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Preliminary communication

Ion-pairing in salts of $[Rh(CO)_2I_2]^-$

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Abstract

Spectroscopic evidence shows that the protonic Rh^I contact ion-pair, $[H^+ \ldots Rh(CO)_2I_2^-]$ rather than the Rh^{III} hydride, $[HRh(CO)_2I_2]$, is obtained by adding HI to $[Rh_2(CO)_4I_2]$ in anhydrous solution. Similar species also exist in RNH_3^+ $Rh(CO)_2I_2^-$ and related salts.

The carbonylations (of methanol, methyl acetate, etc.) promoted by rhodium/iodide are among the most important homogeneously catalysed reactions [1]. The active species has been established as the anion $[Rh(CO)_2I_2]^-$ [2,3], but the nature of the counterion remains obscure.

In the course of spectroscopic and kinetic investigations [4] we have established that the salts, A^+ $[Rh(CO)_2I_2]^-$, for most A^+ exist as solvent-separated ion pairs in solvent systems in which they are soluble. This is shown by the IR spectra (Table 1): for example the bands shown by Bu_4N $[Rh(CO)_2I_2]$ in CH_2Cl_2 (ν(CO) 1990, 2060 cm^{-1}) are found in almost identical positions for a wide range of cations and solvents. In methanol, salts of all cations A^+ showed the same bands, which we interpret to mean that all are completely dissociated.

However, although the IR spectra of salts of cations bearing protons (RNH_3^+, $R_2NH_2^+$, R_3NH^+), showed the same bands in methanol, the bands were moved to higher frequencies in less solvating media (CH_2Cl_2, MeOAc), indicating less back-bonding from the metal to the CO. This may be taken to imply a lower effective charge on the metal, due to contact ion-pair formation, $[A^+ \ldots Rh(CO)_2I_2^-]$.

We have also attempted to make the hydride, $[HRh(CO)_2I_2]$. For example, addition of an excess of a freshly prepared anhydrous solution of HI to the dinuclear $[Rh_2(CO)_4I_2]$ in dry CH_2Cl_2 (under CO, 1 atm, 20 °C) gave a red solution (ν(CO) 2003, 2071 cm^{-1}). These are very close to the bands found for $C_{12}H_{25}NH_3^+$ $[Rh(CO)_2I_2]^-$, at 2004 and 2071, in the same solvent. We suggest that both are due to the contact ion-pair $[\ldots H^+ \ldots Rh(CO)_2I_2^-]$.

The solution of $C_{12}H_{25}NH_3^+$ $[Rh(CO)_2I_2]^-$ is more stable and the ^1H NMR spectrum shows $\delta(NH)$ at 6.9 (in dry $CDCl_3$), compared to δ 7.6 in $C_{12}H_{25}NH_3^+$

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I^- itself. We interpret the higher field shift to result from the proton now coming close to the metal in $C_{12}H_{25}NH_3^+$ $[Rh(CO)_2I_2]^-$, but the fact that the signal is still much further downfield than for most transition metal hydrides implies that it has a predominantly protonic rather than hydridic character. We cannot exclude the presence of small amounts of $[HRh(CO)_2I_2]$ in equilibrium with the ion paired $[H\ldots Rh(CO)_2I_2]$, but since the IR spectra show no sign of other species, the concentration of any Rh^{III} hydride must be less than ca. 1%.

On standing in anhydrous solution, the species $[H\ldots Rh(CO)_2I_2]$ reverts to $[Rh_2(CO)_4I_2]$ and HI. Addition of excess HI causes a redox reaction, with formation of the rhodium(III) salt, ν(CO) 2083 cm^{-1}, probably $[Rh(CO)I_4]^-$ [5]. The reaction between HI and $[Rh_2(CO)_4I_2]$ in aqueous methanol occurs more readily, with evolution of gas, to give a black solid, impure RhI_3.

Addition of HBF_4 to a solution of $n\text{-}Bu_4N[Rh(CO)_2I_2]$ in dry CH_2Cl_2 causes the formation of $[Rh_2(CO)_4I_2]$ by the following reaction:

$$\mathrm{n\text{-}Bu_4N[Rh(CO)_2I_2] + HBF_4 \rightleftharpoons Bu_4N[BF_4] + \tfrac{1}{2}[Rh_2(CO)_4I_2] + HI}$$

We can therefore summarise the equilibria which occur as:

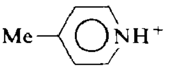
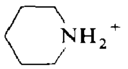
$$\begin{tikzcd} \mathrm{2HI + [Rh_2(CO)_4I_2]} \arrow[r, shift left] & \mathrm{2[H^+\ldots Rh(CO)_2I_2^-]} \arrow[l, shift left] \arrow[r, shift left] \arrow[d, shift left] & \mathrm{2H^+(solvent)_n[Rh(CO)_2I_2]^-} \arrow[l, shift left] \\ & \mathrm{[HRh(CO)_2I_2]} \arrow[u, shift left] & \end{tikzcd}$$

The reaction with LiI [3] is rather similar to that with HI, but no interaction at all was detected with $[Rh_2(CO)_4I_2]$ in solvents which do not solvate lithium. In coordinating solvents (ethers, esters, alcohols, etc.), the product is the solvent-separated $Li(solvent)_n^+$ $[Rh(CO)_2I_2]^-$ (ν(CO) 1981, 2054 cm^{-1} in methyl acetate, very close to that for the Bu_4N^+ salt, see Table 1).

Braca et al. have made rather similar observations for the ruthenium carbonyl iodide system, and noted that "$HRu(CO)_3I_3$", although isolable as an unstable red-brown oil, shows spectroscopic behaviour consistent with its formulation as a tight ion pair, $[H^+\ldots Ru(CO)_3I_3^-]$, rather than as a ruthenium hydride [6].

Table 1

IR carbonyl stretching frequencies (ν(CO) (cm^{-1})) for $A^+[Rh(CO)_2I_2]^-$ and $[Rh_2(CO)_4I_2]$ [a]

Solvent [b]	Salts of $[Rh(CO)_2I_2]^-$				$[Rh_2(CO)_4I_2]$
	Bu_4N^+			$n\text{-}C_{12}H_{25}NH_3^+$	
MeOH	1990	1990	1990	1990	2009
	2060	2060	2060	2060	2029
					2080
MeOCOMe	1985	1986	1993	1993	2030
	2056	2057	2063	2063	2082
					2099
CH_2Cl_2	1988	1998	2001	2004	2028
	2060	2068	2070	2071	2080
					2096

[a] Measured on a Perkin-Elmer 1710 FTIR spectrometer. [b] Solvents were carefully dried and degassed.

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