

The σ -Bonded Palladium(II) Complex of 2-Pyridylferrocene

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2-Pyridylferrocene reacts with lithium tetrachloropalladate(II) in the presence of sodium acetate to give an *ortho*-palladated binuclear complex (**4**). The σ -bonded structure of **4** was confirmed by studies of the IR and NMR spectra and of the reactions of **4** with thallium(I) acetylacetonate and lithium aluminum deuteride. The reactions of **4** with carbon monoxide, butyllithium, and bromine were also examined.

Following the first report of the intramolecular *ortho*-palladation of azobenzene and *N,N*-dimethylbenzylamine¹⁾ there has been considerable interest in the intramolecular *ortho*-metalation of nitrogen, phosphorus, and sulfur donor ligands by transition metals.²⁾ With reference to the *ortho*-metalation, Alper³⁾ reported the first example of the intramolecular *ortho*-palladation of a metallocene by the reaction of thiopivaloylferrocene with sodium tetrachloropalladate(II); Gaunt and Shaw⁴⁾ also described the intramolecular *ortho*-palladation of (dimethylaminomethyl)ferrocene. One might, therefore, expect that 2-pyridylferrocene (**1**) would undergo palladation very readily, since it is well known that a ring in ferrocene is much more susceptible to electrophilic attack than a benzene ring.⁵⁾ In this report, we wish to report on the intramolecular *ortho*-palladation of **1** and the reaction of the metalation product with various reagents.

Results and Discussion

The treatment of **1** in methanol or dioxane with lithium tetrachloropalladate(II) gave dichlorobis(2-pyridylferrocene)palladium(II) (**2**) containing the unpalladated ligand. The **2** structure was consistent with the results of the elemental analysis and the IR spectrum of the compound. Rosenblum and Howells⁶⁾ have previously suggested that the IR spectra may serve to define the structures of homoannularly-disubstituted ferrocene derivatives; the 1,2-isomer possesses one band near 917 cm^{-1} . Compound **2** exhibited no absorption near 917 cm^{-1} . Furthermore, the reaction of **2** with triphenylphosphine in a ligand-replacement reaction gave a quantitative yield of dichlorobis(triphenylphosphine)palladium(II) (**3**), as identified by comparison with an authentic sample.

On the other hand, when mole equivalents of lithium tetrachloropalladate(II), **1**, and sodium acetate trihydrate were stirred together in methanol, a new complex (**4**) was obtained. On the basis of the microanalytical and spectroscopic data, the molecular weight, and the reactions, **4** was shown to be an intramolecularly *ortho*-palladated complex. It has previously been shown that the acetate ion promoted an internal metalation reaction.⁷⁾ The **4** complex shows reactions typical of a chlorine-bridged binuclear complex of palladium; the reactions with thallium(I) acetylacetonate and triphenylphosphine produce the monomeric acetylacetonate (**5**) and triphenylphosphine (**6**) derivatives respectively. The IR spectra of the ferrocene derivatives prepared in this study are recorded in Table 1. Compounds **4**, **5**, and **6** exhibited absorptions near 1100, 1000, and

910 cm^{-1} characteristic of homoannularly 1,2-disubstituted ferrocene derivatives.⁶⁾ In addition, in the far-infrared spectrum of **4** there are three bands, assigned to bridged Pd-Cl stretching absorptions at 317, 296, and 255 cm^{-1} . Presumably the band at 296 cm^{-1} is due to a solid-state effect. The lithium aluminum hydride reduction of **4** gave **1**, whose mass spectrum was identical with that of an authentic sample. On the other hand, the lithium aluminum deuteride reduction of **4** gave 1-(2-pyridyl)ferrocene-2- d_1 (**7**). The position of the deuterium and, therefore, the site of the carbon-to-palladium σ -bond were established by a comparison of the NMR spectrum of **7** with that of the undeuterated **1**. The above evidence established that a σ -bond has been formed between the palladium and the ferrocene moiety.

Recently, the reactions of *ortho*-palladation products from numerous α -arylnitrogen derivatives with carbon monoxide,^{8,9)} chlorine,¹⁰⁾ and alkyllithium or a Grignard reagent^{11,12)} have been reported. The carbonylation of *ortho*-palladation products of azobenzene, Schiff bases, and tertiary benzylamines usually gives a variety of heterocyclic compounds.^{8,9)} The attempted carbonylation of the **4** complex in ethanol was unsuccessful, even at 100 °C; however, the triphenylphosphine derivative, **6**, in ethanol was readily carbonylated at 100 °C to produce an uncyclized ester, 2-ethoxycarbonyl-1-(2-pyridyl)ferrocene (**8**), in a 37% yield. The **6** complex was also smoothly brominated in chloroform at room temperature, forming 2-bromo-1-(2-pyridyl)ferrocene (**9**) in a 35% yield. Furthermore, the treatment of **6** with

