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The Reaction of *ortho*-Palladated Ferrocene Complexes with Olefins

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Synopsis. *ortho*-Palladation products of (dimethylaminomethyl)ferrocene and 2-pyridylferrocene were treated with various olefins under mild conditions. A variety of unusual 1,2-disubstituted ferrocene derivatives were obtained from these reactions.

Following the first report that a palladium-carbon bond is formed directly upon the reaction of palladium(II) salt with azobenzene,[1] considerable interest developed in this area.[2] The *ortho*-palladation reaction is ideally suited for use in the synthesis of *ortho*-disubstituted compounds, since the metalated complexes can be made directly from monosubstituted aromatics. Previously, for example, the reactions of *ortho*-palladation products from numerous α-aryl nitrogen derivatives with carbon monoxide,[3,4] halogen,[5] alkyllithium or a Grignard reagent,[6] and olefins[7-9] have been reported. Furthermore, we ourselves have reported the reactions of an *ortho*-palladated complex of 2-pyridylferrocene with carbon monoxide, alkyllithium, and bromine.[10] In this report, we wish to report on the reactions of various olefins with *ortho*-palladated ferrocenyl derivatives: di-μ-chloro-bis[2-(dimethylaminomethyl)ferrocenyl]dipalladium(II) (**1**) and di-μ-chloro-bis[2-(2-pyridyl)ferrocenyl]dipalladium(II) (**2**).

Tsuji[7] has previously reported that the reaction of the *ortho*-palladated *N*,*N*-dimethylbenzylamine complex with styrene in acetic acid led to the formation of the arylated styrene derivative. Holton[9] has also reported the reaction of *ortho*-palladated benzylamine-type complexes with enones in the presence of triethylamine. The attempted reaction of olefin with **1** in acetic acid was unsuccessful even at 100 °C. On the other hand, in the presence of triethylamine, the **1** complex reacted with simple olefins, such as styrene, ethyl acrylate, methyl methacrylate, acrylonitrile, methyl vinyl ketone, and phenyl vinyl ketone, in toluene at 100 °C, leading to the formation of 1-dimethylaminomethyl-2-alkenyl ferrocene (**3**—**8**) in moderate yields. Compounds **3**—**8** exhibited absorptions near 1100, 1000, and 910 cm^{-1} characteristic of homoannularly 1,2-disubstituted ferrocene derivatives.[11] Moreover, the NMR and mass spectra of Compounds **3**—**8** were all consistent with the proposed structures. Complex **2**, similarly, reacted with olefins, such as methyl vinyl ketone and phenyl vinyl ketone, to afford the substitution products (**9** and **10**). The order of the reactivity of the complexes with olefin is **1**>**2**. The reactions carried out are summarized in Table 1, while the properties of the products are given in Table 2.

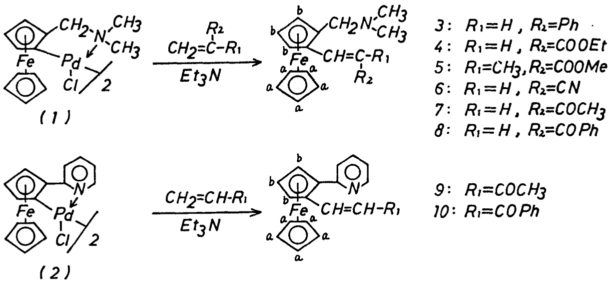

Fig. 1.

Experimental

Materials. The following compounds were synthesized by the methods described in the literature: di-μ-chloro-bis[2-(dimethylaminomethyl)ferrocenyl]dipalladium(II) (**1**)[12] and di-μ-chloro-bis[2-(2-pyridyl)ferrocenyl]dipalladium(II) (**2**).[10]

General Procedure for the Reaction of a Complex with Olefins. A mixture of 2 mmol of a complex (**1** or **2**), 5 mmol of olefin, and 0.29 g (5 mmol) of triethylamine in toluene (40 ml) was heated at 100 °C under a nitrogen atmosphere. The reaction mixture was then cooled and filtered to remove the precipitated palladium, 100 ml of toluene was added, and the mixture was washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was then purified by column chromatography (Al_2O_3–benzene or chloroform). The structure of the products

