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# Relative Stabilities of Some Halide Complexes of Rhodium and Iridium

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Halide-exchange equilibria in the systems $Rh(CO)_2I_2^-$–$Cl^-$, $Ir(CO)_2I_2^-$–$Cl^-$, $Ir(CO)_2I_2^-$–$Br^-$, $Rh(Ph_3P)_2(CO)I$–$Cl^-$, and $Ir(Ph_3P)_2(CO)I$–$Cl^-$ have been investigated spectrophotometrically in both aqueous and nonaqueous media. Overall replacement constants have been determined for the systems and show that the lighter halides are preferred in nonaqueous solvents in all cases. In the aqueous media this preference is inverted for the anionic complexes but is retained for the phosphine complexes. Qualitative equilibrium data in nonaqueous solvents have also been obtained for the systems $Ir(CO)_2Cl_4^-$–$I^-$, $Rh(CO)I_5^{2-}$–$Cl^-$, and $Rh(CO)I_5$–$Br^-$ by infrared spectroscopy. The rhodium(III) systems show a preference for the heavier halide. The iridium(III) anion displays novel ambivalent acceptor behavior, displaying soft acceptor halide preference at two halide positions and hard acceptor behavior at the other halide positions (probably trans to the carbonyls).

Rhodium and iridium are regarded as soft acceptors and thus rhodium has been observed to prefer to bind heavier halides over lighter halides in its complexes in aqueous media.[1,2] However, the equilibrium constants observed for the rhodium systems were sufficiently small that it was apparent[2] that the halide solvation energy was most likely the dominant factor in the equilibria. No studies of relative halide complex stability in nonaqueous solvents have been reported and solvation effects are frequently ignored in consideration of the halide preference exhibited by a particular metal. We, therefore, undertook a limited study of halide exchange and preference in rhodium and iridium systems, in both protic and aprotic media.

## Experimental Section

Electronic spectra were recorded with a Coleman-Hitachi 124 spectrophotometer. Infrared spectra were recorded with a Beckman IR-12 spectrophotometer.

**Preparation of Complexes.**—The following compounds were prepared according to the references indicated: $[(C_6H_5)_4As][Ir(CO)_2Cl_2]$, $[(C_6H_5)_4As][Ir(CO)_2Br_2]$, and $[(C_6H_5)_4As][Ir(CO)_2I_2]$;[3] $[(C_6H_5)_4As][Rh(CO)_2Cl_2]$, $[(C_6H_5)_4As][Rh(CO)_2I_2]$, and $[(C_4H_9)_4N][Rh(CO)I_4]$;[4] $[Ir([C_6H_5]_3P)_2(CO)Cl]$;[5] $[Ir[(C_6H_5]_3P)_2(CO)I]$;[6] $[(C_2H_5)_4N][Ir(CO)_2I_4]$ and $[(C_2H_5)_4N][Ir(CO)_2Cl_4]$;[7] $[(C_2H_5)_4N]_2[Rh(CO)Cl_5]$;[8] $Rh[(C_6H_5)_3P]_2(CO)Cl$;[9] and $Rh[(C_6H_5)_3P]_2(CO)I$.[10]

**$[(C_2H_5)_4N][Ir(CO)_2Cl_2I_2]$.**—$[(C_6H_5)_4As][Ir(CO)_2Cl_2]$ (0.5 g) and $(C_2H_5)_4NCl$ (0.15 g) were dissolved in chloroform (3 ml). Iodine (0.20 g) was dissolved in the minimum volume of cold chloroform and added to the above solution. Dark red crystals rapidly separated and were filtered off, washed with ethanol and diethyl ether, and air-dried; yield 0.25 g. *Anal.* Calcd for $C_{10}H_{20}Cl_2I_2IrN$: C, 17.08; H, 2.87; Cl, 10.08; I, 36.08. Found: C, 17.53; H, 2.74; Cl, 9.71; I, 35.77.

**Determination of Equilibrium Constants.**—The preferred halide in a particular rhodium(I) or iridium(I) system was first established qualitatively and then the complex containing the preferred halide was studied in solutions containing known excess amounts of the less preferred halide (added as the tetrabutylammonium salt). Equilibrium data are expressed as overall replacement constants ($\gamma_i$), *i.e.*

$$\gamma_i = \frac{[MA_i][B]^i}{[MB_i][A]^i}$$

for $MB_i + iA \rightleftharpoons MA_i + iB$.