TABLE 1. THE IR ABSORPTION FREQUENCIES (cm^{-1}) OF 2-PYRIDYLFERROCENE DERIVATIVES

Compound	1100—100 rule	917 rule	Other bands
1	1102, 1002	absent	
2	1104, 1000	absent	344, 336 (terminal Pd-Cl)
4	1100, 1003	910	332, 296, 255 (bridged Pd-Cl)
5	1100, 1009	921, 910	1580, 1550 (Acac group), 1200 (H-C bending of Acac group)
6	1102, 1000	920, 903	315 (terminal Pd-Cl)
7	1105, 1000	absent	
8	1102, 1000	918	1703 (ester group)
9	1100, 1004	920	
10	1105, 1000	915	
11	1100, 1002	908	

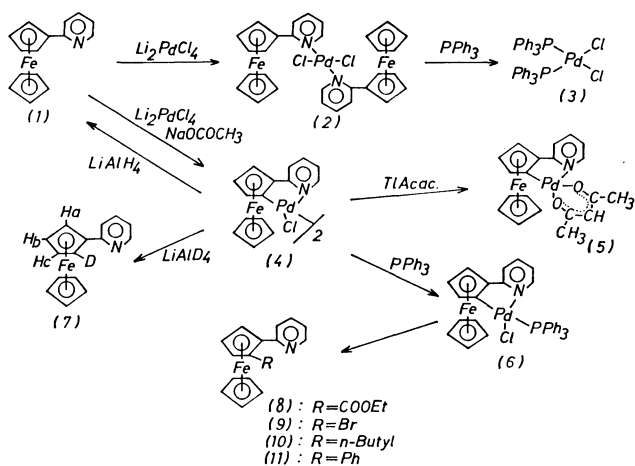


Fig. 1.

butyllithium and phenyllithium gave 2-butyl-1-(2-pyridyl)ferrocene (**10**) (34% yield) and 2-phenyl-1-(2-pyridyl)ferrocene (**11**) (27% yield) respectively. Compounds **8**, **9**, **10**, and **11** exhibit absorptions near 1100, 1000, and 910 cm^{-1} characteristic of homoannularly 1,2-disubstituted ferrocene derivatives.⁶⁾ Moreover, the NMR and mass spectra of the compounds were all consistent with the proposed structures.

Experimental

Materials and Analysis. All the melting points are uncorrected. The 2-pyridylferrocene (**1**) was prepared by the method previously reported.¹³⁾ The IR spectra were measured on KBr disks (4000–650 cm^{-1}) or in Nujol mulls mounted on thin polythene windows (700–200 cm^{-1}), using Hitachi 215 and EPI-L spectrometers. The NMR spectra were taken in CDCl_3 with TMS as the standard and were recorded with a Hitachi R-22 spectrometer at 90 MHz. The mass spectra were obtained with a Hitachi RMU-6M mass spectrometer, using a direct inlet and an ionization energy of 70 eV. The molecular weight was determined in CHCl_3 , using a Hitachi 115 vapor-pressure osmometer.

Dichlorobis(2-pyridylferrocene)palladium(II) (2). A solution of 1.31 g (5 mmol) of lithium tetrachloropalladate(II) in 30 ml of methanol or 30 ml of a mixture of dioxane and water (1 : 1) was stirred drop by drop at room temperature, into a solution of 1.31 g (5 mmol) of **1** in 20 ml of methanol or dioxane. The brownish precipitate which formed immediately was filtered and washed successively with several portions of water and then ether. The solid (3.4 g, 97% yield) was insoluble in all common solvents; mp 185–190 °C (dec). Found: C, 51.02; H, 3.56; N, 3.77%. Calcd for $\text{C}_{30}\text{H}_{26}\text{Cl}_2\text{Fe}_2\text{N}_2\text{Pd}$: C, 51.21; H, 3.72; N, 3.98%.

Ligand-replacement Reaction of 2 with Triphenylphosphine. 0.35 g of **2** and 0.13 g of triphenylphosphine were placed in 15 ml of ethanol, and the mixture was stirred at 80 °C for 24 h. The resultant solid was collected and washed several times with ethanol to give a quantitative yield of dichlorobis(triphenylphosphine)palladium(II) (**3**) (mp 250–260 °C (dec)), whose IR spectrum was identical to that of an authentic sample.¹⁴⁾ The concentration of the filtrate *in vacuo* gave **1** (mp 91–92 °C (lit.¹³⁾ mp 92–93 °C)).

