Halocarbonyl Derivatives of Rhodium

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New[1] halocarbonyl anions of rhodium of the type $RhX_5(CO)^{2-}$ are described. It is shown that the species previously formulated as $Rh^I{}_2X_4(CO)_2{}^{2-}$ ions are better formulated as rhodium(III) species. An attempt is made to rationalize the chemistry of the various halocarbonyl species by a series of interconversion reactions.

Introduction

The first rhodium halocarbonyl species to be described were the neutral dicarbonylhalorhodium(I) dimers[2a] $[Rh(CO)_2X]_2$. Vallarino showed[2b] that treatment of these neutral species in solution with halide salts of large cations gave solids containing dicarbonyldihalorhodate(I) anions, $Rh(CO)_2X_2{}^-$. Vallarino described several reactions of the basic rhodium(I) species, $Rh(CO)_2X_2{}^-$, principally reactions giving species formulated as dimeric anions $Rh_2(CO)_2X_4{}^{2-}$ (X = Br, I), and the only rhodium(III) halocarbonyl species previously known, $RhI_4(CO)^-$. This work is an attempt to rationalize and correlate the chemistry of the various halocarbonyl species of rhodium.

Experimental Section

Infrared spectra were obtained with Perkin-Elmer 221 or Beckman IR-12 spectrometers. Analytical data were obtained by Galbraith Laboratories, Knoxville, Tenn. X-Ray powder diagrams were obtained by D. J. Dahm and A. L. Ashbaugh of the Physical Sciences Center, Monsanto Co. Mass spectral data were obtained with a CEC 21-104 by Dr. W. E. Dahl. Rhodium carbonyl chloride was obtained from Strem Chemicals and rhodium chloride hydrate was from Engelhard Industries.

Preparation of Compounds. Tetraphenylarsonium and Tetrabutylammonium Dihalodicarbonylrhodate(I).—These compounds were prepared by the method of Vallarino.[2b]

Tetrabutylammonium Tetraiodocarbonylrhodate(III).—This compound was prepared by the method of Vallarino.[2b]

$[(C_2H_5)_4N]_2[Rh(CO)Cl_5]$.—Rhodium carbonyl chloride (0.10 g) and $[(C_2H_5)_4N]Cl$ (0.20 g) were dissolved in chloroform (~3 ml). Chlorine was passed through the solution for several minutes. Gas evolution occurred and pale orange crystals rapidly separated. These were filtered off and washed with chloroform: yield 0.25 g. *Anal.* Calcd for $C_{17}H_{40}Cl_5NORh$: C, 35.91; H, 7.04; Cl, 31.19; N, 4.93. Found: C, 36.47; H, 7.51; Cl, 30.72; N, 4.94.

Tetramethylammonium Pentachlorocarbonylrhodate(III).—Rhodium carbonyl chloride (0.20 g) and tetramethylammonium chloride (0.20 g) were dissolved in methanol (~2 ml). Chlorine was bubbled through the solution. Gas evolution was noted and precipitation of a pale orange solid rapidly occurred. This solid was filtered off and washed with methanol and dimethyl ether; yield 0.26 g. *Anal.* Calcd for $C_9H_{24}Cl_5NORh$: C, 23.67; H, 5.26; Cl, 38.85; N, 6.14. Found: C, 24.24; H, 5.37; Cl, 38.94; N, 6.78.

Tetraethylammonium Pentabromocarbonylrhodate(III).—Rhodium carbonyl chloride (0.20 g) was dissolved in CH_3NO_2 (~3

ml) containing a large excess of tetraethylammonium bromide and excess bromine added. Gas evolution occurred and orange crystals separated. The precipitate was filtered off, washed with nitromethane and diethyl ether, and air dried; yield 0.20 g. *Anal.* Calcd for $C_{17}H_{40}Br_5NORh$: C, 25.81; H, 5.06; Br, 50.55; N, 3.54. Found: C, 26.18; H, 5.16; Br, 49.53; N, 3.51.

