
*Australian National University, Canberra, A.C.T., Australia.*

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**Abstract**: Four groups of popular extrathermodynamic assumptions give much the same solvent activity coefficients for transfer of silver cation from acetonitrile to 14 other solvents at 25°. It is therefore strongly recommended that chemists adopt the simplest of these, the assumption of negligible liquid junction potential between $Ag|AgClO_4$ (0.01 *M*) half-cells in different solvents, when linked by a salt bridge of 0.1 *M* tetraethylammonium picrate in either solvent. We note that the $Ph_4AsBPh_4$ assumption gives very similar values.

The evaluation of single-ion solvent activity coefficients, ${}^0\gamma^S{}_{A^+}$ and ${}^0\gamma^S{}_{B^-}$, for transfer of cations, $A^+$, or of anions, $B^-$, from a reference solvent (superscript 0) to another solvent (superscript S) is one of the unresolved classical problems of solution chemistry.[3] It is a problem outside the realm of rigorous thermodynamics and so is of no interest to a few chemists. Those of us who are interested are seeking a universally acceptable means of communicating, interpreting, and predicting the chemistry of ions in different solutions.

In part XIII[5] we were preparing to interpret and predict rates and mechanism of reactions in a variety of solvents. The reactants were usually 0.01–0.04 *M* so we decided to use the molar concentration scale, to compare behavior in 0.01–0.04 *M* solutions, rather than calculate salt (Debye–Hückel) activity coefficients and to not use log ${}^0\gamma^S{}_{Ag^+}$ as derived from any *one* assumption, but rather to take biased mean values. The numbers obtained, by an intuitive estimate of log ${}^0\gamma^S{}_{Ag^+}$ from many assumptions, were most useful.[9,10] In this paper we are anxious to establish an acceptable scale

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(1) Part XV: A. J. Parker and E. C. F. Ko, *J. Amer. Chem. Soc.*, 90, 6447 (1968).

(2) Author to whom enquiries should be addressed at the Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, A.C.T., Australia.

(3) The current status of the problem has been reviewed splendidly by Popovych[4] and less comprehensively in part XIII.[5] Some other useful reviews and papers have appeared.[6–8] The reader is referred to ref 4–8 for a more detailed introduction and acknowledgment of the important work of others in this area. We would like, however, to acknowledge the influence of E. Grunwald, G. Baughman, and G. Kohnstam, *J. Amer. Chem. Soc.*, **82**, 5801 (1960), on our work. Some authors[7] prefer the term "medium effect" or "medium activity coefficient" to "solvent activity coefficient," and we have no strong feelings about such terminology.

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