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Reaction of Optically Active 1-Dimethylaminoethylferrocene Palladium Complexes

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Synopsis. *ortho*-Palladation products of optically active 1-dimethylaminoethylferrocene were treated with phenyl vinyl ketone and carbon monoxide and a variety of optically active 1,2-disubstituted ferrocene derivatives were obtained.

Recently, the reactions of *ortho*-palladation products from aromatic nitrogen derivatives with various reagents have been reported.[1] The carbonylation of *ortho*-palladation products of azobenzene, Schiff bases, and tertiary benzylamines usually give a variety of heterocyclic compounds.[2] The reaction of *ortho*-palladated benzylamine-type complexes with enones result in the formation of aryl-substituted enone derivatives.[3] On the other hand, it has been reported that stereoselective metallation of optically active α-ferrocenyl tertiary amines produce lithio amines with a high degree of asymmetric induction.[4] Sokolov *et al.*[5] described the *ortho*-palladation of optically active 1-dimethylaminoethylferrocene [(+)-**1** and (−)-**1**] with sodium tetrachloropalladate(II) in methanol in the presence of sodium acetate and found it to proceed with moderate stereoselectivity. For example, the *ortho*-palladation of (+)-**1** with sodium tetrachloropalladate(II) produced a mixture of two diastereoisomers [(−)-**2a** (major product) and (+)-**2b** (minor product)].[5a] The *ortho*-palladation products [(+)-**3a** and (−)-**3b**] were similarly obtained from (−)-**1**.[5b] In this paper, the reactions of optically active dimeric 2-chloropalladio-1-(1′-dimethylaminoethyl) ferrocene [(−)-**2a** and (+)-**3a**] with phenyl vinyl ketone and carbon monoxide, affording optically active 1,2-disubstituted ferrocene derivatives with a plane of chirality will be reported.

In the presence of triethylamine, the (−)-**2a** complex reacted with phenyl vinyl ketone in benzene, leading to the formation of (−)-1-(2′-benzoylvinyl)-2-(1″-dimethylaminoethyl)ferrocene (**4**). Treatment of (−)-**4** with methyl iodide resulted in the formation of (−)-1-(2′-benzoylvinyl)-2-vinylferrocene (**5**). In the presence of triphenylphosphine in ethanol, (−)-**2a** was carbonylated under carbon monoxide pressure, affording (+)-1-(1′-dimethylaminoethyl)-2-ethoxycarbonylferrocene (**6**). Elimination of the chiral center from (+)-**6** by the treatment with methyl iodide led to the formation of (+)-1-ethoxycarbonyl-2-vinyl-ferrocene (**7**).

On the other hand, the reaction of the (+)-**3a** complex with phenyl vinyl ketone, gave (+)-1-(2′-benzoylvinyl)-2-(1″-dimethylaminoethyl)ferrocene (**8**), and subsequent elimination of a chiral carbon center of (+)-**8** with methyl iodide afforded (+)-1-(2′-benzoylvinyl)-2-vinylferrocene (**9**). The carbonylation of the (+)-**3a** complex in ethanol also led to the formation of (−)-1-(1′-dimethylaminoethyl)-2-ethoxycarbonylferrocene (**10**), and subsequent treatment with methyl iodide afforded (−)-1-ethoxycarbonyl-2-vinylferrocene (**11**).

The structures of these compounds were identified by elemental analyses, IR, NMR, and MS spectra. There is no rapid interconversion (−)-**2a**⇌(+)-**2b** or (+)-**3a**⇌(−)-**3b**, the reaction of (−)-**2a** or (+)-**3a** with phenyl vinyl ketone is not the stereoselectivity determining process for (−)-**2a**→(−)-**4** or (+)-**3a**→(+)-**8** in the sence of the Curtin-Hammett principle,[6] and the carbonylation of σ-bonded palladium complexes proceeds with retention of configuration.[7] On the basis of the work of Uri,[4c] Sokolov *et al.*[5] suggested (*R*)-(*S*)-configuration to (−)-**2a** (the major product of the direct palladation of (+)-**1**). Consequently, one may assign a (*R*)-(*S*)-configuration to (−)-**4** and (+)-**6**; and *S*-configuration to (−)-**5** and (+)-**7**. It is similarly inferred that (*S*)-(*R*)-configuration to (+)-**3a** (the major product of the palladation of (−)-**1**), (+)-**8**, and (−)-**10**; and *R*-configuration to (+)-**9** and (−)-**11** were assigned.

