The σ-Bonded Palladium(II) Complex of (Dimethylaminomethyl)ruthenocene

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The reaction between (dimethylaminomethyl)ruthenocene with lithium tetrachloropalladate(II) in the presence of sodium acetate gave di-μ-chloro-bis[2-(dimethylaminomethyl)ruthenocenyl]dipalladium(II) (**2**). The σ-bonded structure of **2** has been confirmed by IR analysis and the reactions of **2** with triphenylphosphine, thallium(I) acetylacetonate, and lithium aluminum deuteride. The reactions of chloro[2-(dimethylaminomethyl)ruthenocenyl](triphenylphosphine)palladium(II) with carbon monoxide and **2** with methyl vinyl ketone, phenyl vinyl ketone, and styrene have been examined. 1,2-Disubstituted ruthenocene derivatives have been obtained in higher yields than those of the corresponding ferrocene derivatives.

Cope has reported the first intramolecular *ortho*-palladation of azobenzene[1] and *N*,*N*-dimethylbenzylamine.[2] For the regioselective syntheses of *ortho*-substituted aromatic compounds, there has been considerable interest in the intramolecular *ortho*-metalation by transition metals of aromatic compounds containing donor ligands such as nitrogen, phosphorus and sulfur.[3] In addition, the reactions of ferrocene derivatives with palladium(II) halides have been studied.[4] Generally, there have been few synthetic investigations of the ruthenocenes in contrast to those of the ferrocenes. This paper will deal with the intramolecular *ortho*-palladation of (dimethylaminomethyl)ruthenocene and the reactions of the palladium complexes.

Results and Discussion

The reaction between (dimethylaminomethyl)ruthenocene (**1**) with lithium tetrachloropalladate(II) in the presence of sodium acetate[5] gave di-μ-chlorobis[2-(dimethylaminomethyl)ruthernocenyl]dipalladium(II) (**2**) in 78% yield. The complex **2** was shown to be an intramolecularly *ortho*-palladated complex on the basis of the reactions of **2** and the microanalytical and spectroscopic results. Measurement of the molecular weight using a vapor pressure osmometer was not conducted because of the low solubility of **2** in all common solvents. The treatment of **2** with triphenylphosphine and thallium(I) acetylacetonate afforded the monomeric triphenylphosphine (**3**) and acetylacetonate (**4**) complexes, respectively (Fig. 1). In the IR spectrum of **2**, the three bands at 323, 258, and 216 cm^{-1} have been assigned to the bridged Pd–Cl stretching absorption.[6] The single band at 357 cm^{-1} of **3** has been assigned to the terminal Pd–Cl stretching absorption. Thus, it has been confirmed that **2** is a typical chlorine-bridged binuclear complex. The low solubility of **2** in all common solvents precluded any NMR studies at room temperature. However, the ^{1}H NMR spectra of **3** and **4** clearly demonstrated that a palladium-carbon σ bond and a palladium-nitrogen coordinated bond existed in these complexes (Table 1). *N*-Methyl and *N*-methylene protons of **1** appear as a singlet, whereas the *N*-methyl protons appear as two broad singlets and the *N*-methylene protons as two doublets in **3** and **4**. The nonequivalence of the *N*-methyl and *N*-methylene protons in **3** and **4** can be explained in terms of a cyclic system in which the nitrogen is coordinated to the palladium and a palladium-carbon σ bond is involved.[7] To ascertain the formation of the σ-bond between pal-

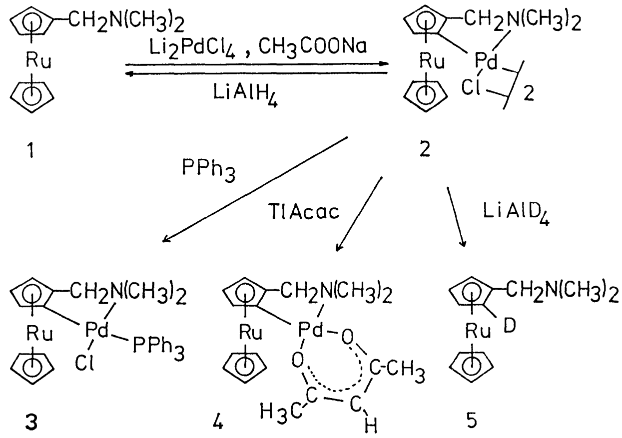

Fig. 1. Syntheses of palladium(II) complexes.