The following absorption peaks were used to determine the concentration of the various species studied: $Ir(CO)_2Cl_2^-$, $\lambda_{max}$ 352 m$\mu$ ($\epsilon_{max}$ 2.8 × $10^3$), 317 m$\mu$ ($\epsilon_{max}$ 2.7 × $10^3$); $Ir(CO)_2Br_2^-$, $\lambda_{max}$ 355 m$\mu$ ($\epsilon_{max}$ 2.7 × $10^3$), 312 m$\mu$ ($\epsilon_{max}$ 3.0 × $10^3$); $Ir(CO)_2I_2^-$, $\lambda_{max}$ 342 m$\mu$ ($\epsilon_{max}$ 3.7 × $10^3$); $Rh(CO)_2Cl_2^-$, $\lambda_{max}$ 334 m$\mu$ ($\epsilon_{max}$ 3.2 × $10^3$); $Rh(CO)_2I_2^-$, $\lambda_{max}$ 290 m$\mu$ ($\epsilon_{max}$ 2.0 × $10^3$); $Rh(Ph_3P)_2(CO)Cl$, $\lambda_{max}$ 365 m$\mu$ ($\epsilon_{max}$ 3.2 × $10^3$), $\epsilon$ at 335 m$\mu$ is 3.0 × $10^3$; $Rh(Ph_3P)_2COI$, $\lambda_{max}$ 360 m$\mu$ ($\epsilon_{max}$ 3.5 × $10^3$), $\epsilon$ at 335 m$\mu$ is 4.5 × $10^3$; $Ir(Ph_3P)_2COCl$, $\lambda_{max}$ 385 m$\mu$ ($\epsilon_{max}$ 2.5 × $10^3$), 336 m$\mu$ ($\epsilon_{max}$ 2.9 × $10^3$); $Ir(Ph_3P)_2COI$, $\lambda_{max}$ 395 m$\mu$ ($\epsilon_{max}$ 2.1 × $10^3$), 350 m$\mu$ ($\epsilon_{max}$ 2.4 × $10^3$). No attempt was made to determine concentrations of intermediate species. Equilibration was essentially instantaneous with all of the above systems.

Equilibrium positions in the iridium(III) and rhodium(III) systems studied were determined, qualitatively, by observation of the infrared spectra in the carbonyl region of the complexes dissolved in nonaqueous solvents containing equal amounts of the competing halides.

## Results and Discussion

The results obtained for the iridium(I) and rhodium(I) systems are summarized in Table I. It can be seen that the lighter halides are strongly preferred in all cases in nonaqueous solvents. These results presumably reflect the higher bond strength of metal–chloride and metal–bromide bonds when compared with metal–iodide bonds.[11] The importance of the relative halide ion solvation energies in these equilibria is illustrated by the inversion of halide preference which occurs with the anionic complexes in $CH_3CN$–$H_2O$.[12] In the case of the neutral phosphine complexes, the preference for the lighter halide is much reduced in the protic medium as compared to the aprotic medium but an inversion is not observed. This observation is noteworthy with respect to the preparative techniques used for $Rh(Ph_3P_2)_2(CO)I$[10] and $Ir(Ph_3P)_2(CO)I$[6] which both involve halide exchange with sodium iodide. In both cases it appears that the insolubility of sodium chloride in the reaction medium is actually the principal driving force rather than the halide preference of the transition metal.

The results obtained by infrared measurements with the systems $RhX_5(CO)^{2-} + Y^-$ [X and Y are either (a) iodide or chloride or (b) iodide or bromide] and $IrX_4(CO)_2^- + Y^-$ (X and Y are iodide or chloride) are summarized in Scheme I. It is apparent that, in both rhodium systems studied, iodide is preferred in all

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(1) H. L. Bott and A. J. Poë, *J. Chem. Soc.*, 5931 (1965).

(2) E. J. Bounsall and A. J. Poë, *J. Chem. Soc. A*, 286 (1966).

