

Preliminary communication

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

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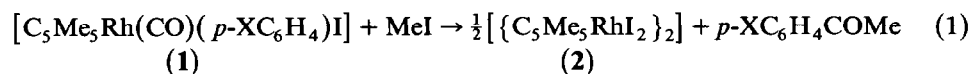
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Abstract

$[\text{C}_5\text{Me}_5\text{Rh}(\text{aryl})(\text{CO})\text{I}]$ reacts with methyl iodide to give $[(\text{C}_5\text{Me}_5\text{RhI}_2)_2]$ and arylCOMe; similar reactions occur between $[\text{C}_5\text{Me}_5\text{Rh}(\text{Me})(\text{CO})\text{I}]$ and RI to give the ketones RCOMe (R = Ph, Me, Et, or Pr).

The preceding communication described the promoted formation of acetophenone from $[\text{C}_5\text{Me}_5\text{Rh}(\text{Ph})(\text{CO})(\text{Me})]$ [1]; we here report the bimolecular formation of ketones (RCOR') by reaction of $[\text{C}_5\text{Me}_5\text{Rh}(\text{R})(\text{CO})\text{I}]$ with organic iodides (R'I), normally in R'I as solvent.

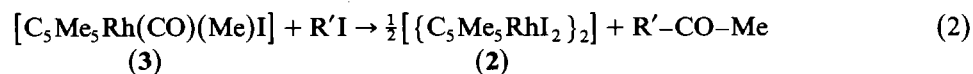
The aryl-iodo-carbonyl complexes (1a–1e) reacted with methyl iodide (sealed tube, 60 °C) to give the corresponding acetophenones (80–90%) and the rhodium diiodide complex 2 (eq. 1). Only traces (1–2%) of the toluenes were formed.



(a, X = C₆H₅; b, *p*-MeC₆H₄; c, *p*-NCC₆H₄; d, *p*-NO₂C₆H₄; e, *p*-CHOC₆H₄)

The relative rates of the reactions (1) decreased in the order, X = Me (10) > H (25) > CHO (32) > NC (44) > NO₂ (76) (*t*_{1/2} in h; 60 °C).

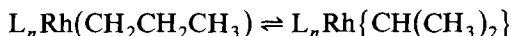
The inverse reaction (eq. 2; R' = C₆H₅), of iodobenzene with $[\text{C}_5\text{Me}_5\text{Rh}(\text{CO})(\text{Me})\text{I}]$ (3) also gave acetophenone (80%) and the iodo complex 2.



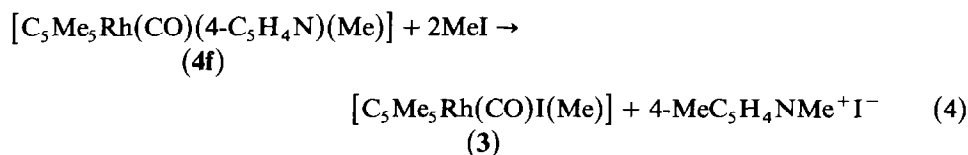
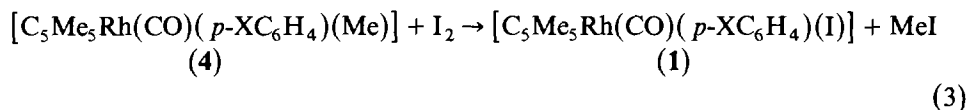
Complex 3 also reacted with alkyl iodides (R'I). Thus acetone was formed in methyl iodide (90%; 60 °C), and reaction with CD₃I gave largely CH₃COCD₃, (mass spectroscopy, *m/e* 61). Reaction with ethyl iodide gave methyl ethyl ketone

(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,

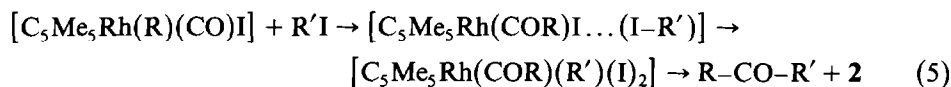


Complexes **1a–1e** were prepared by reaction of $[C_5Me_5Rh(aryl)(CO)Me]$ (**4a–4e**) [2] with I_2/CH_2Cl_2 ($< 0^\circ C$; 80–90% yields; eq. 3). Complex **3** was not conveniently accessible by reaction of $[C_5Me_5Rh(CO)Me_2]$ with iodine since that gave considerable amounts of $[C_5Me_5Rh(CO)I_2]$ (**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.



When reaction 4 was carried out with CD_3I , the labelling in the dimethylpyridinium salt was $4-CH_3C_5H_4NCD_3^+ I^-$ (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.



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References

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