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The Carbonylation of 1,1′-Bis(chloromercuri)ferrocene with Palladium Salt: A Synthesis of [1.1]Ferrocenophane-1,12-dione

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It has recently been found that palladium or palladium chloride can be used as a catalyst for the carbonylation reaction of various compounds:[1] olefins,[2] dienes,[3] acetylene,[4] allyl halides,[5] and amines.[6,7] Furthermore, Henry[7] has reported that arylpalladium salts, prepared *in situ* from arylmercuric salts and palladium compounds, react with carbon monoxide to form arenecarboxylic acids or their derivatives; Heck[8] has also described that diaryl ketones could be formed in moderate yields from arylmercuric salts and carbon monoxide with a palladium-salt catalyst. In this paper, we wish to report that the reaction of 1,1′-bis(chloromercuri)ferrocene (**1**) and carbon monoxide in the presence of a palladium salt results in the formation of [1.1]ferrocenophane-1,12-dione (**2**) and ferrocenedicarboxylic acid derivatives (**3**), plus a small amount of bi-1,1′-ferrocenylene (**4**), while the diferrocenyl ketone (**6**) and methyl ferrocenecarboxylate (**7**) are also produced by the carbonylation reaction of chloromercuriferrocene (**5**) in methanol with a palladium-salt catalyst.

Experimental

Measurements. All the melting points are uncorrected. The NMR spectra were determined in $CDCl_3$ at 60 MHz with a Hitachi H-60 NMR spectrometer, using TMS as the internal reference. A Hitachi EPI-S2 infrared spectrometer was used for the measurements of the infrared absorption spectra. The molecular weight was determined in benzene or in chloroform, using a Hitachi 115 vapor-pressure osmometer.

Materials. 1,1′-Bis(chloromercuri)ferrocene (**1**) and chloromercuriferrocene (**5**) were prepared according to the method described by Fish and Rosenblum.[9]

Carbonylation of 1,1′-Bis(chloromercuri)ferrocene (1). The lithium palladium chloride solution was prepared by stirring 1.68 g (40 mmol) of anhydrous lithium chloride with 3.54 g (20 mmol) of anhydrous palladium chloride overnight at room temperature in 200 m*l* of methanol. Into this lithium chloropalladite solution, **1** (6.56 g, 10 mmol) was then carbonylated at 70°C under a carbon monoxide pressure (50 atm) for 6 hr with shaking; a pressure drop was thus observed. The products were isolated by filtering to remove a precipitated palladium and by distilling under reduced pressure to remove the solvent. The residue was dissolved in benzene and chromatographed on neutral alumina. The first elution with benzene and recrystallization from benzene afforded orange crystals (0.15 g, 8% yields); they were identified as bi-1,1′-ferrocenylene (**4**) by a comparison of the IR spectrum with that of an authentic sample and by a mixed-melting-point determination.[10] Mp 370°C. IR spectrum (KBr): 3090, 1101, 998 cm^{-1}. Found: C, 65.41; H, 4.46%; mol wt (in $CHCl_3$) 363. Calcd for $C_{20}H_{16}Fe_2$: C, 65.54; H, 4.39%; mol wt 368.

The second elution with benzene and recrystallization gave dimethyl 1,1′-ferrocenedicarboxylate[11] (**3**) (1.12 g, 36.8%); this was identified by a comparison of the IR and NMR spectra, and by a mixed-melting-point determination, with an authentic sample. Mp 114—115°C. IR spectrum (KBr): 1704 cm^{-1} (ester). NMR spectrum (ppm): 3.78 ($COOCH_3$, singlet), 4.35 (ring protons, triplet), 4.77 (ring protons, triplet).

Further elution with chloroform and recrystallization from chloroform afforded yellow orange crystals (1.19 g, 29%); they were identified as [1.1]ferrocenophane-1,12-dione[12] (**2**). Mp 350°C. IR spectrum (KBr): 1615, 1104, 998 cm^{-1}. NMR spectrum (ppm): 4.40 (ring protons, triplet); 4.80 (ring protons, triplet). Found: C, 62.17; H, 3.72%; mol wt (in $CHCl_3$) 419. Calcd for $C_{22}H_{16}O_2Fe_2$: C, 62.28; H, 3.80%; mol wt 424.2.

