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Iodide and Acetate Promotion of Oxidative Addition of MeI to Rh(I) Carbonyl Complexes

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Soluble rhodium/iodide catalysts carbonylate methanol to acetic acid [1] (eqn. 1) and methyl acetate to acetic anhydride [2] (eqn. 2). The $[\mathrm{RhI_2(CO)_2}]^-$ anion, **1**, is the major observable Rh complex present in both catalyst systems. The first order kinetics in Rh and methyl iodide exhibited by both systems have been interpreted in terms of rate determining oxidative addition of MeI to **1** [1, 3] (eqn. 3):

$$\mathrm{MeOH + CO \longrightarrow MeCO_2H} \qquad (1)$$

$$\mathrm{MeO_2CMe + CO \longrightarrow MeCO{\cdot}O{\cdot}OCMe} \qquad (2)$$

$$\mathrm{MeI} + \underset{\mathbf{1}}{[\mathrm{RhI_2(CO)_2}]^-} \longrightarrow \underset{\mathbf{2}}{[\mathrm{Me\text{-}RhI_3(CO)_2}]^-} \qquad (3)$$

Hickey and Maitlis recently described [3] the promotional effect of 1-methyl imidazole and several halide salts on the kinetics of reaction 3 (and on catalytic methyl acetate carbonylation) in aprotic solvents. Publication of their results prompts us to publish our studies of the oxidative addition of methyl iodide to Rh(I) carbonyl complexes which were completed before submission of the Hickey–Maitlis communication. Our results were obtained in acetic acid solvent (instead of the aprotic solvents used by these authors) and indicated a significant promotional effect by lithium iodide and acetate on the oxidative addition of methyl iodide to lithium salts of $[\mathrm{RhI_2(CO)_2}]^-$. Some of our catalytic work to be published in a future paper also indicates that the promotional effect can be obtained with iodide and acetate salts of other cations.

Thus, our work is not only compatible with that of Hickey–Maitlis but also extends the scope of their results, allowing a better understanding of the effect of salts in the promotion of this important reaction. Because salts of simple inorganic cations produce similar effects to those produced by complicated organic bases and salts of organic cations used by Hickey–Maitlis, the importance of the anion in the catalysis is emphasized. Catalysis probably occurs via a ligand effect to produce a five-coordinate intermediate. Cation effects appear to be less important.

We have carried out spectroscopic and kinetic studies (at 25 °C) of the reaction of $[\mathrm{RhI_2(CO)_2}]^-$ with MeI in acetic acid (AcOH) solvent, a model for the rate determining step in Rh catalyzed carbonylation reactions. The acetic acid soluble salt $\mathrm{Li[RhI_2(CO)_2]}$, **3**, can be rapidly and stoichiometrically prepared via eqn. 4. IR spectra of the stable (but air sensitive) complex in AcOH solution show only two sharp absorptions at 2058 and 1988 $\mathrm{cm^{-1}}$:

$$1/2[\mathrm{RhCl(CO)_2}]_2 + 2\mathrm{LiI} \xrightarrow[\mathrm{AcOH}]{25\ ^\circ\mathrm{C}} \underset{\mathbf{3}}{\mathrm{Li[RhI_2(CO)_2]}} + \mathrm{LiCl} \qquad (4)$$

Similar to the behavior in aprotic solvents, [1, 3] addition of MeI to acetic acid solutions of **3** at 25 °C caused the smooth disappearance of the IR bands of **3**, and appearance of a band at 2061 $\mathrm{cm^{-1}}$ attributable to $[\mathrm{MeCORhI_3(CO)}]^-$, **3** (which is a product of rearrangement of **2**) [1]. Interestingly, the kinetics of this organometallic reaction have not been published until recently [3]. In the presence of excess MeI, the disappearance of the IR bands of **3** was a first order process. The observed pseudo-first order rate constants for the disappearance of **3** showed a first order dependence on MeI concentration, either in the presence or absence of added salts. The observed first order dependences on MeI and $[\mathrm{RhI_2(CO)_2}]^-$ indicate that the IR technique accurately measures the rate of reaction 3.

The effects of various additives on the rate of reaction 3 were then investigated. From a base rate obtained in the absence of additives, the addition of polar solvents such as nitromethane gave only very small proportional effects on the rate of reaction 3. The effects of salts were larger than those of the polar solvents. $\mathrm{Li[BF_4]}$ (presumably an inert salt) slightly increased rates, while lithium iodide or acetate (LiOAc) gave significantly larger rate increases. See Fig. 1.†

Figure 1 demonstrates that the differing properties of iodide, acetate, and tetrafluoroborate anions are important factors in the size of the promotional effect observed. We hypothesize that the relatively small promotional effects of $\mathrm{Li[BF_4]}$ and polar solvents on the rates of reaction 3 are largely due to

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†The Rh reaction products in all runs gave broad IR absorptions in the immediate vicinity of 2061 $\mathrm{cm^{-1}}$ which can be attributed [1] to **4**. We were unable to conclusively determine (via IR spectroscopy) whether ligand substituted acyl–Rh complexes are formed in the presence of acetate.