Table 1. The ^{1}H NMR spectra of complexes **3** and **4** (δ)

Compound	-N-CH$_3$	Rc-CH$_2$-N-	Ruthenocene ring proton	Others
Pd complex (**3**)	2.97(br s)[b] 3.07(br s)	3.74(d)[c,e] 4.02(d)[e]	4.3—4.4(m)[d]	7.2—7.7(m) PPh$_3$
Pd complex (**4**)	2.82(s)[a] 3.02(s)	3.13(d)[f] 3.52(d)[f]	4.3—4.7(m)	1.91(s) CH$_3$ of acac group 5.21(s) -CH- of acac group
(Dimethylaminomethyl)-ruthenocene (**1**)	2.20(s)	3.10(s)	4.5—4.6(m)	

a) Singlet. b) Broad singlet. c) Doublet. d) Multiplet. e) J=1.8 Hz. f) J=7.8 Hz.

Table 2. The ^{1}H NMR spectra of 1,2-disubstituted ruthenocenes (δ)

Ruthenocene	-N-CH$_3$	Rc-CH$_2$-N-	Ruthenocene ring proton	Others
1-(2-Acetylvinyl)- 2-(dimethylaminomethyl)- (**6**)	2.15(s)[a]	3.08(d)[b] 3.37(d) (J=14 Hz)	H$_a$ 4.70(m)[d] H$_b$ 4.92(m) H$_c$ 4.70(m) H$_d$ 4.45(s)	2.18(s, -COCH$_3$) 6.32(d, J=16 Hz, -C=CH-CO-) 7.40(d, J=16 Hz, Rc-CH=C-CO-)
1-(2-Benzoylvinyl)- 2-(dimethylaminomethyl)- (**7**)	2.16(s)	3.09(d) 3.42(d) (J=13 Hz)	H$_a$ 4.71(m) H$_b$ 4.98(m) H$_c$ 4.71(m) H$_d$ 4.45(s)	7.16(d, J=16 Hz, -C=CH-CO-) 7.51(d, J=16 Hz, Rc-CH=C-CO-) 7.3—8.0(m, Ph)
1-(Dimethylaminomethyl)- 2-styryl- (**8**)	2.18(s)	3.12(d) 3.39(d) (J=13 Hz)	H$_a$ 4.60(m) H$_b$ 4.91(m) H$_c$ 4.60(m) H$_d$ 4.43(s)	6.63(d, J=16 Hz, -C=CH-Ph) 6.85(d, J=16 Hz, Rc-CH=C-Ph) 7.1—7.3(m, Ph)
1-(Dimethylaminomethyl)- 2-(ethoxycarbonyl)- (**9**)	2.4—3.1(m)		H$_a$ 4.85(m) H$_b$ 5.18(m) H$_c$ 4.85(m) H$_d$ 4.60(s)	1.25(t[c]), J=6 Hz, CH$_3$ of COOEt) 2.4—3.1(m, -CH$_2$- of COOEt)

a) Singlet. b) Doublet. c) Triplet. d) Multiplet.

ladium and the cyclopentadienyl ring in **2**, **3**, and **4**, **2** was reduced with lithium aluminum deuteride to give 1-(dimethylaminomethyl)ruthenocene-2-*d* (**5**) quantitatively. Again, the starting material (**1**) was obtained by the lithium aluminum hydride reduction of **2**. The presence of deuterium in **5** was established by a comparison of the ^{1}H NMR and mass spectra of **5** with those of the undeuterated sample (**1**). The intramolecular palladation of α-aryl nitrogen derivatives gave the *ortho*-palladated complexes.[3,4] It appears therefore that the deuterium exists at the *ortho*-position of the dimethylaminomethyl group in **5**.