TABLE 1. REACTIONS OF *ortho*-PALLADATED FERROCENYL COMPLEXES WITH OLEFINS

Complex	olefin	Reaction time (h)	Product	Yield[a]
1	Styrene	5	1-Dimethylaminomethyl-2-styrylferrocene (**3**)	33
1	Ethyl acrylate	5	1-Dimethylaminomethyl-2-(2-ethoxycarbonylvinyl)ferrocene (**4**)	55
1	Methyl methacrylate	5	1-Dimethylaminomethyl-2-(2-methoxycarbonyl-2-methylvinyl)-ferrocene (**5**)	28
1	Acrylonitrile	5	1-(2-Cyanovinyl)-2-(dimethylaminomethyl)ferrocene (**6**)	30
1	Methyl vinyl ketone	5	1-(2-Acetylvinyl)-2-(dimethylaminomethyl)ferrocene (**7**)	27
1	Phenyl vinyl ketone	5	1-(2-Benzoylvinyl)-2-(dimethylaminomethyl)ferrocene (**8**)	59
2	Methyl vinyl ketone	19	1-(2-Acetylvinyl)-2-(2-pyridyl)ferrocene (**9**)	8
2	Phenyl vinyl ketone	12	1-(2-Benzoylvinyl)-2-(2-pyridyl)ferrocene (**10**)	20

a) The yields are based upon Complex **1** or **2**.

Table 2. Properties and analyses of reaction products[a)]

