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The σ-Bonded Palladium(II) Complex of [π-(Dimethylaminomethyl)cyclopentadienyl]tetraphenylcyclobutadienecobalt(I)

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[π-(Dimethylaminomethyl)cyclopentadienyl]tetraphenylcyclobutadienecobalt(I) reacts with lithium tetrachloropalladate(II) in the presence of sodium acetate to give an ortho-palladated binuclear complex. The σ-bonded structure of the complex was confirmed by studies of the IR and ^{1}H-NMR spectra and of the reactions with triphenylphosphine, thallium(I) acetylacetonate, and lithium aluminum deuteride. The reactions of the σ-bonded complex with carbon monoxide and olefins have been examined.

Following the first observation by Cope and Siekman1) that azobenzene reacts with palladium(II) chloride to give an intramolecular ortho-palladation product with a carbon-to-metal σ-bond, considerable interest developed in this area and numerous ortho-metalated complexes have been prepared.2) In connection with 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); subsequently the intramolecular ortho-palladations of (dimethylaminomethyl)ferrocene,4) acetylferrocene *N,N*-dimethylhydrazone,5) 2-pyridylferrocene,6) and (dimethylaminomethyl)ruthenocene7) were also reported. In this report, we wish to report on the intramolecular ortho-palladation of [π-(dimethylaminomethyl)cyclopentadienyl]tetraphenylcyclobutadienecobalt(I) (**1**) and the reaction of the metalation product (**2**) with carbon monoxide and olefins.

Results and Discussion

In the presence of sodium acetate trihydrate, the reaction of **1** with mole equivalents of lithium tetra-

Table 1. The ^{1}H-NMR spectra (δ, ppm) of [π-(dimethylaminomethyl)cyclopentadienyl]tetraphenylcyclobutadienecobalt(I) derivatives

Compound	-N-C$\underline{H}_3$	-C$\underline{H}_2$-	Cp-$\underline{H}$	Other
1	2.23 (s, 6H)	2.71 (s, 2H)	4.63 (s, 4H)	7.10—7.65 (m, 20H, Ar-$\underline{H}$).
3	2.43 (s, 3H) 2.82 (s, 3H)	3.00 (d, 1H) 3.18 (d, 1H)	4.61 (m, 3H)	7.02—7.90 (m, 35H, Ar-$\underline{H}$).
4	2.20 (s, 3H) 2.62 (s, 3H)	2.75 (d, 1H) 3.25 (d, 1H)	4.20—4.60 (t, 3H)	1.67 and 1.82 (each s, 3H, C$\underline{H}_3$ of Acac group), 5.11 (s, 1H, -C$\underline{H}$- of Acac group), 7.07—7.62 (m, 20H, Ar-$\underline{H}$).
6	2.11 (s, 6H)	2.78 (br-s, 2H)	4.93 (t, 3H)	1.02 (t, 3H, -COOCH$_2$C$\underline{H}_3$), 3.63 (q, 2H, -COOC$\underline{H}_2$CH$_3$), 7.13—7.47 (m, 20H, Ar-$\underline{H}$).
7	2.15 (s, 6H)	2.98 (br-s, 2H)	4.68—4.94 (m, 3H)	6.35 (d, 1H, J=16 Hz, -C=C$\underline{H}$-Ph), 6.71 (d, 1H, J=16 Hz, -C$\underline{H}$=C-Ph), 7.25—770 (m, 25H, Ar-$\underline{H}$).
8	2.15 (s, 6H)	2.99 (br-s, 2H)	4.72—4.98 (m, 3H)	1.91 (s, 3H, -CO-C$\underline{H}_3$), 600 (d, 1H, J=16 Hz, -C=C$\underline{H}$-CO-), 6.84 (d, 1H, J=16 Hz, -C$\underline{H}$=C-CO-), 7.15—7.50 (m, 20H, Ar-$\underline{H}$).
9	2.00 (s, 6H)	2.85 (br-s, 2H)	4.65—4.95 (m, 3H)	6.71 (d, 1H, J=16 Hz, -C=C$\underline{H}$-CO-), 7.10—7.75 (m, 26H, Ar-$\underline{H}$+-C$\underline{H}$=C-CO-).
10	2.11 (s, 6H)	2.93 (br-s, 2H)	4.51—4.78 (m, 3H)	3.97—4.16 (m, 9H, Cp-$\underline{H}$ of ferrocene), 5.87 (d, 1H, J=16 Hz, -C=C$\underline{H}$-Fc), 6.31 (d, 1H, J=16 Hz, -C$\underline{H}$=C-Fc), 7.11—7.53 (m, 20H, Ar-$\underline{H}$).
11	2.01 (s, 6H)	2.96 (br-s, 2H)	4.51—4.79 (m, 3H)	4.82 and 5.13 (each d-d, 2H, -C=C$\underline{H}_2$), 5.99 (d-d, 1H, -C$\underline{H}$=C), 7.09—7.56 (m, 20H, Ar-$\underline{H}$).
12	2.44 (s, 12H)	3.17 (s, 4H)	4.74—4.90 (m, 3H)	7.16—7.51 (m, 42H, Ar-$\underline{H}$+-C$\underline{H}$=C$\underline{H}$-).