Carbonylation of Chloromercuriferrocene (5). In a lithium chloropalladite solution (prepared from 0.84 g of lithium chloride and 1.77 g of palladium chloride in 100 m*l* of methanol), **5** was carbonylated at 50°C under carbon monoxide (50 atm) for 3 hr with shaking. The isolation of the product in the same manner as was used for **1** gave biferrocenyl[13] (**8**) (mp 236—238°C, 0.21 g, 11.2%), methyl ferrocenecarboxylate[14] (**7**) (mp 70—71°C, 0.78 g, 32.3%), and diferrocenyl ketone[15] (**6**) (mp 205—206°C, 0.54 g, 31.5%). These products were identified by a comparison of the IR and NMR spectra, and by a mixed-melting-point determination, with an authentic sample.

Results and Discussion

The carbonylation of **1** was carried out at 70°C under a carbon monoxide pressure of 50 atm in the presence

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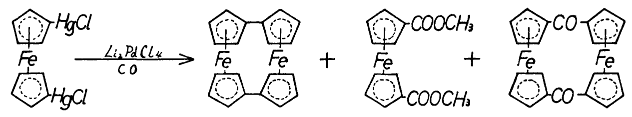
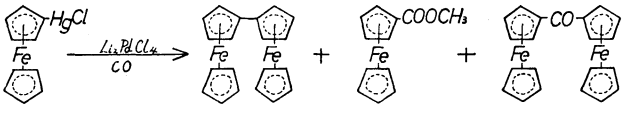


(1) (4) (3) (2)



(5) (8) (7) (6)

of lithium chloropalladite in methanol; the main products were **2** and **3**, plus a small amount of **4**. Under the same conditions, the carbonylation of **5** in methanol resulted in the formation of **6**, **7**, and **8**. Heck[8] reported that arylmercuric chlorides react with palladium salts in the absence of carbon monoxide to form biaryls in good yields. We also observed that the reaction of **1** with palladium salts led to the formation of **4** in good yields.[16] The addition of carbon monoxide to the reaction mixture results in the formation of **2** and **3** at the expense of **4**. In the carbonylation of arylmercuric salts, the use of rhodium catalysts for the diaryl ketone has been reported. However, in the carbonylation of **1**, the use of rhodium trichloride as a catalyst did not bring about better results in the formation of **2** compared with the use of the palladium catalyst.

The mechanism of the formation of **2** from **1**, as Heck pointed out in his carbonylation study,[8] probably involves the reaction of an acyl-palladium compound with a ferrocenylene palladium compound or a ferrocenylene mercuric compound. **3** and **4** are probably formed by side reactions.

$$[C_5H_4(HgCl)]_2Fe + PdCl_2 \rightleftarrows [C_5H_4(PdCl)]_2Fe + 2HgCl_2$$

$$[C_5H_4(PdCl)]_2Fe + 2CO \rightleftarrows [C_5H_4(COPdCl)]_2Fe$$

$$[C_5H_4(COPdCl)]_2Fe + [C_5H_4(PdCl)]_2Fe \longrightarrow \mathbf{2} + 2PdCl_2 + 2Pd$$

or

$$[C_5H_4(COPdCl)]_2Fe + [C_5H_4(HgCl)]_2Fe \longrightarrow \mathbf{2} + 2HgCl_2 + 2Pd$$

$$2[C_5H_4(PdCl)]_2Fe \longrightarrow \mathbf{4} + 2PdCl_2 + 2Pd$$

or

$$[C_5H_4(PdCl)]_2Fe + [C_5H_4(HgCl)]_2Fe \longrightarrow \mathbf{4} + 2HgCl_2 + 2Pd$$

$$[C_5H_4(COPdCl)]_2Fe \longrightarrow [C_5H_4(COCl)]_2Fe + 2Pd$$

$$[C_5H_4(COCl)]_2Fe + CH_3OH \longrightarrow \mathbf{3} + 2HCl$$

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