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# Rhodium Carbonyl Catalyzed Carbonylation of Unsaturated Compounds. IV.[1) Carbonylation and Oligomerization of Diphenylacetylene Catalyzed by $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, and $Ir_4(CO)_{12}$ under Pressure of Carbon Monoxide

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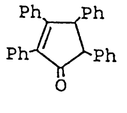
**Synopsis.** In the presence of $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, and $Ir_4(CO)_{12}$ catalysts the reaction of diphenylacetylene (**1**) in 2-propanol under pressure of carbon monoxide gave the hydrocarbonylation products **2** and/or **3** and the oligomers **4** and/or **5**, in which the ratios depended on the catalyst employed.

Carbonylation of acetylenes with carbon monoxide in the presence of a soluble group VIII metal catalyst is a useful synthetic reaction because it yields a variety of valuable products according to the catalysts employed and the reaction conditions.[2) We have previously reported that cross-hydrocarbonylation of acetylenes and ethylene catalyzed by $Rh_4(CO)_{12}$ yields 5-ethyl-2(5*H*)-furanones[3) and 1-penten-3-one,[1,4) and that alkoxycarbonylation of acetylenes catalyzed by $Rh_4(CO)_{12}$-base yields 5-alkoxy-2(5*H*)-furanones.[5) The corresponding cobalt and iridium catalysts showed very low activities for these reactions, and gave some carbonylation and oligomerization products of acetylenes. In order to investigate in detail whether there is any significant difference in the catalytic behavior of $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, and $Ir_4(CO)_{12}$ we have examined the reaction of diphenylacetylene (**1**) under carbon monoxide pressure and the results are now reported.

## Results and Discussion

Under CO pressure (30 kg cm$^{-2}$) a mixture of diphenylacetylene (**1**, 4 mmol) and $M_4(CO)_{12}$ (0.01 mmol for M=Rh and Ir, and 0.1 mmol for M=Co) in 2-propanol was heated at 220 °C for 6 h. A mixture of 2,3,4,5-tetraphenyl-2-cyclopenten-1-one (**2**), 2-phenyl-1-indanone (**3**), 1-benzylidene-2,3-diphenyl-1*H*-indene (**4**), hexaphenylbenzene (**5**), and (*E*)/(*Z*)-stilbene (**6**) were formed in different ratios, depending on the catalysts employed. The products **2** and **3** are the hydrocarbonylation ones, in which the hydrogens required are supplied by the dehydrogenation of 2-propanol,[3) and the latter is derived via aromatic C–H activation. The product **4** is a cyclic dimer of **1**, which is formed via the C–H activation of a phenyl group in **1**,[6) and **5** is the usual trimer. (*E*)/(*Z*)-Stilbene is formed by the hydrogen transfer from 2-propanol to **1**. These results are listed in Table 1.



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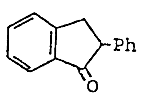

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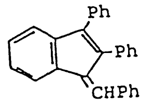

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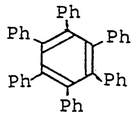

5

PhCH=CHPh

6

The reaction in which $Rh_4(CO)_{12}$ was used as the catalyst gave **2**, **4**, and **6** in 42%, 35%, and 17% yields, respectively. In the reaction using benzene as the solvent, the catalytic cleavage of C–H bond(s) of benzene occurs to give triphenylethylene (45%) and 2,3-diphenyl-1*H*-inden-1-one (10%), and **2** (16%) and **4** (8%) are obtained as the by-products.[6) These results show that the yields of **2** and **4** increase by replacement of the solvent benzene with a hydrogen-donating solvent such as 2-propanol.

In the presence of $Ir_4(CO)_{12}$ catalyst, **4** was obtained as the major product (51%), together with **2** (9%), **5** (23%), and **6** (4%). In spite of the reaction under

Table 1. Reaction of Diphenylacetylene in 2-Propanol under Pressure of Carbon Monoxide[a)

| Catalyst | Conv. (%) | Product (%) | | | | |
|---|---|---|---|---|---|---|
| | | **2**[b) | **3**[c) | **4**[b) | **5**[b) | **6** ((*E*)/(*Z*))[c) |
| $Co_4(CO)_{12}$ | 100 | 41 | 24 | — | 11 | 5 (71/29) |
| $Rh_4(CO)_{12}$ | 100 | 42 | — | 35 | 1 | 17 (83/17) |
| $Ir_4(CO)_{12}$ | 100 | 9 | — | 51 | 23 | 4 (86/14) |
| $Fe_3(CO)_{12}$ | 31 | — | — | — | — | 29 (37/63) |
| $Ru_3(CO)_{12}$ | 100 | — | — | — | — | 99 (84/16) |
| $Os_3(CO)_{12}$ | 13 | — | — | — | — | 3 (35/65) |

a) Reactions were carried out under conditions described in the text. b) Isolated yields based on the acetylene used. c) Yields determined by GC.

pressure of CO, the combined yield of the oligomers **4** and **5** was much higher than the yield of the carbonylation product **2**.

