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The Formation of 1,1′-Oligomeric Ferrocenes from Chloromercuriferrocene and Bis(chloromercuri)ferrocene

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Synopsis. A series of 1,1′-oligomeric ferrocenes, including biferrocene, 1,1′-biferrocenylene, 1,1′-terferrocene, 1,1′-quaterferrocene, 1,1′-quinqueferrocene, and 1,1′-sexiferrocene, was formed by the reaction between chloromercuriferrocene and 1,1′-bis(chloromercuri)ferrocene in the presence of palladium(II) salt.

The increasing interest in systems containing directly bonding ferrocene nuclei has been focused on the study of the synthesis of oligomeric ferrocene.[1] Nesmeyanov *et al.*[2] reported a mixed Ullmann reaction with bromoferrocene and 1,1′-dibromoferrocene to give a series of 1,1′-oligomeric ferrocenes. Watanabe *et al.*[3] also described the formation of the 1,1′-oligomeric ferrocenes from the reaction of a mixture of mono- and dilithioferrocenes with cobalt chloride. More recently, Roling and Rausch[4] reported a mixed Ullmann reaction between haloferrocene and 1,1′-diiodoferrocene.

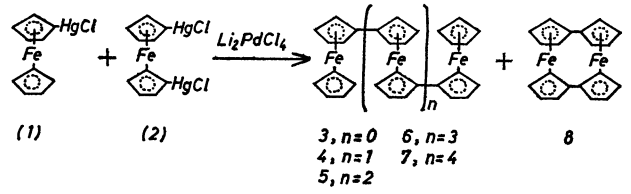

Fig. 1.

In this report, we wish to describe the synthesis of ferrocene oligomers from the reaction between a palladium(II) salt and a mixture of chloromercuriferrocene (**1**) and 1,1′-bis(chloromercuri)ferrocene (**2**).

In the presence of lithium chloropalladite, the reaction between **1** and **2** was accomplished in a polar solvent, such as ethanol or acetonitrile, under an atmosphere of nitrogen. The reaction products were separated by a combination of crystallization and chromatography on alumina and were found to be biferrocene (**3**), 1,1′-terferrocene (**4**), 1,1′-quaterferrocene (**5**), 1,1′-quinqueferrocene (**6**), 1,1′-sexiferrocene (**7**), and 1,1′-biferrocenylene (**8**). As may be seen in Table 1, different product ratios were obtained depending on the ratio of **1** to **2**. Roling and Rausch[4] reported that **8** could not be detected in a mixed Ullmann reaction; however, the **8** prepared in this study agreed in its properties with the 1,1′-biferrocenylene obtained by Hedberg and Rosenberg.[5]

Table 1. Reaction of chloromercuriferrocene (**1**) and 1,1′-bis(chloromercuri)ferrocene (**2**) with palladium(II) salt

Run	Ratio of **1** to **2**	Solvent	Percentage yields[a] of products						
			3	**4**	**5**	**6**	**7**	**8**	total
1	2 : 1[b]	EtOH	44	9	2			3	58
2	2 : 1[b]	CH_3CN	48	10	2	1		4	65
3	1 : 1[c]	EtOH	31	16	4	1	1	4	57
4	1 : 1[c]	CH_3CN	30	18	6	2	1	3	59
5	1 : 2[d]	EtOH	16	24	6	3	1	6	56
6	1 : 2[d]	CH_3CN	20	18	5	3	1	4	51

a) Yields are based on the limiting reagent in each reaction. b) Six mmol of **1** and 3 mmol of **2** were used. c) Four mmol of **1** and 4 mmol of **2** were used. d) Two point four mmol of **1** and 4.8 mmol of **2** were used.

Heck[6] previously reported that the reaction of olefins with arylmercuric chloride and palladium(II) salt produces the arylated olefinic compounds, accompanied by biaryl; he suggested that the mechanism of the formation of biaryl as a by-product involves a coupling reaction of arylpalladium chloride or a reaction of arylpalladium chloride and arylmercuric chloride. The formation of ferrocene oligomers may, therefore, be accounted for as follows:

$$FcHgCl + Li_2PdCl_4 \rightarrow [FcPdCl] + HgCl_2 + 2LiCl$$

$$Fcl(HgCl)_2 + 2Li_2PdCl_4 \rightarrow [Fcl(PdCl)_2] + 2HgCl_2 + 4LiCl$$

$$2[FcPdCl] \rightarrow Fc\text{-}Fc + PdCl_2 + Pd$$

or

$$[FcPdCl] + FcHgCl \rightarrow Fc\text{-}Fc + HgCl_2 + Pd$$

$$2[FcPdCl] + Fcl(HgCl)_2 \rightarrow Fc\text{-}Fc\text{-}Fc + 2HgCl_2 + 2Pd$$

$$2[FcPdCl] + [Fcl(PdCl)_2] \rightarrow Fc\text{-}Fc\text{-}Fc + 2PdCl_2 + 2Pd$$

$$[FcPdCl] + [Fcl(PdCl)_2]_n \rightarrow [Fc\text{-}FcPdCl] + PdCl_2 + Pd$$

$$2[Fc\text{-}FcPdCl] \rightarrow Fc\text{-}Fc\text{-}Fc\text{-}Fc + PdCl_2 + 2Pd$$

$$2[Fc\text{-}FcPdCl] + [Fcl(PdCl)_2] \rightarrow Fc\text{-}Fc\text{-}Fc\text{-}Fc\text{-}Fc + 2PdCl_2 + 2Pd$$

$$[Fc\text{-}FcPdCl] + [Fcl(PdCl)_2] \rightarrow [Fc\text{-}Fc\text{-}FcPdCl] + PdCl_2 + Pd$$

$$2[Fc\text{-}Fc\text{-}FcPdCl] \rightarrow Fc\text{-}Fc\text{-}Fc\text{-}Fc\text{-}Fc\text{-}Fc + PdCl_2 + Pd$$

$$2[Fcl(PdCl)_2] \rightarrow Fcl\text{-}Fcl + 2PdCl_2 + 2Pd$$

$$[Fcl(PdCl)_2] + Fcl(HgCl)_2 \rightarrow Fcl\text{-}Fcl + 2HgCl_2 + 2Pd$$

Fc=ferrocenyl, $FeC_{10}H_9$; Fcl=1,1′-ferrocenylene, $Fe(C_5H_4)_2$.

Experimental

Materials. All the melting points are uncorrected. The chloromercuriferrocene[7] (**1**) and 1,1′-bis(chloromercuri)-ferrocene[7] (**2**) were prepared by the standard literature method. The IR spectra were measured using a Hitachi 215 spectrometer. The NMR spectra were measured using a Hitachi R-22 (90 MHz) spectrometer. The chemical shifts were expressed in downfield from TMS as an internal standard. The mass spectra were recorded on a Hitachi RMU-6E mass spectrometer at 70 eV.

General Procedure for the Preparation of Oligomeric Ferrocenes. The lithium chloropalladite solutions were prepared by stirring 1.01 g (24 mmol) of anhydrous lithium chloride and 2.12 g (12 mmol) of anhydrous palladium chloride overnight at room temperature in 100 ml of ethanol. On the other hand, in the case of acetonitrile, a 12-mmol portion instead of a 24-mmol portion of lithium chloride was used.

To this lithium chloropalladite solution, a mixture of **1** and **2** was added, after which the mixture was stirred at room temperature for 48 hr under nitrogen. After the separation of the precipitated palladium, the solvent was evaporated under reduced pressure to yield Substance A. The precipitated palladium was further extracted with boiling toluene until the toluene extracts were colorless; the toluene was then evaporated to yield Substance B. Finally, the precipitated palladium was extracted with boiling bromobenzene, the extracts were allowed to cool, and the resulting precipitate was collected to give Substance C.

Substance A was dissolved in 30 ml of benzene, and 30 ml of hexane was added. The precipitate, thus formed was collected to yield a yellow product, which was crystallized from benzene and identified as 1,1′-quinqueferrocene (**6**); mp 258—260 °C (lit, 240—245 °C,[3] 262—264 °C[4]). IR (KBr) 1105, 1100, 1020, 998, 805 cm^{-1}. The NMR spectrum of **6** is not available, for **6** is insoluble in the solvent necessary for the observation of the NMR spectrum.

Found: C, 64.88; H, 4.47%; mol wt, 922 (mass spectrometry). Calcd for $C_{50}H_{42}Fe_5$: C, 65.13; H, 4.59%; mol wt, 922.