Tetraethylammonium Pentaiodocarbonylrhodate.—Rhodium carbonyl chloride (0.20 g) and tetraethylammonium bromide (0.30 g) were heated in a Carius tube with methyl iodide (2 ml) and nitromethane (2 ml) for 16 hr at 70°. The tube was cooled and opened, and the product was filtered off as black crystals which were washed with methyl iodide and air dried; yield 0.30 g. *Anal.* Calcd for $C_{17}H_{40}I_5NORh$: C, 19.89; H, 3.90; I, 61.88; N, 2.73. Found: C, 19.60; H, 3.97; I, 60.97; N, 3.26.

The above compound can be obtained by several other routes (see text) but the above method allows the growth of large crystals.

Reactions of Halogens with Dihalodicarbonylrhodate Ions in Alcohols. $[(C_6H_5)_4As][Rh(CO)_2Cl_2]$ + Cl_2 in Methanol.—$[(C_6H_5)_4As][Rh(CO)_2Cl_2]$ (0.20 g) was dissolved in chloroform (1 ml) and then excess methanol (~5 ml) added. Chlorine was bubbled through the solution for ~2 min whereupon gas evolution occurred. Diethyl ether (~10 ml) was added and the reaction mixture cooled at −60° for 10 min. The pale orange crystals which formed were filtered off and air dried; yield 0.15 g. Mass spectrographic examination of this solid indicates the presence of methanol. *Anal.* Calcd for $[(C_6H_5)_4As][RhCl_4(CO)]\cdot2CH_3OH$ (*i.e.*, $C_{27}H_{28}AsCl_4O_3Rh$): C, 45.02; H, 3.89; Cl, 19.70. Calcd for $[(C_6H_5)_4As][RhCl_4(CO)]\cdot CH_3OH$: C, 45.37; H, 3.49; Cl, 20.62. Found: C, 46.30; H, 3.65; Cl, 19.37.

$[(C_6H_5)_4As][Rh(CO)_2Br_2]$ + Br_2 in Methanol.—$[(C_6H_5)_4As][Rh(CO)_2Br_2]$ (0.20 g) was dissolved in boiling methanol (10 ml). Excess bromine was added whereupon gas evolution occurred. The solution was allowed to cool and red crystals separated. This solid was filtered, washed with diethyl ether, and air dried; yield 0.16 g. *Anal.* Calcd for $C_{27}H_{28}AsBr_4O_3Rh$ (*i.e.*, $[(C_6H_5)_4As][RhBr_4(CO)]\cdot2CH_3OH$): C, 36.10; H, 3.12; Br, 35.61. Found: C, 36.61; H, 2.97; Br, 34.92.

Attempt to Prepare $[(C_6H_5)_4As]_2[Rh_2(CO)_2Br_4]$.—In attempts to prepare $[(C_6H_5)_4As]_2[Rh_2(CO)_2Br_4]$ by the method of Vallarino,[2b] *i.e.*, by refluxing $[(C_6H_5)_4As][Rh(CO)_2Br_2]$ with CH_3OH–HBr for 1 hr, only uncharged starting material was recovered when air was rigorously excluded. However, when the reaction was carried out in an open beaker, a product with melting point and carbonyl stretching frequency close to that described by Vallarino for $[(C_6H_5)_4As]_2[Rh_2(CO)_2Br_4]$ was obtained. This solid was shown by X-ray diffraction to be the same as the solid described above as $[(C_6H_5)_4As][RhBr_4(CO)]\cdot2CH_3OH$ (see text for discussion of stoichiometry of this compound).

Partial Carbonylation of Rhodium(III) Halides in Methanol.—$RhCl_3\cdot xH_2O$ (1.0 g) and $(C_6H_5)_4AsCl$ (2.0 g) were heated in a mixture of methanol (~60 ml) and concentrated HBr solution (~15 ml) with a stream of carbon monoxide bubbling through the solution. After 1 hr the solution was filtered hot. Orange-red crystals separated from the filtrate on cooling. These crystals were filtered off, washed with cold methanol and diethyl

(1) Since completion of this work a report has appeared of the preparation of $RhCl_5(CO)^{2-}$ and $RhBr_5(CO)^{2-}$ by a route different from those described herein: M. J. Cleare and W. P. Griffith, *J. Chem. Soc., A*, 372 (1969).

