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Preliminary communication

The direct formation of ketones by reaction of methyl- and aryl-(carbonyl)(iodo)pentamethylcyclopentadienylrhodium complexes with organic iodides

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Abstract

[C_5Me_5Rh(aryl)(CO)I] reacts with methyl iodide to give [$(C_5Me_5RhI_2)_2$] and arylCOMe; similar reactions occur between [C_5Me_5Rh(Me)(CO)I] and RI to give the ketones RCOMe (R = Ph, Me, Et, or Pr).

The preceding communication described the promoted formation of acetophenone from [C_5Me_5Rh(Ph)(CO)(Me)] [1]; we here report the bimolecular formation of ketones (RCOR′) by reaction of [C_5Me_5Rh(R)CO(I)] with organic iodides (R′I), normally in R′I as solvent.

The aryl-iodo-carbonyl complexes (**1a**–**1e**) reacted with methyl iodide (sealed tube, 60 °C) to give the corresponding acetophenones (80–90%) and the rhodium diiodide complex **2** (eq. 1). Only traces (1–2%) of the toluenes were formed.

$$\underset{(\mathbf{1})}{[C_5Me_5Rh(CO)(p\text{-}XC_6H_4)I]} + MeI \rightarrow \tfrac{1}{2}\underset{(\mathbf{2})}{[\{C_5Me_5RhI_2\}_2]} + p\text{-}XC_6H_4COMe \qquad (1)$$

(a, X = C_6H_5; b, p-MeC_6H_4; c, p-NCC_6H_4; d, p-$NO_2C_6H_4$; e, p-$CHOC_6H_4$)

The relative rates of the reactions (1) decreased in the order, X = Me (10) > H (25) > CHO (32) > NC (44) > NO_2 (76) ($t_{1/2}$ in h; 60 °C).

The inverse reaction (eq. 2; R′ = C_6H_5), of iodobenzene with [C_5Me_5Rh(CO)(Me)I] (**3**) also gave acetophenone (80%) and the iodo complex **2**.

$$\underset{(\mathbf{3})}{[C_5Me_5Rh(CO)(Me)I]} + R'I \rightarrow \tfrac{1}{2}\underset{(\mathbf{2})}{[\{C_5Me_5RhI_2\}_2]} + R'\text{–CO–Me} \qquad (2)$$

Complex **3** also reacted with alkyl iodides (R′I). Thus acetone was formed in methyl iodide (90%; 60 °C), and reaction with CD_3I gave largely CH_3COCD_3, (mass spectroscopy, m/e 61). Reaction with ethyl iodide gave methyl ethyl ketone

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(60%; 100 °C, 2 h) together with ethylene and ethane, while reaction with n-propyl iodide (3 h, 80 °C) gave a mixture of n-propyl methyl ketone (30%) and isopropyl methyl ketone (23%), together with propane and propylene; the same products (25% each of the two ketones) were obtained when **3** was treated with isopropyl iodide.

The observation of isomerisation in the last reactions suggests the intermediacy of rhodium-σ-alkyl (Rh–R′) species, in this case propyl in equilibrium with isopropyl species,

$$L_nRh(CH_2CH_2CH_3) \rightleftharpoons L_nRh\{CH(CH_3)_2\}$$

Complexes **1a**–**1e** were prepared by reaction of [$C_5Me_5Rh(aryl)(CO)Me$] (**4a**–**4e**) [2] with I_2/CH_2Cl_2 (< 0 °C; 80–90% yields; eq. 3). Complex **3** was not conveniently accessible by reaction of [$C_5Me_5Rh(CO)Me_2$] with iodine since that gave considerable amounts of [$C_5Me_5Rh(CO)I_2$] (**5**) even at low temperatures and with a deficiency of iodine. A better route to **3** was via reaction of methyl iodide with the 4-pyridyl complex **4f** (from [$C_5Me_5Rh(Me_2SO)(Me)_2$] and 4-pyridinecarboxaldehyde). The other product from this reaction (eq. 4) was *N*,4-dimethylpyridinium iodide.

$$\underset{(\mathbf{4})}{[C_5Me_5Rh(CO)(p\text{-}XC_6H_4)(Me)]} + I_2 \rightarrow \underset{(\mathbf{1})}{[C_5Me_5Rh(CO)(p\text{-}XC_6H_4)(I)]} + MeI \qquad (3)$$

$$\underset{(\mathbf{4f})}{[C_5Me_5Rh(CO)(4\text{-}C_5H_4N)(Me)]} + 2MeI \rightarrow \underset{(\mathbf{3})}{[C_5Me_5Rh(CO)I(Me)]} + 4\text{-}MeC_5H_4NMe^+I^- \qquad (4)$$

When reaction 4 was carried out with CD_3I, the labelling in the dimethylpyridinium salt was $4\text{-}CH_3C_5H_4NCD_3^+\ I^-$ (^1H and ^2H NMR spectra), indicating that the methyl which coupled to the pyridine carbon was originally on the rhodium.

Reaction of methyl iodide with [$C_5Me_5Rh(COMe)(CO)I$] [3] also gave acetone (80% yield; 50 °C, 72 h) and complex **5**. The somewhat milder conditions needed suggests that the first steps in reactions 1 or 2 may also be an R′–I promoted migration of R onto coordinated CO [1], then followed by oxidative addition and reductive elimination of RCOR′ (eq. 5). Studies of mechanisms and further applications are in progress.

$$[C_5Me_5Rh(R)(CO)I] + R'I \rightarrow [C_5Me_5Rh(COR)I\ldots(I\text{–}R')] \rightarrow [C_5Me_5Rh(COR)(R')(I)_2] \rightarrow R\text{–}CO\text{–}R' + \mathbf{2} \qquad (5)$$

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