The filtrate was chromatographed on neutral alumina. The first elution with hexane-benzene (4 : 1) afforded orange-yellow crystals; they were identified as biferrocene (**3**) (mp 236—238 °C) by a mixed-melting-point determination with an authentic sample (mp 238—239 °C[8]). IR (KBr) 1105, 1100, 1028, 1000, 818 cm^{-1}. NMR ($CDCl_3$) δ 3.95 (s, 10H, unsubstituted cyclopentadienyl ring protons), 4.17 (m, 4H, β protons on the substituted ring), 4.31 ppm (m, 4H, α protons on the substituted ring). Found: mol wt, 370 (mass spectrometry). Calcd for $C_{20}H_{18}Fe_2$: mol wt, 370.

The second band was eluted with hexane-benzene (1 : 1) to yield a yellow material, which was then cryatallized from a mixture of hexane-benzene. This material was 1,1′-terferrocene (**4**); mp 223—224 °C (dec.) (lit,[3] 226.5—227.2 °C (dec.)). IR (KBr) 1105, 1100, 1020, 1000, 815 cm^{-1}. NMR ($CDCl_3$) δ 3.94 (s, 10H, unsubstituted cyclopentadienyl ring protons), 4.06—4.28 ppm (m, 16H, α and β protons on the substituted ring).

Found: C, 64.92; H, 4.61%; mol wt 554 (mass spectrometry). Calcd for $C_{30}H_{26}Fe_3$: C, 65.03; H, 4.73%; mol wt, 554.

The third band was eluted with benzene to give a orange-yellow compound, which was then crystallized from benzene to yield 1,1′-quaterferrocene (**5**); mp 275—280 °C (dec.) (lit,[3] mp 280 °C). IR (KBr) 1105, 1100, 1025, 1000, 810 cm^{-1}. The NMR spectrum of **5** is not available, for **5** is insoluble in the solvent necessary for the observation of the NMR spectrum.

Found: C, 64.89; H, 4.60%; mol wt, 738 (mass spectrometry). Calcd for $C_{40}H_{34}Fe_4$: C, 65.09; H, 4.64%; mol wt 738.

The last band was eluted with benzene-chloroform (1 : 1) to give reddish-orange crystals, which were then crystallized from benzene to yield 1,1′-biferrocenylene (**8**) (mp 370 °C (dec) (lit,[5] mp 380 °C (dec))). IR (KBr) 1110, 1105, 1027, 1005, 824 cm^{-1}. NMR (C_6D_6) δ 3.79 (t, 8H), 5.25 ppm (t, 8H).

Found: C, 65.48; H, 4.31%; mol wt 368 (mass spectrometry). Calcd for $C_{20}H_{16}Fe_2$: C, 65.54; H, 4.39%; mol wt, 368.

Substance B was purified in a similar manner to yield **3**, **4**, **5**, **6**, and **8**.

Substance C was extracted with boiling benzene until the extracts were colorless. The benzene was then allowed to cool to yield a yellow-brown material, 1,1′-sexiferrocene (**7**) (mp 265—268 °C (dec.), (lit, mp 252—256 °C,[3] mp 270—272 °C[4])). IR (KBr) 1105, 1100, 1020, 995, 802 cm^{-1}. The NMR spectrum of **7** is not available, for **7** is insoluble in the solvent necessary for the observation of the NMR spectrum.

Found: C, 65.01, H, 4.46%; mol wt, 1106 (mass spectrometry). Calcd for $C_{60}H_{50}Fe_6$: C, 65.15; H, 4.56%; mol wt, 1106.

The results are summarized in Table 1.

The Preparation of Biferrocene (3) and 1,1′-Biferrocenylene (8). To a solution of 10 mmol of lithium chloropalladite in acetonitrile, a 5-mmol portion of **1** was added, after which the mixture was stirred at room temperature for 24 hr under nitrogen. The product was isolated by filtration to remove a precipitated palladium and by distillation under reduced pressure to remove the solvent. The residue was dissolved in hexane-benzene (1 : 1); subsequent chromatography on alumina afforded yellow crystals (mp 236—238 °C, 66% yield), which were identical as biferrocene (**3**) by a comparison of the IR and NMR spectra and by a mixed-melting-point determination with an authentic sample.[8]

1,1′-Biferrocenylene (**8**) (mp 370 °C, 48% yield) was also obtained from the reaction of 10 mmol of lithium chloropalladite and 2.5 mmol of **2** in a manner similar to that used for **3**.

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