(2) (a) W. Hieber and H. Lagally, *Z. Anorg. Allgem., Chem.*, **251**, 98 (1943); (b) L. M. Vallarino, *Inorg. Chem.*, **4**, 161 (1965).

ether, and dried *in vacuo;* yield 2.3 g. This complex was shown to be isomorphous with the solid formulated above as $[(C_6H_5)_4As]$-$[RhBr_4(CO)] \cdot 2CH_3OH$ by its X-ray diffraction powder pattern.

Results and Discussion

Reactions of the Dihalodicarbonylrhodate(I) Ions.—

It is described elsewhere[3] that halogens will oxidatively add to $Rh(CO)_2X_2^-$ ions in solvents such as $CHCl_3$ and C_6H_5Cl to give $Rh(CO)_2X_4^-$ ions. It has now been found that choice of solvent is important in conducting this reaction. Thus if chlorine or bromine is allowed to react with $Rh(CO)_2X_2^-$ ions in methanol,[4] carbon monoxide is evolved and salts of monocarbonylrhodium-(III) species can be isolated. The specific rhodium(III) species obtained as a solid depended also on the cation used. Thus use of $(CH_3)_4N^+$ gives salts of the new class of rhodium halocarbonyl species, the $Rh(CO)X_5^{2-}$ ions, whereas $(C_6H_5)_4As^+$ gives rise to salts formulated as $[(C_6H_5)_4As][Rh(CO)X_4] \cdot (1 \text{ or } 2)CH_3OH$ (X = Cl or Br). The structure of these latter species remains in some doubt. The low-frequency vibrational spectrum of the chloro complex shows only one rhodium–chlorine stretching mode at 342 cm^{-1}, which is in the region observed for terminal rhodium(III)–chlorine stretching modes favoring the structure of either *trans*-Rh(CO)-Cl$_4 \cdot$CH$_3$OH$^-$ or Rh(CO)Cl$_4^-$. A similar problem is apparent in the iridium halocarbonyls where the compounds originally formulated[5] as [cation][IrBr$_4$]$\cdot$(2 or 3)-C$_2$H$_5$OH were later suggested[6] to contain IrBr$_4$(CO)$^-$ ions. This problem will probably require a crystallographic investigation for a definitive solution.

The species $Rh(CO)X_5^{2-}$ (X = Cl or Br) described above which can be obtained as solids with $(CH_3)_4N^+$ or $(C_2H_5)_4N^+$ cations from methanol can also be readily obtained from CHCl$_3$ by conducting the halogen addition to the $Rh(CO)_2X_2^-$ ions in the presence of $(CH_3)_4N^+$ or $(C_2H_5)_4N^+$ halide salts. The series of salts $[(C_2H_5)_4N]_2[Rh(CO)X_5]$ (X = Cl, Br, or I) is an isomorphous series. A single-crystal X-ray diffraction study[7] of the iodo compound has confirmed the formulation.

The reaction of the $RhI_2(CO)_2^-$ ion with methyl iodide gives salts of the $[RhI_3(CO)(CH_3CO)]_2^{2-}$ ion initially.[3] It has now been observed that long reaction of $[(C_2H_5)_4N][Rh(CO)_2I_2]$ with either CH$_3$I or C$_2$H$_5$I gives a black crystalline solid. This can be shown to be $[(C_2H_5)_4N]_2[Rh(CO)I_5]$, described above, by its X-ray powder diffraction pattern. This "halogen abstraction" reaction is related to the formation of $RhCl_3(CO)[(C_2H_5)_3P]_2$ by reaction of $RhCl(CO)$-$[(C_2H_5)_3P]_2$ with CCl$_4$[8] and formation of IrClI$_2$(CO)-$[P(C_6H_5)_3]_2$ by reaction of IrCl(CO)$[(C_6H_5)_3]_2$ with CH$_2$ICH$_2$I.[9]