The evidence indicates a five-membered chelate-ring exists between palladium and the ruthenocene moiety in **2**, **3**, and **4**. A simple model for **2**, **3**, and **4** suggests that the chelate-ring may be five-membered rather than six-membered. This conclusion has been unambiguously supported by the reactions of **2** and **3** with various reagents (Fig. 2). The reactions of *ortho*-palladation products from numerous α-aryl nitrogen derivatives with carbon monoxide,[8] halogens,[9] alkyllithium,[10] Grignard reagents,[10] and olefins[11] have been reported. Recently, the *ortho*-palladation complexes of ferrocene derivatives have been converted into a variety of 1,2-disubstituted ferrocenes.[4,12] Complexes **2** and **3** failed to react with bromine or butyllithium. However, **2** reacted with methyl vinyl ketone, phenyl vinyl ketone and styrene in the presence of triethylamine to readily give 1-alkenyl-2-(dimethylaminomethyl)ruthenocenes (**6**, **7**, **8**) in 89—94% yields. The yields of these ruthenocene derivatives were higher than those of the corresponding ferrocene derivatives.[12] 1-(Dimethylaminomethyl)-2-(ethoxycarbonyl)ruthenocene (**9**) was obtained by the carbonylation of **3** in ethanol; the carbonylation of **2** was unsuccessful. The ^{1}H NMR, IR, and mass spectra of these products were all consistent with those of the proposed structures.

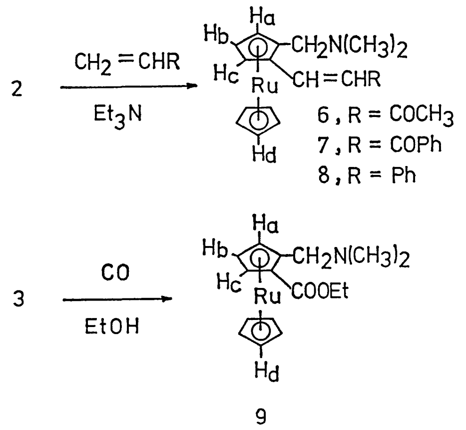

Fig. 2. Reactions of palladium(II) complexes.

1,2-Disubstituted ferrocenes exhibited one peak, while the 1,3-isomers showed two peaks in the region near 900 cm^{-1}, as the characteristic absorption band of

Table 3. Properties and analyses of 1,2-disubstituted ruthenocenes (**6**—**9**)

6	Pale yellow oil. Found: C, 57.18; H, 5.80; N, 3.74%. Calcd for $C_{17}H_{21}NORu$: C, 57.40; H, 5.92; N, 3.91%; mol wt, 356. IR(Nujol): 1655 (C=O); 1615, 965 cm^{-1} (*trans* -CH=CH-). MS: M$^+$ 356.
7	Pale yellow heavy oil. Found: C, 63.28; H, 5.41; N, 3.16%. Calcd for $C_{22}H_{23}NORu$: C, 63.52; H, 5.53; N, 3.34%; mol wt, 418. IR(Nujol): 1660 (C=O); 1605, 965 cm^{-1} (*trans* -CH=CH-). MS: M$^+$ 418.
8	Pale yellow oil. Found: C, 64.22: H, 4.80; N, 3.37%. Calcd for $C_{21}H_{23}NRu$: C, 64.59; H, 4.93; N, 3.58%; mol wt, 390. IR(Nujol): 1625, 955 cm^{-1} (*trans* -CH=CH-). MS: M$^+$ 390.
9	Pale yellow oil. Found: C, 53.15; H, 5.71: N, 3.66%. Calcd for $C_{16}H_{21}NO_2Ru$: C, 53.32; H, 5.87; N, 3.88%; mol wt, 360. IR(Nujol): 1715 cm^{-1} (COOEt). MS: M$^+$ 360.