Compound	
3	Heavy, reddish-brown oil. Found: C, 72.87; H, 6.56; N, 3.91%; M$^+$, 345. Calcd for $C_{21}H_{23}FeN$; C, 73.05; H, 6.71; N, 4.05%; mol wt, 345. IR: 1100, 1000, 915 (1,2-disubstituted ferrocene); 1630, 960 (*trans* -CH=CH-); 1600, 1500, 745, 690 cm^{-1} (phenyl). NMR: δ 2.25 (s, 6H, -N(**CH**$_3$)$_2$), 3.34 (d-d, 2H, -**CH**$_2$N-:), 4.10 (s, 5H, **H**$_a$), 4.40 (m, 3H, **H**$_b$), 6.72 (d, J=12 Hz, 1H, -C=**CH**-Ph), 7.11—7.28 ppm (m, 6H,-**CH**=C-Ph+phenyl protons).
4	Heavy, reddish-brown oil. Found: C, 63.51; H, 6.88; N, 4.25% M$^+$, 341. Calcd for $C_{18}H_{23}FeNO_2$:C, 63.38; H, 6.75; N, 4.18%; mol wt, 341. IR: 1710 (ester); 1100, 1000, 910 (1,2-disubstituted ferrocene); 1625, 960 cm^{-1} (*trans* -CH=CH-). NMR: δ 1.23 (t, 3H, -COOCH$_2$-**CH**$_3$), 2.09 (s, 6H, -N(**CH**$_3$)$_2$), 3.29 (d-d, 2H, -**CH**$_2$N-), 3.99 (s, 5H, **H**$_a$), 4.11 (q, 2H, -CO-O**CH**$_2$CH$_3$), 4.33 (m, 3H, **H**$_b$), 5.95 (d, J=14 Hz, 1H, -C=**CH**-COOEt), 7.53 ppm (d, J=14 Hz, 1H, Fc-**CH**=C-).
5	Heavy, reddish brown oil. Found: C, 63.44; H, 6.85; N, 4.20%; M$^+$, 341. Calcd for $C_{18}H_{23}FeNO_2$: C, 63.38; H, 6.75; N, 4.18%; mol wt, 341. IR: 1710 (ester); 1100, 1000, 915 (1,2-disubstituted ferrocene); 1620, 810 cm^{-1} (-C=CH-). NMR: δ 1.93 (d, 3H, -CH=C(**CH**$_3$)-), 2.04 (s, 6H, -N(**CH**$_3$)$_2$), 3.24 (d-d, 2H, -**CH**$_2$N-), 3.69 (s, 3H, -COO**CH**$_3$), 3.98 (s, 5H, **H**$_a$), 4.30 (m, 3H, **H**$_b$), 7.44 ppm (q, 1H, Fc-**CH**=C-).
6	Heavy, reddish oil. Found: C, 65.27; H, 6.03; N, 9.43%; M$^+$, 294. Calcd for $C_{16}H_{18}FeN_2$: C, 65.35; H, 6.12; N, 9.52%; mol wt, 294. IR: 2200 (-CN); 1610, 955 (*trans* -CH= CH-), 1100, 1000, 910 (1,2-disubstituted ferrocene). NMR: δ 2.13 (s, 6H, -N(**CH**$_3$)$_2$), 3.33 (d-d, 2H, -**CH**$_2$N-), 4.08 (s, 5H, **H**$_a$), 442 (m, 3H, **H**$_b$), 5.13 (d, J=12 Hz, 1H, -C=**CH**-CN), 7.07 ppm (d, J=12 Hz, 1H, Fc-**CH**=C-).
7	Heavy, reddish-brown oil. Found: C, 65.58; H, 6.69; N, 4.41%; M$^+$, 311. Calcd for $C_{17}H_{21}FeNO$: C, 65.63; H, 6.75; N, 4.50%; mol wt, 311. IR: 1660 (C=O); 1610, 960 (*trans* -CH=CH-); 1100, 1000, 910 cm^{-1} (1,2-disubstituted ferrocene). NMR: δ 2.07 (s, 6H, -N(**CH**$_3$)$_2$), 2.19 (s, 3H, -CO**CH**$_3$), 3.33 (d-d, 2H, -**CH**$_2$N-), 4.00 (s, 5H, **H**$_a$), 4.40 (m, 3H, **H**$_b$), 6.27 (d, J=12 Hz, 1H, -C=**CH**-CO-), 7.40 ppm (d, J=12 Hz, 1H, Fc-**CH**=C-).
8	Heavy, reddish-brown oil. Found: C, 70.68; H, 6.08; N, 3.70%; M$^+$, 373. Calcd for $C_{22}H_{23}FeNO$: C, 70.81; H, 6.16; N, 3.75%; mol wt, 373. IR: 1660 (C=O); 1610, 965 (*trans* -CH=CH-); 1100, 1010, 910 (1,2-disubstituted ferrocene); 1600, 1500, 745, 690 cm^{-1} (phenyl). NMR: δ 2.15 (s, 6H, -N(**CH**$_3$)$_2$), 3.43 (d-d, 2H, -**CH**$_2$N-), 4.08 (s, 5H, **H**$_a$), 4.56 (m, 3H, **H**$_b$), 7.08 (d, J=12 Hz, -C=**CH**-CO-), 7.28 (broad s, 5H, phenyl protons), 7.82 ppm (d, J=12 Hz, 1H, -**CH**=C-CO-).
9	Heavy, reddish brown oil. Found: C, 68.81; H, 5.06; N, 4.21%; M$^+$, 331. Calcd for $C_{19}H_{17}FeNO$: C, 68.92; H, 5.13; N, 4.23%; mol wt, 331. IR: 1660 (C=O); 1610, 960 (*trans* -CH=CH-); 1100, 1005, 915 cm^{-1} (1,2-disubstituted ferrocene). NMR: δ 2.31 (s, 3H, -CO-**CH**$_3$), 4.00 (s, 5H, **H**$_a$), 4.56 (m, 3H, **H**$_b$), 6.27 (d, J=12 Hz, 1H, -C=**CH**-CO-), 7.19 (d, J=12 Hz, 1H, Fc-**CH**=C-), 7.31—8.39 ppm (m, 4H, pyridyl protons).
10	Reddish crystals, mp 149—150°C. Found: C, 73.39; H, 4.88; N, 3.53%; M$^+$, 393. Calcd for $C_{24}H_{19}FeNO$: C, 73.31; H, 4.83; N, 3.56%; mol wt, 393. IR: 1655 (C=O); 1630, 960 (*trans* -CH=CH-); 1100, 1000, 910 (1,2-disubstituted ferrocene); 1600, 1500, 745, 690 cm^{-1} (phenyl). NMR: δ 4.02 (s, 5H, **H**$_a$), 4.68 (m, 3H, **H**$_b$), 6.98 (d, J=12 Hz, 1H, -C=**CH**-CO-), 7.18—8.13 ppm (m, 10H, Fc-**CH**=C-+phenyl and pyridyl protons).

a) The IR and mass spectra were measured using a Hitachi 215 spectrophotometer and a Model RMU-6M mass spectrometer at 70 eV. The NMR spectra were observed in $CDCl_3$ on a Hitachi Model R-22 (90 MHz), using TMS as the internal standard (δ, ppm). The chemical shifts were followed by means of the splitting pattern (s, singlet; d, doublet; d-d, double doublet; t, triplet; q, quartet; m, multiplet) and the relative strengths.

was confirmed by an elemental analysis and by the observation of the IR, NMR, and mass spectra. The results are summarized in Tables 1 and 2.

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