It is described elsewhere[3] that reaction of $Rh(CO)_2I_2^-$ with hydriodic acid in aqueous acetic acid gives hydrogen and a rhodium(III) iodocarbonyl species. By

conducting this reaction in the presence of excess $(C_2$-$H_5)_4N^+I^-$ a solid was obtained which can be shown to be $[(C_2H_5)_4N]_2[Rh(CO)I_5]$. By contrast oxidation of $Rh(CO)_2I_2^-$ in CH$_3$OH–HI gives salts of $Rh(CO)I_4^-$ with $(C_4H_9)_4N^+$ or $(C_6H_5)_4As^+$ cations, as described by Vallarino.[2b] These latter compounds give no evidence for containing methanol, unlike the chloro and bromo analogs described above. Thus, choice of cation is important in determining the nature of the solid formed from a particular reaction mixture.

Vallarino described[2b] the formation of salts of $Rh^I_2(CO)_2X_4^{2-}$ (X = Br or I). This author obtained a solid with the melting point and carbonyl stretching frequency reported[2b] for $[(C_6H_5)_4As]_2[Rh_2(CO)_2Br_4]$, but an X-ray diffraction powder pattern of this material shows it to be identical with the compound formulated above as $[(C_6H_5)_4As][Rh(CO)Br_4] \cdot xCH_3OH$. The carbonyl stretching frequency observed for this compound (2103 cm^{-1}) in nitromethane is in better agreement with a formulation based on rhodium(III) than with that based on rhodium(I). All rhodium(I) species so far described containing one carbonyl per rhodium have carbonyl stretching bands less than 2050 cm^{-1}.

Carbonylation of Rhodium(III) Halides in Solution.

—Carbonylation of solid hydrated rhodium trihalides gives[1] the well-known rhodium dihalocarbonyl dimers. In aqueous[10] and aqueous–alcoholic solutions, carbonylation of rhodium chloride eventually gives the $Rh(CO)_2X_2^-$ ions. However, an infrared investigation of the alcoholic solutions during the course of the reaction gives evidence for initial formation of another carbonyl species. Thus carbonylation of a methanol solution of rhodium chloride containing 5% of concentrated HCl leads initially to a solution with a strong infrared absorption of 2110 cm^{-1}. The corresponding bromide-containing solution shows a band at 2100 cm^{-1} and the iodide solution a band at 2091 cm^{-1}. All of these frequencies are in the region observed for formally rhodium(III) carbonyl-containing species. By using suitable cations solids have been obtained from the solutions at these "intermediate" stages. Thus carbonylation of rhodium(III) chloride in CH$_3$OH–H$_2$O in the presence of excess $[(C_2H_5)_4N]I$ at 30° gives a black crystalline precipitate within 2 hr which can be shown to be the compound $[(C_2H_5)_4N]_2[Rh(CO)I_5]$ described above. Carbonylation of rhodium chloride in methanol–HBr in the presence of $[(C_6H_5)_4As]Cl$ for a relatively short period gives a solution from which a solid which X-ray diffraction shows to be the compound described above as $[(C_6H_5)_4As][RhBr_4(CO)] \cdot CH_3OH$ may be isolated. It appears safe to conclude that carbonylation, at least in aqueous–alcoholic media, proceeds *via* a rhodium(III) carbonyl species.

Transformations in Solution.—

The compound $[(C_2H_5)_4N]_2[RhI_5(CO)]$ on dissolution in nitromethane gives an infrared spectrum with two carbonyl stretching frequencies, 2076 and 2047 cm^{-1}. On addition of excess iodide ion the 2047-cm^{-1} band increases in intensity while the 2076-cm^{-1} band decreases. The