Experimental

Materials. All melting points are uncorrected. The optically pure (1*R*)-(1*S*)-di-μ-chlorobis[2-(1′-dimethylaminoethyl)ferrocenyl]dipalladium(II) ((−)-**2a**) (mp 146 °C (dec), $[\alpha]_D^{20}$ −435.5° (*c* 0.053, $CHCl_3$)) and (1*S*)-(1*R*)-di-μ-chlorobis[2-(1′-dimethylaminoethyl)ferrocenyl]dipalladium-(II) ((+)-**3a**) (mp 145—146 °C (dec), $[\alpha]_D^{20}$ +438.1° (*c* 0.041, $CHCl_3$)) were synthesized by the methods in the literature.[5]

The Reaction of ortho-*Palladated Complexes with Phenyl Vinyl Ketone.* A mixture of complex ((1*R*)-(1*S*)-**2a** or (1*S*)-(1*R*)-**3a**) (2.0 g; 2.3 mmol), phenyl vinyl ketone (0.6 g; 4.6 mmol), and triethylamine (0.45 g; 4.6 mmol) in benzene (50 ml) was heated at 75 °C under nitrogen. The reaction mixture was then cooled and filtered to remove the precipitated palladium, benzene (100 ml) was added, and the mixture 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).

(1*R*)-(1*S*)-**4**: yield 90%, reddish viscous oil, $[\alpha]_D^{20}$ −1982° (*c*, 0.045, $CHCl_3$). IR: 1660 (C=O), 1600 and 970 (*trans* –CH=CH–), 1100. 1000, and 908 cm^{-1} (1,2-disubstituted Fc ring). NMR: δ 1.44 (d, 3H, $-CH_3$), 2.05 (s, 6H, $-N(CH_3)_2$), 3.85 (q, 1H, –CH–), 4.07, 4.44, and 4.67 (m, 8H, Fc protons), 7.14 (d, 1H, –C=CH–CO–), 7.45 (m, 5H, Ph), and 7.87 ppm (d, 1H, –CH=C–CO–). MS: *m/e* 387 (M^+). Found: C, 70.93; H, 6.58; N, 3.55%. Calcd for $C_{23}H_{25}FeNO$: C, 71.07; H, 6.53; N, 3.61%; mol wt, 387.

(1*S*)-(1*R*)-**8**: yield 92%, reddish viscous oil, $[\alpha]_D^{20}$ +1972° (*c* 0.043, $CHCl_3$). IR: 1660 (C=O), 1600 and 970 (*trans* –CH=CH–), 1100, 1000, and 910 cm^{-1} (1,2-disubstituted Fc ring). NMR: δ 1.45 (d, 3H, $-CH_3$), 2.06 (s, 6H, $-N(CH_3)_2$), 3.85 (q, 1H, –CH–), 4.06, 4.44, and 4.67 (m, 8H, Fc protons), 7.13 (d, 1H, –C=CH–CO–), 7.45 (m, 5H, Ph), and 7.86 ppm (d, 1H, –CH=C–CO–). MS: *m/e* 387 (M^+).