the C–H out-of-plane bending mode on the ferrocene ring.[13] The IR spectra of compounds **6**, **7**, **8**, and **9** showed one peak at *ca.* 910 cm^{-1}. The infrared frequencies of the C–H bending modes of ruthenocene are similar to those of ferrocene.[14] Taking the evidences into account, it has been confirmed that **6**, **7**, **8**, and **9** are 1,2-disubstituted ruthenocenes. Furthermore, in the ^{1}H NMR spectra of **6**, **7**, and **8**, the *N*-methylene protons appear as doublets in contrast to those of **1** containing no substituent at the *ortho*-position of the dimethylaminomethyl group (Tables 1 and 2). This result, intimating the steric heterogeneity of the *N*-methylene protons in **6**, **7**, and **8**, supports the above conclusions. The coupling constnats of the doublets corresponding to olefinic protons are 16 Hz, and the absorption bands of the C=C linkage are located at *ca.* 1600 and 960 cm^{-1} in **6**, **7**, and **8** (Tables 2 and 3). This indicates that the olefinic protons occupy a *trans* position relative to each other.

Experimental

Materials. All the melting points are uncorrected. (Dimethylaminomethyl)ruthenocene (**1**) was prepared according to the method described by Hofer and Schlögl.[15]

Measurements. The ^{1}H NMR spectra were determined in CDCl$_3$ with a JEOL JNM-PMX-60 spectrometer (60 MHz) and a Hitachi R-22 spectrometer (90 MHz) at room temperature. All the chemical shifts are expressed in δ (ppm; downfield from the internal standard Me$_4$Si). The IR spectra were measured using KBr disks, Nujol mulls (4000—650 cm^{-1}) and Nujol mulls mounted on thin polythene windows (700—200 cm^{-1}) with Hitachi 215 and ÉPI-L spectrometers. The mass spectra were obtained on a JEOL JMS-07S mass spectrometer and a Hitachi RMU-6M mass spectrometer, using a direct insertion probe at an ionization energy of 70 eV. The molecular weight was determined in CHCl$_3$ with a Hitachi 115 vapor pressure osmometer.

*Di-μ-chloro-bis[2-(dimethylaminomethyl)ruthenocenyl]dipalladium(II) (**2**).* A mixture of lithium tetrachloropalladate(II) (2.28 g, 8.7 mmol) and sodium acetate trihydrate (1.18 g, 8.7 mmol) in ethanol (50 ml) was stirred for 20 min at room temperature. To the reaction mixture, a solution of (dimethylaminomethyl)ruthenocene (**1**) (2.5 g, 8.7 mmol) in ethanol (100 ml) was added, and the mixture was stirred for 5 min at room temperature. The yellow precipitate was filtered and dried, and the crude product was column-chromatographed on silica gel. The first band, eluted with chloroform, yielded di-μ-chloro-bis[2-(dimethylaminomethyl)-ruthenocenyl]dipalladium(II) (**2**) (2.9 g, 78%). The solid (**2**) was insoluble in all common solvents; mp 163—166 °C (dec). IR(Nujol): 323, 258, and 216 cm^{-1} (bridged Pd-Cl).

*Chloro[2-(dimethylaminomethyl)ruthenocenyl](triphenylphosphine)-palladium(II) (**3**).* A mixture of the complex **2** (1.9 g, 2.2 mmol) and triphenylphosphine (1.16 g, 4.4 mmol) in benzene (50 ml) was stirred for 12 h at room temperature. After removal of the solvent *in vacuo*, the column chromatography of the residue on silica gel (chloroform) gave chloro[2-(dimethylaminomethyl)ruthenocenyl](triphenylphosphine)palladium(II) (**3**) (2.7 g, 88%); mp 220—225 °C (dec) (chloroform). IR(Nujol): 357 cm^{-1} (terminal Pd-Cl). Found: C, 53.84; H, 4.39; N, 2.20%. Calcd for C$_{31}$H$_{31}$ClRuPPd: C, 53.85; H, 4.52; N, 2.03%; mol wt, 691.