(3) D. Forster, to be submitted for publication.
(4) Reactions with iodine are complicated by the insolubility of salts of the I$_5^-$ ion.
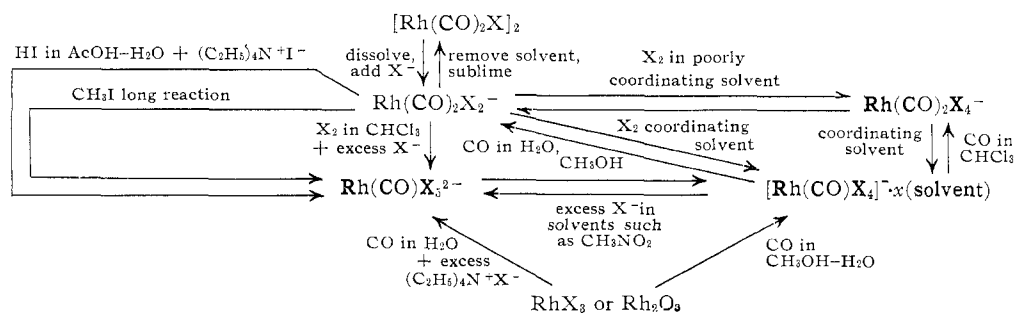(5) L. Malatesta and F. Canziani, *J. Inorg. Nucl. Chem.*, **19**, 81 (1961).
(6) L. Malatesta, L. Naldini, and F. Cariati, *J. Chem. Soc.*, 961 (1964).
(7) D. J. Dahm and D. Forster, to be submitted for publication.
(8) R. F. Heck, *J. Am. Chem. Soc.*, **86**, 2796 (1964).
(9) P. B. Chock and J. Halpern, *ibid.*, **88**, 3511 (1966).

(10) B. R. James and G. L. Rempel, *Chem. Commun.*, 158 (1967).

Scheme I

Interconversion Reactions of the Halocarbonyl Derivatives of Rhodium

$[Rh(CO)_2X]_2$

HI in AcOH–H₂O + (C₂H₅)₄N⁺I⁻   dissolve, add X⁻ | ↑remove solvent, sublime   X₂ in poorly coordinating solvent

CH₃I long reaction   Rh(CO)₂X₂⁻ ⇌   Rh(CO)₂X₄⁻

X₂ in CHCl₃ + excess X⁻ | CO in H₂O, CH₃OH   X₂ coordinating solvent   coordinating solvent | ↑ CO in CHCl₃

Rh(CO)X₅²⁻ ⇌   [Rh(CO)X₄]⁻·x(solvent)

excess X⁻ in solvents such as CH₃NO₂

CO in H₂O + excess (C₂H₅)₄N⁺X⁻   CO in CH₃OH–H₂O

RhX₃ or Rh₂O₃

2047-cm⁻¹ band is close to that of $[(C_2H_5)_4N]_2[Rh(CO)-I_5]$ in the solid state (see Table I) and is most reasonably assigned to the $Rh(CO)I_5{}^{2-}$ ion in this solvent. The band at 2076 cm⁻¹ is also observed when $[(C_4H_9)_4N]-[Rh(CO)I_4]$ is dissolved in this solvent and is thus best assigned as $RhI_4(CO)^-$ or $Rh(CO)I_4 \cdot CH_3NO_2{}^-$. The compound formulated as $[(C_6H_5)_4As][Rh(CO)-Br_4] \cdot xCH_3OH$ has a carbonyl stretching band at 2103 cm⁻¹ in CH₃NO₂. Addition of excess bromide results in a gradual formation (over ~30 min at 25°) of a band at 2072 cm⁻¹ at the expense of the 2103-cm⁻¹ band. The band at 2072 cm⁻¹ is that of $Rh(CO)Br_5{}^{2-}$ in this solvent (see Table I). The slowness of the transformation may be evidence for the rhodium being hexacoordinate in the starting material. The chloride complex behaves similarly.

