

Preliminary communication

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

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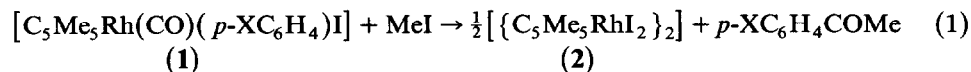
(Received April 27th, 1987)

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 ($\text{R} = \text{Ph}, \text{Me}, \text{Et}, \text{or Pr}$).

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 ($\text{R}'\text{I}$), normally in $\text{R}'\text{I}$ as solvent.

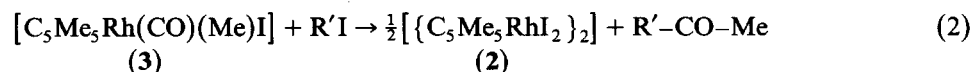
The aryl-iodo-carbonyl complexes (**1a–1e**) reacted with methyl iodide (sealed tube, 60°C) to give the corresponding acetophenones (80–90%) and the rhodium diiodide complex **2** (eq. 1). Only traces (1–2%) of the toluenes were formed.



(a, $\text{X} = \text{C}_6\text{H}_5$; b, $p\text{-MeC}_6\text{H}_4$; c, $p\text{-NCC}_6\text{H}_4$; d, $p\text{-NO}_2\text{C}_6\text{H}_4$; e, $p\text{-CHOC}_6\text{H}_4$)

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

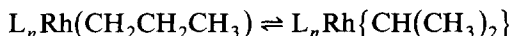
The inverse reaction (eq. 2; $\text{R}' = \text{C}_6\text{H}_5$), of iodobenzene with $[\text{C}_5\text{Me}_5\text{Rh}(\text{CO})(\text{Me})\text{I}]$ (**3**) also gave acetophenone (80%) and the iodo complex **2**.



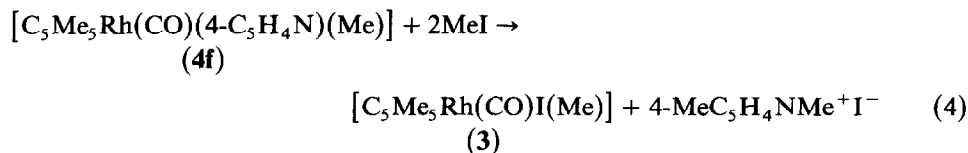
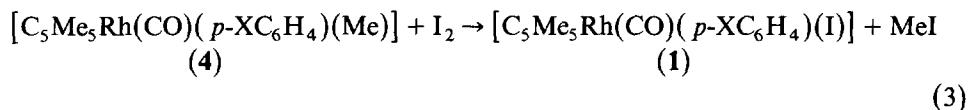
Complex **3** also reacted with alkyl iodides ($\text{R}'\text{I}$). Thus acetone was formed in methyl iodide (90%; 60°C), and reaction with CD_3I gave largely CH_3COCD_3 , (mass spectroscopy, m/e 61). Reaction with ethyl iodide gave methyl ethyl ketone

(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,

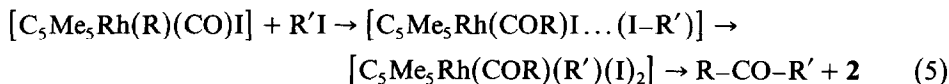


Complexes **1a–1e** were prepared by reaction of $[C_5Me_5Rh(aryl)(CO)Me]$ (**4a–4e**) [2] with I_2/CH_2Cl_2 ($< 0^\circ C$; 80–90% yields; eq. 3). Complex **3** was not conveniently accessible by reaction of $[C_5Me_5Rh(CO)Me_2]$ with iodine since that gave considerable amounts of $[C_5Me_5Rh(CO)I_2]$ (**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 $4\text{-}CH_3C_5H_4NCD_3^+ I^-$ (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.



Acknowledgement. We thank the SERC, ICI New Science Group (CASE award to GJS), and the Italian Ministero della Pubblica Istruzione (grant to FPF) for support, and Johnson Matthey for the loan of rhodium salts.

References

- 1 G.J. Sunley, F.P. Fanizzi, I.M. Saez, and P.M. Maitlis, *J. Organomet. Chem.*, 330 (1987) C27.
- 2 M. Gomez, J.M. Kisenyi, G.J. Sunley, and P.M. Maitlis, *J. Organomet. Chem.*, 296 (1985) 197.
- 3 J.W. Kang and P.J. Maitlis, *J. Organomet. Chem.*, 26 (1971) 393.