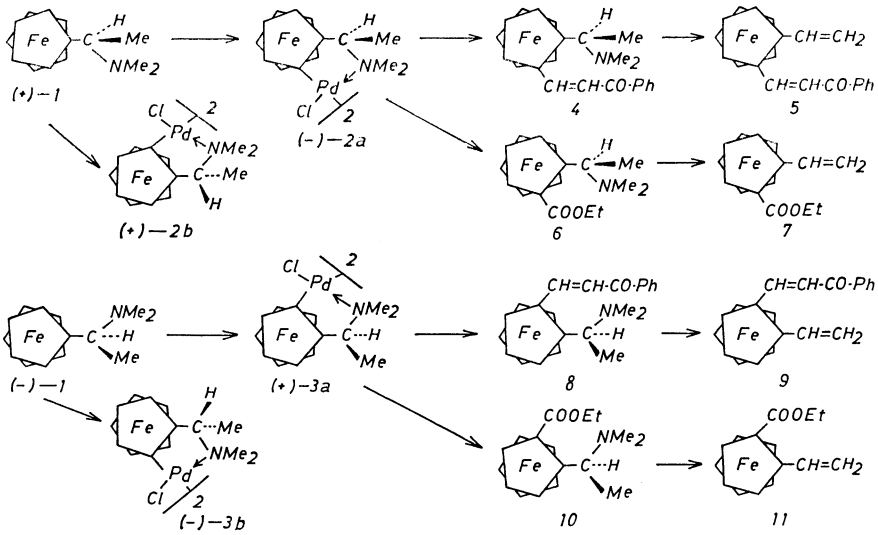

Fig. 1.

Found: C, 71.18; H, 6.55; N, 3.61%. Calcd for $C_{23}H_{25}FeNO$: C, 71.07; H, 6.53; N, 3.61%; mol wt, 387.

*Synthesis of (1S)-**5** and (1R)-**9** Compounds.* In acetone (15 ml), the (1*R*)-(1*S*)-**4** or (1*S*)-(1*R*)-**8** compound (1.00 g), and methyl iodide (10.0 g) were refluxed for 20 min; the solution was then diluted with ether (30 ml), washed with 8% aqueous phosphoric acid and saturated sodium hydrogencarbonate solution, dried over anhydrous magnesium sulfate, and evaporated. The residue was purified by column chromatography (silica gel-benzene).

(*1S*)-**5**: yield 34%, mp 91—92 °C, $[\alpha]_D^{20}$ −2229° (*c* 0.084, $CHCl_3$). IR: 1660 (C=O), 1600 and 980 (*trans* -CH=CH-), 1100, 1000, and 910 (1,2-disubstituted Fc ring), 990 and 900 cm^{-1} (-C=CH_2). NMR: δ 4.08, 4.53, and 4.73 (m, 8H, Fc protons), 5.18 and 5.43 (m, 2H, Fc-C=CH_2), 6.85 (m, 1H, Fc-CH=C-), 7.16 (d, 1H, -C=CH-CO-), 7.45 (m, 5H, Ph), 7.92 ppm (d, 1H, -CH=C-CO-). MS: *m/e* 342 (M^+). Found: C, 73.58: H, 5.22%. Calcd for $C_{21}H_{18}FeO$: C, 73.70; H, 5.30%; mol wt, 342.

(1*R*)-**9**: yield 40%, mp 91—92 °C, $[\alpha]_D^{20}$ +2238° (*c*, 0.082, $CHCl_3$). IR: 1660 (C=O), 1600 and 980 (*trans* -CH=CH-), 1100, 1000, and 910 (1,2-disubstituted Fc ring), 990 and 900 cm^{-1} (-CH=CH_2). NMR: δ 4.08, 4.53, and 4.72 (m, 8H, Fc protons), 5.18 and 5.43 (m, 2H, Fc-C=CH_2), 6.85 (m, 1H, Fc-CH-C-), 7.16 (d, 1H, -C=CH-CO-), 7.45 (m, 5H, Ph), 7.92 ppm (d, 1H, -CH=C-CO-). MS: *m/e* 342 (M^+). Found: C, 73.61; H, 5.18%. Calcd for $C_{21}H_{18}FeO$: C, 73.70; H, 5.30%; mol wt, 342.

*Synthesis of (1R)-(1S)-**6** and (1S)-(1R)-**10**.* In the presence of triphenylphosphine (1.2 g; 4.6 mmol) in ethanol (70 ml), (1*R*)-(1*S*)-**2a** or (1*S*)-(1*R*)-**3a** (2.0 g, 2.3 mmol) was carbonylated with shaking at 100 °C under carbon monoxide at 70 atm for 10 h. The reaction mixture was filtered to remove precipitated palladium and evaporated to dryness and the residue purified by column chromatography (silica gel-benzene).