(3) D. Forster, *Inorg. Nucl. Chem. Lett.*, **5**, 433 (1969).

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(8) D. Forster, *Inorg. Chem.*, **8**, 2556 (1969).

(9) J. A. McCleverty and G. Wilkinson, *Inorg. Syn.*, **8**, 214 (1966).

(10) L. M. Vallarino, *J. Chem. Soc.*, 2287 (1957).

(11) R. G. Pearson and R. J. Mawby, "Halogen Chemistry," Vol. 3, V. Gutmann, Ed., Academic Press, New York, N. Y., 1967, p 55.

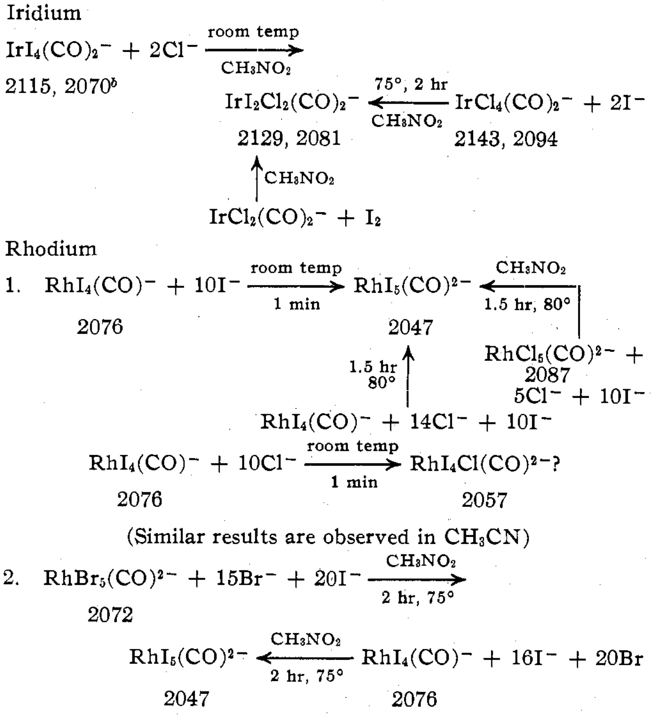
(12) The hardness of the position trans to the carbonyl in $[M(Ph_3P)_2(CO)X]$ is also reflected in the bonding mode adopted by pseudohalides: see J. L. Burmeister and N. J. DeStefano, *Chem. Commun.*, 1698 (1970).

TABLE I
HALIDE PREFERENCES IN SOME RHODIUM(I) AND IRIDIUM(I) SYSTEMS

| System | Solvent | Favored halide | Replacement constant (±20%)[a] |
|---|---|---|---|
| $Rh(CO)_2Cl_2^-$–$I^-$ | 1,2-Dichloroethane | $Cl^-$ | 80 |
| $Rh(CO)_2Cl_2^-$–$I^-$ | $CH_3CN$ | $Cl^-$ | 200 |
| $Rh(CO)_2Cl_2$–$I^-$ | $CH_3CN$–$H_2O$ (10% $H_2O$) | $I^-$ | 30 |
| $Ir(CO)_2Cl_2^-$–$I^-$ | 1,2-Dichloroethane | $Cl^-$ | 5000 |
| $Ir(CO)_2Cl_2^-$–$I^-$ | $CH_3CN$ | $Cl^-$ | 400 |
| $Ir(CO)_2Cl_2^-$–$I^-$ | $CH_3CN$–$H_2O$ (10% $H_2O$) | $I^-$ | 20 |
| $Ir(CO)_2Br_2^-$–$I^-$ | 1,2-Dichloroethane | $Br^-$ | 11 |
| $Ir(CO)_2Br_2^-$–$I^-$ | $CH_3CN$ | $Br^-$ | 50 |
| $Ir(CO)_2Br_2^-$–$I^-$ | $CH_3CN$–$H_2O$ (10% $H_2O$) | $I^-$ | 60 |
| $[Rh(Ph_3P)_2(CO)Cl]$–$I^-$ | DMF | $Cl^-$ | 250 |
| $[Rh(Ph_3P)_2(CO)Cl]$–$I^-$ | DMF–$H_2O$ (10% $H_2O$) | $Cl^-$ | 20 |
| $[Ir(Ph_3P)_2(CO)Cl]$–$I^-$ | 1,2-Dichloroethane | $Cl^-$ | $>10^3$ |
| $[Ir(Ph_3P)_2(CO)Cl]$–$I^-$ | DMF–$H_2O$ (10% $H_2O$) | $Cl^-$ | 60 |

[a] Expressed with the preferred halide ion on the left-hand side of the equilibrium.