Di-μ-chlorobis[2-(2-pyridyl)ferrocenyl]dipalladium(II) (4). A solution of 1.31 g (5 mmol) of **1** in methanol (30 ml) was added to a mixture of lithium tetrachloropalladate(II) (1.31 g, 5 mmol) and sodium acetate trihydrate (0.68 g, 5 mmol) in

methanol (50 ml). The new mixture was then stirred for 20 h at room temperature, and the reddish precipitate which formed was filtered off and dried (yield: 4.20 g; 99% yield). A portion was recrystallized from chloroform–cyclohexane; mp 240–244 °C (dec). NMR δ : 4.31 (6H, **H_b** + unsubstituted ferrocene ring protons, singlet); 5.14 (1H, **H_a**, multiplet); 5.33 (1H, **H_c**, multiplet); 7.01–8.64 ppm (4H, pyridyl protons, multiplet). Found: C, 44.46; H, 2.87; N, 3.41%; mol wt 786. Calcd for $\text{C}_{30}\text{H}_{24}\text{Cl}_2\text{Fe}_2\text{N}_2\text{Pd}_2$: C, 44.60; H, 2.99; N, 3.46%; mol wt, 808.

Acetylacetonato[2-(2-pyridyl)ferrocenyl]palladium(II) (5).

A solution of thallium(I) acetylacetonate (0.30 g, 1 mmol) and the **4** complex (0.40 g, 0.5 mmol) in benzene (20 ml) was stirred for 24 h at room temperature and then filtered. The filtrate was then evaporated under reduced pressure, giving a red oil. After purification by column chromatography on silica gel (benzene), the product, **5**, was obtained as orange prisms from hexane–benzene; mp 151–152 °C, NMR δ : 2.06 (6H, CH_3 of acac group, singlet); 4.18 (5H, unsubstituted ferrocene ring protons, singlet); 4.40 (1H, **H_b**, double-doublet); 4.63 (1H, **H_a**, doublet); 4.76 (1H, **H_c**, doublet); 5.41 (1H, **H-C** of acac group, singlet); 6.97–8.70 ppm (4H, pyridyl protons, multiplet). Found: C, 51.25; H, 3.97; N, 2.91%; M^+ , 467. Calcd for $\text{C}_{20}\text{H}_{19}\text{FeNO}_2\text{Pd}$: C, 51.37; H, 4.09; N, 2.99%; M , 467.

Chloro[2-(2-pyridyl)ferrocenyl](triphenylphosphine)palladium(II) (6).

Triphenylphosphine (0.26 g, 1 mmol) and the **4** complex (0.40 g, 0.5 mmol) were dissolved in benzene (20 ml), and then the mixture was stirred for 4 h. The solvent was removed under reduced pressure, and the product (0.60 g, 90% yield) was obtained as orange plates from ethanol; mp 136–138 °C (dec). Found: C, 59.25; H, 3.96; N, 2.03%; mol wt, 654 (in CHCl_3). Calcd for $\text{C}_{33}\text{H}_{27}\text{ClFeNPPd}$: C, 59.49; H, 4.07; N, 2.12%; mol wt, 666.

Reduction of the 4 Complex with Lithium Aluminum Hydride.

Lithium aluminum hydride (0.02 g, 0.5 mmol) in anhydrous ether (50 ml) was slowly added to a solution of the **4** complex (0.4 g, 0.5 mmol) in anhydrous ether (50 ml). The resulting black mixture was stirred at room temperature for 4 h; then water (10 ml) was added with cooling. The ether layer was washed with water and dried over anhydrous magnesium sulfate. After the removal of the solvent, **1** was obtained as reddish plates from benzene–cyclohexane; mp 91–92 °C (lit.¹³⁾ mp 92–93 °C). NMR δ : 4.07 (5H, unsubstituted ferrocene ring protons, singlet); 4.42 (2H, **H_b**, multiplet); 4.94 (2H, **H_a**, multiplet); 7.01–8.59 ppm (4H, pyridyl protons, multiplet). MS: M^+ 263. Calcd for $\text{C}_{15}\text{H}_{13}\text{FeN}$: M , 263.

Reduction of the 4 Complex with Lithium Aluminum Deuteride.

The reduction of **4** (0.40 g) in anhydrous ether with lithium aluminum deuteride (0.02 g) was carried out as in the preceding experiment; this gave a product (mp 92–93 °C) which can be identified as 1-(2-pyridyl)ferrocene-2- d_1 (**7**) on the basis of the following evidence: NMR δ : 4.07 (5H, unsubstituted ferrocene ring protons, singlet); 4.42 (2H, **H_b**, multiplet); 4.92 (1H, **H_a**, multiplet); 7.00–8.60 ppm (4H, pyridyl protons, multiplet). Found: C, 68.05; H, 5.31; N, 5.19%; M^+ , 264. Calcd for $\text{C}_{15}\text{H}_{12}\text{DFeN}$: C, 68.13; H, 5.38; N, 5.30%; M , 264.

Carbonylation of the 6 Complex in Ethanol.