*Acetylacetonato[2-(dimethylaminomethyl)ruthenocenyl]palladium(II) (**4**).* A suspension of the complex **2** (1.0 g, 1.16 mmol) and thallium(I) acetylacetonate (0.07 g, 2.3 mmol) in benzene (50 ml) was stirred for 3 h at room temperature, and filtered. The filtrate was evaporated *in vacuo*, and the residue was purified by column chromatography on silica gel (chloroform) to give acetylacetonato[2-(dimethylaminomethyl)ruthenocenyl]palladium(II) (**4**) (0.68 g, 60%); mp 162—165 °C(dec) (chloroform). IR(KBr): 1620 and 1550 cm^{-1} (acac group). Found: C, 43.66; H, 4.75; N, 2.91%. Calcd for C$_{18}$H$_{23}$RuNPd: C, 43.87; H, 4.70; N, 2.84%; mol wt, 493.

*Reduction of Complex **2** with Lithium Aluminum Hydride.* A mixture of the complex **2** (1.0 g, 1.16 mmol) and lithium aluminum hydride (0.044 g, 1.16 mmol) in dry ether (100 ml) was stirred for 4 h at room temperature. After the addition of moist ether and water, the reaction mixture was extracted three times with ether which had been washed with water and brine, and then dried over anhydrous sodium sulfate. The removal of the solvent gave **1** in 95% yield as brownish plates from petroleum ether; mp 38—41 °C (lit,[15] 39—42 °C). The ^{1}H NMR, IR, and mass spectra of **1** were consistent with those of an authentic sample.

*Reduction of Complex **2** with Lithium Aluminum Deuteride.* The reduction of the complex **2** (1.0 g) with lithium aluminum deuteride (0.044 g) in dry ether (100 ml) was conducted under the same conditions as in the proceeding experiment. After recrystallization from petroleum ether, the product (mp 39—42 °C) was identified as 1-(dimethylaminomethyl)ruthenocene-2-*d* (**5**) on the basis of the following evidence: ^{1}H NMR(CDCl$_3$): δ 2.20 (s, 6H, -N(CH$_3$)$_2$); 3.10 (s, 2H, -CH$_2$-); 4.5—4.6 ppm (m, 8H, ruthenocene ring protons). MS: M$^+$ 289. Found: C, 54.08; H, 5.43; N. 4.91%. Calcd for C$_{13}$H$_{16}$DRuN: C, 53.96; H, 5.57; N, 4.84%; mol wt, 289.

*General Procedure for the Reaction of Complex **2** with Olefins.* In a closed vessel, a mixture of the complex **2** (1.0 g, 1.16 mmol) and an olefin (5 mmol) and triethylamine (0.30 g, 3 mmol) in toluene (50 ml) was stirred for 5 h at 80 °C under a nitrogen atmosphere. The reaction mixture was cooled and filtered to remove precipitated palladium, and the filtrate was evaporated *in vacuo*. The residue was dissolved in chloroform which had been washed with water and brine, and dried over anhydrous magnesium sulfate. After removal of the solvent, purification of the crude product by column chromatography (silica gel-chloroform) gave 1-alkenyl-2-(dimethylaminomethyl)ruthenocenes (**6**, **7**, **8**) in 91, 89, and 94% yields, respectively.

*Carbonylation of Complex **3** in Ethanol.* In an autoclave, a suspension of the complex **3** (1.3 g, 1.9 mmol) in ethanol (50 ml) was stirred for 50 h at 100 °C under a carbon monoxide pressure of 80 atm. The reaction mixture was filtered to remove precipitated palladium, and the filtrate was evaporated *in vacuo*. The residue was dissolved in chloroform and column chromatographed on silica gel (chloroform) to afford 1-(dimethylaminomethyl)-2-(ethoxycarbonyl)ruthenocene (**9**) (0.27 g, 40%). The structure of the 1,2-disubstituted ruthenocenes has been confirmed by elemental analysis and the ^{1}H NMR, IR, and mass spectra (Tables 2 and 3).

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