SCHEME I
INFRARED STUDIES OF HALIDE EXCHANGE IN THE SYSTEMS $RhX_5(CO)^{2-} + Y^-$ AND $IrX_4(CO)_2^- + Y^-$ IN NONAQUEOUS SOLVENTS (WHERE X AND Y ARE DIFFERENT HALIDES)[a]



[a] Stoichiometries in the equations refer to molar ratios used in the experiments. [b] Carbonyl frequencies ($cm^{-1}$) throughout the scheme refer to solution measurements.

halide coordination sites in the two aprotic solvents studied. These results contrast markedly with the results described above for rhodium(I) systems in nonaqueous solvents. This finding is somewhat unexpected since it has been predicted that higher valence states of metals would behave "harder" than lower valence states,[13] although the differing charges and stereochemistry of the species involved make comparisons of doubtful value in this case.

The results obtained with the iridium(III) tetrahalodicarbonyl anions are particularly intriguing. The following conclusions may be reached from the experiments described in Scheme I: (1) two of the halide acceptor sites on iridium in $IrX_4(CO)_2^-$ prefer a lighter halide ($Cl^-$) over a heavier halide ($I^-$); (2) the other two halide acceptor sites prefer the heavier halide ($I^-$) over the lighter halide ($Cl^-$);[14] (3) two of the halide positions exchange rapidly at room temperature whereas the other two exchange very slowly at room temperature and require elevated temperatures to effect facile exchange. The two halide positions which exchange rapidly at room temperature are most probably those trans to the carbonyl groups in view of the well known trans-labilizing influence of carbonyls. These considerations strongly suggest that the species observed with the carbonyl bands at 2129 and 2081 $cm^{-1}$ is $IrCl_2I_2(CO)_2^-$ with both chlorides trans to the carbonyl groups. Thus the equilibrium position in the system studied with equal amounts of chloride and iodide (in excess) available to the iridium is such that two chlorides and two iodides are coordinated. It is thus apparent that the iridium(III) is displaying "ambivalent"[15] acceptor behavior in the solvent used, with the positions trans to the carbonyls being "hardened" relative to the positions cis to the carbonyls.

In view of the above results obtained with the iridium(III) system it is worth reconsidering the rhodium(III) systems where only one type of acceptor behavior was found. It seems probable that there is a difference in relative "hardness" or "softness" of the two sites in $RhX_5(CO)^{2-}$ also but that a different solvent might be required to allow the rhodium to manifest "ambivalent" acceptor behavior. However, the greater electron density on the metal in the dinegative rhodium anion may serve to lessen differences between the acceptor sites since it is likely that the marked difference in the iridium system is brought about by the electron-withdrawing properties of the carbonyl groups.

Fluorocarbonyl derivatives of transition metals are rare but the trends found in this work suggest that in rigorously aprotic solvents, fluoro derivatives may frequently be found to be the most stable halocarbonyl species.

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(13) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3433 (1963).

(14) Attempts were made to determine the equilibrium constants of these systems accurately for more direct comparison with the iridium(I) systems but apparently reactions of the type $IrX_4(CO)_2^- + Y^- \rightarrow IrX_2(CO)_2^- + YX_2^-$ become important with relatively small excesses of halide in these systems. The overlap of electronic spectra of the resulting mixture of iridium(I) and iridium(III) complexes made quantification difficult. A similar reaction in which halide ion reduces $Pt(CN)_4X_2^{2-}$ ions has been reported previously: A. J. Poë and D. H. Vaughan, *Inorg. Chim. Acta*, **2**, 159 (1968).

(15) Ambivalent acceptor is used here to mean an acceptor displaying *simultaneous* hard and soft acceptor behavior.