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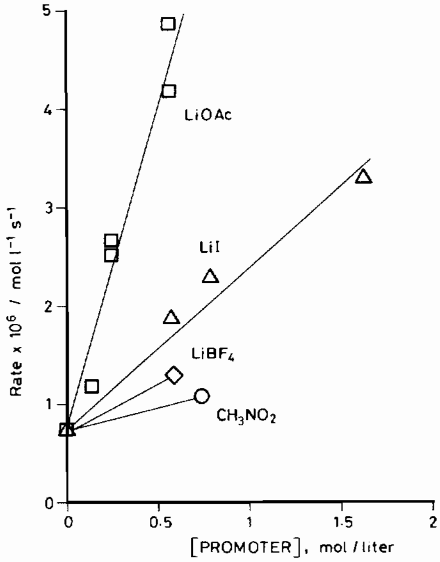
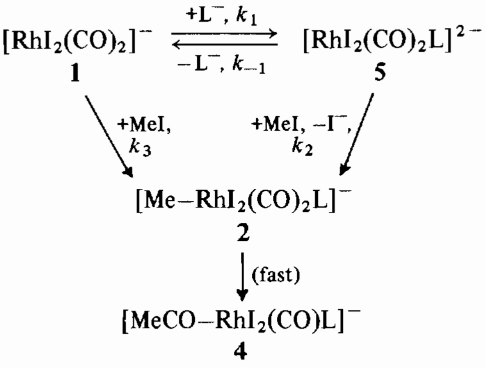


Fig. 1. $Li[RhI_2(CO)_2]$ + MeI. Reaction rate *vs.* promoter concentration. $Li[RhI_2(CO)_2]$ = 0.014 M, MeI = 1.63 M in AcOH, 25 °C.

slight changes in the solvation and/or ion-pairing behavior of **3** in solution.†† It is expected that ion-pair interactions will be relatively more important in aprotic media such as methyl acetate [2, 3].

We suggest that iodide and acetate anions may be significantly better promoters than tetrafluoroborate because of their ability to serve as ligands for transition metals. The $[RhI_2(CO)_2]^-$ anion is a four coordinate, sixteen electron, coordinatively unsaturated complex, and may be in equilibrium with small amounts of five-coordinate, dianionic complexes in which iodide or acetate anions are a fifth ligand. The $[RhI_2(CO)_2L]^{2-}$ complexes formed (**5**, L^- = iodide or acetate) would be electronically analogous to $[Mn(CO)_5]^-$, and might be expected to behave as strong S_N2 nucleophiles toward MeI. Five-coordinate species have also been proposed by others [3, 6] as reactive intermediates in $[RhI_2(CO)_2]^-$ chemistry. Hickey and Maitlis [3] detect weak IR bands in iodide containing systems which they attribute to five-coordinate Rh species, but we were unable to detect similar bands for **3** dissolved in iodide containing acetic acid solvent.

The promotional effects of iodide and acetate on reaction 3 can be rationalized as a competition between four-coordinate and five-coordinate pathways for rate determining reactions with MeI. See Scheme 1.



Scheme 1. ($L = I^-$ or $CH_3CO_2^-$)

The steady-state rate law derived from Scheme 1 is shown in eqn. 5. With the assumption that $k_{-1} \gg k_2$ [MeI], eqn. 5 reduces to a simple linear equation which readily rationalizes Fig. 1. A non-promoted pathway (k_3) gives a non-zero intercept, and a ligand promoted pathway (k_2) provides rate increases directly dependent on salt concentration. It is significant to note that iodide and acetate salts, and a variety of organic bases have been proposed as promoters of acetic anhydride synthesis via carbonylation of methyl acetate [2d, 3, 7].

$$-\frac{d[RhI_2(CO)_2^-]}{dt} = \left(\frac{k_1k_2[L^-]}{k_{-1}+k_2[MeI]} + k_3\right)[RhI_2(CO)_2^-][MeI] \quad (5)$$

Further studies are needed to better define the relative importance of ion-pairing and ligation effects in $[RhI_2(CO)_2]^-$ chemistry. We expect to disclose our results with catalytic systems in future publications.

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††Infrared spectral evidence suggests that these solution effects are not related to formation of 'contact ion pairs' between Li+ cations and $[RhI_2(CO)_2]^-$ anions in acetic acid solution. The bandshapes and energies of the CO stretching absorptions of 3 in AcOH solution are little affected (2–3 cm^{-1}) by the addition of excess nitromethane or hexamethylphosphoramide, which might be expected to strongly coordinate Li+ ions and break up 'contact ion pairs' [4, 5]. Likewise, addition of various lithium salts (including iodide or acetate) caused no significant changes in the IR spectra of 3 in acetic acid.

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