Carbonylation of the anionic rhodium(III) monocarbonyl species in CHCl₃ gives the *cis*-dicarbonyl species. Thus passage of CO through $[(C_6H_5)_4As]-[RhBr_4(CO)] \cdot xCH_3OH$ in CHCl₃ at 25° and 1 atm for ~30 min gives a solution with carbonyl stretching bands at 2146, 2115, 2070, and 1992 cm⁻¹. The two higher frequency bands are those of *cis*-$Rh(CO)_2Br_4{}^-$ and the other bands are those of $Rh(CO)_2Br_2{}^-$ formed by reductive elimination of bromine from the rhodium(III) species. Similarly passage of CO through a solution of $[(C_4H_9)_4N][Rh(CO)I_4]$ in CHCl₃ at 25° gives a solution displaying the infrared spectra of *cis*-$Rh(CO)_2I_4{}^-$ and $Rh(CO)_2I_2{}^-$.[11]

(11) Note Added in Proof.—A report of the preparation of $[(C_2H_5)_4N]-[RhI_4(CO)_2]$ containing *cis*-$RhI_4(CO)_2{}^-$ ions by a method different from that described above has recently appeared [J. V. Kingston and G. R. Scollary, *J. Inorg. Nucl. Chem.*, **31**, 2557 (1969)]. However, the carbonyl stretching frequencies were markedly different from those reported above for this species. We therefore repeated the Kingston and Scollary preparation and found that its X-ray powder pattern indicated a mixture of $[(C_2H_5)_4N]_2-[RhI_5(CO)]$ and some other species. We, therefore, repeated the prepara-

Table I

Infrared Data for the Halocarbonylrhodate Species[a]

Compound	Medium	Freq,[b] cm⁻¹
$[(C_6H_5)_4As][Rh(CO)_2Cl_2]$	CH₃NO₂	2073, 1994
$[(C_6H_5)_4As][Rh(CO)_2Br_2]$	CH₃NO₂	2070, 1992
$[(C_6H_5)_4As][Rh(CO)_2I_2]$	CH₃NO₂	2064, 1989
	CH₃CO₂H	2060, 1988
$Rh(CO)_2Cl_4{}^-$	CHCl₃	2160, 2125
$[(C_6H_5)_4As][Rh(CO)_2Br_4]$	CHCl₃	2146, 2115
$Rh(CO)_2I_4{}^-$	CHCl₃	2122, 2092
$[(C_2H_4)_4N]_2[Rh(CO)Cl_5]$	Solid (Nujol)	~2070 br
	CH₃NO₂[c]	2087
$[(CH_3)_4N]_2[Rh(CO)Cl_5]$	Solid (Nujol)	~2090 br
	CH₃NO₂[c]	2087
$[(C_2H_5)_4N]_2[Rh(CO)Br_5]$	Solid [Nujol]	2070
	CH₃NO₂[c]	2072
$[(C_2H_5)_4N]_2[Rh(CO)I_5]$	Solid (Nujol)	~2040
	CH₃NO₂[c]	2047
$[(C_4H_9)_4N][Rh(CO)I_4]$	CH₃NO₂	2076
$[(C_6H_5)_4As][Rh(CO)I_4]$	CH₃NO₂	2076
$[(C_6H_5)_4As][Rh(CO)Cl_4] \cdot xCH_3OH$	Solid (Nujol)	2103
	CH₃NO₂	2112
$[(C_6H_5)_4As][Rh(CO)Br_4] \cdot xCH_3OH$	Solid (Nujol)	2092
	CH₄NO₂	2103

[a] Rhodium–chlorine stretching modes are observed in $[(C_2H_5)_4-N]_2[Rh(CO)Cl_5]$ at 329 (s) and 288 (m) cm⁻¹ and in $[(C_6H_5)_4As]-[Rh(CO)Cl_4] \cdot xCH_3OH$ at 342 (s) cm⁻¹ (both compounds were examined as Nujol mulls). [b] All absorptions are strong. [c] Solution containing excess halide ion.

The various transformations so far observed among the halocarbonyl derivatives of rhodium are summarized in Scheme I.

tion using (C₂H₅)₄NI instead of NaI + (C₂H₅)₄NCl and obtained a solid with only one carbonyl frequency which X-ray diffraction showed to be pure $[(C_2H_5)_4N]_2[RhI_5(CO)]$. We conclude that Kingston and Scollary's preparation is a mixture of $[RhI_5(CO)]^{2-}$ and another species (possibly containing chloride).