When $Co_4(CO)_{12}$ catalyst was used, **2** and **3** were formed in 41% and 24% yields, respectively, together with **5** (11%) and **6** (5%). The dimer **4** was not obtained at all. The cyclic carbonylation product **3** has been recently reported to be formed in the $Co_2(CO)_8/PPh_3$-catalyzed carbonylation of **1** under water gas shift conditions.[7]

Under the present reaction conditions the carbonylation of **1** competes with the oligomerization and the product distributions markedly depends on the catalyst employed. The combined yield of the carbonylation products **2** and **3** decreases in the following order; $Co_4(CO)_{12}$ (65%)>$Rh_4(CO)_{12}$ (42%)≫$Ir_4(CO)_{12}$ (9%). Carbonylation ability was the lowest for $Ir_4(CO)_{12}$ catalyst.

Under similar conditions $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$ catalysts gave no carbonylation and oligomerization products, but gave the hydrogenation product **6**. The catalytic activity was the highest for $Ru_3(CO)_{12}$ and much lower for $Fe_3(CO)_{12}$ or $Os_3(CO)_{12}$, as shown in Table 1. This trend is consistent with that in hydrogenation of 1- and 2-pentyne with molecular hydrogen.[8]

## Experimental

**Materials.** $M_4(CO)_{12}$ (M=Co[9] and Rh[1]) and $M_3(CO)_{12}$ (M=Fe,[10] Ru,[11] and Os[12]) were prepared by the methods described in the literatures. Diphenylacetylene and $Ir_4(CO)_{12}$ were purchased and used without further purification.

**General Procedures.** A 50 cm$^3$ glass tube was charged with diphenylacetylene (**1**, 4 mmol), $M_4(CO)_{12}$ (0.01 mmol for M=Rh and Ir, and 0.1 mmol for M=Co) or $M_3(CO)_{12}$ (0.013 mmol for M=Ru and Os, and 0.13 mmol for M=Fe), and 2-propanol (25 cm$^3$), and the tube was placed in a 100 cm$^3$ stainless-steel autoclave. The autoclave was flushed three times with CO (10 kg cm$^{-2}$), then pressurized to 30 kg cm$^{-2}$, heated and agitated at 220 °C for 6 h. The reaction mixture was analyzed by gas chromatography (3% Silicone OV-17 on Chromosorb W) and separated by column chromatography on silica gel (2 cm×20 cm). The products were identified by $^1$H NMR, IR, and GC/MS spectroscopy.

**Reaction in the Presence of $Rh_4(CO)_{12}$ Catalyst.** Yellow and colorless crystalline precipitates and a orange yellow solution were obtained. After removal of the solvent in vacuo, the residue was recrystallized from benzene/hexane (1/10) to give the product **2** (225 mg, 29%) as colorless crystals. The products **4** (250 mg, 35%), **5** (6 mg, 1%), and **2** (97 mg, 13%) were isolated by column chromatography of the mother liquor. GC analysis of the reaction mixture showed the presence of **6** (125 mg, 17%, (*E*)/(*Z*)=83/17).

**Reaction in the Presence of $Ir_4(CO)_{12}$ Catalyst.** Yellow and colorless crystalline precipitates and a yellow solution were obtained. The reaction mixture was filtered and the precipitate was washed with benzene (20 cm$^3$) to dissolve the yellow precipitate, remaining colorless crystals **5** (163 mg, 23%). The products **4** (366 mg, 51%) and **2** (69 mg, 9%) were isolated by column chromatography of the combined filtrate. GC analysis of the filtrate showed the presence of **6** (28 mg, 4%, (*E*)/(*Z*)=86/14).

**Reaction in the Presence of $Co_4(CO)_{12}$ Catalyst.** A light brown solution and colorless precipitate were obtained. The colorless precipitate (**5**, 62 mg, 9%) was filtered off. GC analysis of the filtrate showed the presence of **6** (33 mg, 5%, (*E*)/(*Z*)=71/29) and **3** (217 mg, 24%). The products **5** (18 mg, 2%) and **2** (316 mg, 41%) were isolated by column chromatography of the filtrate.

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