In ethanol (50 ml), the **6** complex (3.33 g, 5 mmol) was carbonylated at 100 °C under a carbon monoxide pressure of 80 atm for 10 h with shaking. The product was then isolated by filtering to remove a precipitated palladium and distilling under reduced pressure to remove the solvent. The residue was dissolved in chloroform and chromatographed on silica gel to afford red crystals (0.62 g; 37% yield), which can be identified as 2-ethoxycarbonyl-1-(2-pyridyl)ferrocene (**8**); mp 108

—110 °C. NMR δ : 1.21 (3H, CH_3 of ester group, triplet); 4.29 (5H, unsubstituted ferrocene ring protons, singlet); 4.40 (3H, $\text{H}_b + \text{CH}_2$ of ester group, multiplet); 4.68 (1H, H_a , multiplet); 4.87 (1H, H_c , multiplet); 7.06—8.74 ppm (4H, pyridyl protons, multiplet). Found: C, 64.38; H, 5.06; N, 4.05%; M^+ , 335. Calcd for $\text{C}_{18}\text{H}_{17}\text{FeNO}_2$: C, 64.52; H, 5.11; N, 4.17%; M , 335.

Reaction of the 6 Complex with Bromine. Under a nitrogen atmosphere, bromine (0.90 g, 5 mmol) in chloroform (15 ml) was slowly added in a solution of the 6 complex (3.33 g, 5 mmol) in chloroform (50 ml). After stirring at room temperature for 4 h, the reaction mixture was filtered and the chloroform phase washed several times with water, dried over anhydrous magnesium sulfate, and concentrated. The residue was dissolved in chloroform and chromatographed on silica gel afford reddish crystals (0.60 g; 35% yield), which can be identified as 2-bromo-1-(2-pyridyl)ferrocene (**9**); mp 95—97 °C. NMR δ : 3.70 (5H, unsubstituted ferrocene ring protons); 4.32 (2H, $\text{H}_b + \text{H}_c$, multiplet); 4.85 (1H, H_a , multiplet); 7.16—8.64 ppm (4H, pyridyl protons, multiplet). Found: C, 52.21; H, 4.10; N, 3.89%; M^+ , 344. Calcd for $\text{C}_{18}\text{H}_{12}\text{BrFeN}$: C, 52.37; H, 4.01; 4.07%; M , 344.

Reaction of the 6 Complex with Butyllithium. Under a nitrogen atmosphere, the 6 complex (3.33 g, 5 mmol) in dry benzene (50 ml) was reacted with 10 mmol of butyllithium in ether. After stirring at 50 °C for 8 h, the products were isolated by diluting the cooled reaction mixtures with water and chloroform. The chloroform phase was separated, washed several times with water, dried over anhydrous magnesium sulfate, and concentrated. The residue was dissolved in chloroform and chromatographed on silica gel. The first elution with chloroform afforded red crystals (0.21 g, mp 91—93 °C); they were identified as 2-pyridylferrocene (**1**) by a comparison of the IR and NMR spectra with those of an authentic sample and by a mixed-melting-point determination. The second elution with chloroform afforded a heavy reddish oil (0.54 g, 34% yield) which can be identified as 2-butyl-1-(2-pyridyl)ferrocene (**10**) on the basis of the following evidence: NMR δ : 0.92 (3H, CH_3 of butyl group, triplet), 1.15—1.87 (4H, CH_2 of butyl group, multiplet); 2.80 (2H, ferrocenyl- CH_2 -, triplet); 4.11 (5H, unsubstituted ferrocene ring protons, singlet); 4.38 (2H, $\text{H}_b + \text{H}_c$, multiplet); 4.96 (1H, H_a , multiplet); 6.80—8.60 ppm (4H, pyridyl pro-

tons, multiplet). Found: C, 71.28; H, 6.55; N, 4.26%; M^+ , 319. Calcd for $\text{C}_{19}\text{H}_{21}\text{FeN}$: C, 71.49; H, 6.63; N, 4.38%; M , 319.

Reaction of the 6 Complex with Phenyllithium. The reaction of **6** (3.33 g, 5 mmol) with 10 mmol of phenyllithium in ether was carried out as in the preceding experiment; it gave a product (0.46 g, yield, 27%) which can be identified as 2-phenyl-1-(2-pyridyl)ferrocene (**11**); mp 235 °C (dec). NMR δ : 3.93 (5H, unsubstituted ferrocene ring protons); 4.12 (1H, H_b , multiplet); 4.77 (2H, $\text{H}_a + \text{H}_c$, multiplet); 7.18—8.49 ppm (9H, phenyl and pyridyl protons, multiplet). Found: C, 74.25; H, 4.87; N, 4.03; M^+ , 339. Calcd for $\text{C}_{21}\text{H}_{17}\text{FeN}$: C, 74.40; H, 5.05; N, 4.13; M , 339.

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