(1*R*)-(1*S*)-**6**: yield 20%, reddish viscous oil, $[\alpha]_D^{20}$ +141.0° (*c* 0.85, $CHCl_3$). IR: 1705 (ester), 1100, 1000, and 910 cm^{-1} (1,2-disubstituted Fc ring). NMR: δ 1.24 (t, 3H, -O-C-CH_3), 1.35 (d, 3H, -CH_3), 2.08 (s, 6H, -$N(CH_3)_2$), 3.78 (q, 1H, -CH-), 4.22 (q, 2H, -CH_2-), 4.12, 4.52, and 4.84 ppm (m, 8H, Fc protons). MS: *m/e* 329 (M^+). Found: C, 61.93; H, 6.88; N, 4.07%. Calcd for $C_{17}H_{23}FeNO_2$: C, 62.02; H, 7.03; N, 4.25%; mol wt, 329.

(1*S*)-(1*R*)-**10**: yield 25%, reddish viscous oil, $[\alpha]_D^{20}$ −137.0° (*c* 0.85, $CHCl_3$). IR: 1705 (ester), 1100, 1000, and 910 cm^{-1} (1,2-disubstituted Fc ring). NMR: δ 1.24 (t, 3H, -O-C-CH_3), 1.35 (d, 3H, -CH_3), 2.08 (s, 6H, -$N(CH_3)_2$), 3.78 (q, 1H, -CH-), 4.22 (q, 2H, -CH_2-), 4.12, 4.52, and 4.84 ppm (m, 8H, Fc protons). MS: *m/e* 329 (M^+). Found: C, 61.90; H, 6.93; N, 4.11%. Calcd for $C_{17}H_{23}FeNO_2$: C, 62.02; H. 7.03; N, 4.25%; mol wt, 329.

*Synthesis of (1S)-**7** and (1R)-**11**.* In acetone (15 ml), (1*R*)-(1*S*)-**6** or (1*S*)-(1*R*)-**10** (1.00 g), and methyl iodide (10.0 g) were refluxed for 20 min; then the solution was diluted with ether (30 ml), washed with 8% aqueous phosphoric acid and saturated sodium hydrogencarobonate solution, dried over anhydrous magnesium sulfate, and evaporated. The residue was purified by column chromatography (silica gel-benzene).

(1*S*)-**7**: yield 40%, reddish viscous oil, $[\alpha]_D^{20}$ +179.8° (*c* 0.26, $CHCl_3$). IR: 1710 (ester), 1100, 1000, and 910 (1,2-disubstituted Fc ring), 1410, 995, and 900 cm^{-1} (-CH=CH_2). NMR: δ 1.28 (t, 3H, -O-C-CH_3), 4.27 (q, 2H, -CH_2-), 4.13, 4.41, and 4.76 (m, 8H, Fc protons), 5.15 and 5.44 (m, 2H, Fc-C-CH_2), and 7.23 ppm (m, 1H, Fc-CH=C-). MS: *m/e* 284 (M^+). Found: C, 63.33; H, 5.58%. Calcd for $C_{15}H_{16}FeO_2$: C, 63.40; H, 5.67%; mol wt, 284.

(1*R*)-**11**: yield 35%, reddish viscous oil, $[\alpha]_D^{20}$ −175.5° (*c* 0.182, $CHCl_3$). IR: 1710 (ester), 1100, 1000, and 910 (1,2-disubstituted Fc ring), 1410, 995, and 900 cm^{-1} (-CH=CH_2). NMR: δ 1.28 (t, 3H, -O-C-CH_3), 4.27 (q, 2H, -CH_2-), 4.13, 4.41, and 4.75 (m, 8H, Fc protons), 5.15 and 5.44 (m, 2H, Fc-C-CH_2), and 7.23 ppm (m, 1H, Fc-CH=C-). MS: *m/e* 284 (M^+), Found: C, 63.26; H, 5.61%. Calcd for $C_{15}H_{16}FeO_2$: C, 63.40; H, 5.67%; mol wt, 284.

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