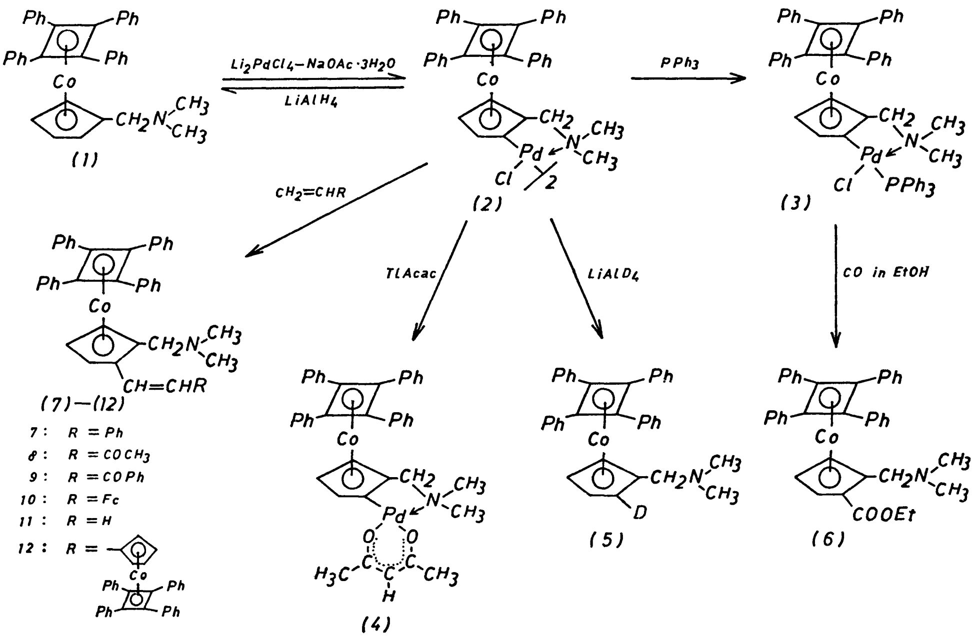

Fig. 1.

chloropalladate(II) gave di-μ-chloro-bis{[π-1-(dimethylaminomethyl)cyclopentadienyl-2*C*, *N*]tetraphenylcyclobutadienecobalt(I)}dipalladium(II) (**2**) in 96% yield. The complex **2** was shown to be an intramolecularly ortho-palladated complex on the bases of its reactions and of 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. However, the binuclearly σ-bonded structure of the complex **2** was supported by the bridged splitting reaction with triphenylphosphine and thallium(I) acetylacetonate to give readily soluble monomeric triphenylphosphine derivative **3** and a monomeric acetylacetonate derivative **4**, respectively. Moreover, the far-infrared spectrum of **2** showed a bridged Pd–Cl streching absorption at about 303, 275, and 255 cm^{-1}. The low solubility of **2** in all common solvents precluded any NMR studies at room temperature. However, the ^{1}H-NMR spectra of derivative **3** and **4** clearly demonstrated that Pd–C σ-bonds and Pd–nitrogen coordination bonds existed in these complexes (Table 1). *N*-Methyl and *N*-methylene protons of **1** appear as singlets, whereas in **3** and **4** the *N*-methyl protons appear as two singlets and the *N*-methylene protons as two doublets. The non-equivalence 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.[8] Furthermore, to ascertain the formation of the σ-bond between palladium and the cyclopentadienyl ring in **2**, **3**, and **4**, the compound **2** was reduced with lithium aluminum deuteride to give [π-1-(dimethylaminomethyl)cyclopentadienyl-2-*d*]tetraphenylcyclobutadienecobalt(I) (**5**). On the other hand, the lithium aluminum hydride reduction of **2** gave **1**, whose mass spectrum was identical with that of an authentic sample. The IR spectrum of the compounds prepared in this study is recorded in Table 2. In ferrocene derivatives, generally, 1,2-disubstituted derivatives exhibited one peak, while the 1,3-isomers showed two peaks in the region near 900 cm^{-1}; this was the characteristic absorption band of the C–H out-of-plane bending mode on the ferrocene ring.[9] The infrared frequencies of the C–H bending modes of ruthenocene derivatives are also similar to those ferrocene.[7,10] Compounds **2**, **3**, and **4** and another derivatives from **2** all exhibited a single peak in the 900 cm^{-1} region. Taking these results into account, it has been confirmed that **2**, **3**, and **4** are 1,2-disubstituted cyclopentadienyl derivatives.

The reactions of ortho-palladation products from α-aryl-nitrogen derivatives with numerous reagents have been reported.[2] The carbonylation of ortho-palladation products of azobenzene, Schiff bases, and *N*,*N*-dialkylbenzylamines usually gives a variety of heterocyclic compounds.[11,12] The derivative **3** in ethanol was readily carbonylated at 100 °C to produce an uncyclic ester [π-1-(dimethylaminomethyl)-2-ethoxycarbonylcyclopentadienyl]tetraphenylcyclobutadienecobalt(I) (**6**) in 42% yield. On the other hand, in the presence of triethylamine, the complex **2** reacted with simple olefins, such as styrene, methyl vinyl ketone, phenyl vinyl ketone, and vinylferrocene, in toluene at 100 °C, leading to the formation of [π-1-(dimethylaminomethyl)-2-alkenylcyclopentadienyl]tetraphenylcyclobutadienecobalt(I) (**7**—**10**) in moderate yields. Moreover, the reaction of the complex **2** with ethylene led to the formation of vinyl derivative (**11**) and disubstituted ethylene derivative (**12**) in 78 and 1.5% yield, respectively. The IR and ^{1}H-NMR spectra of compounds **5**—**12** were all consistent with the proposed structures. The compounds **5**—**12** also exhibited a single peak absorption in the 900 cm^{-1} region characteristic of homoannularly 1,2-disubstituted metallocene derivatives.

Table 2. The IR absorption frequencies (cm^{-1}) of [π-(dimethylaminomethyl)cyclopentadienyl]-tetraphenylcyclobutadienecobalt(I) derivatives

Compound	917 Rule	Other bands
2	910	3050, 2900, 2850, 1600, 1500, 740, 690; 303, 275, 255 (bridged Pd-Cl).
3	910	3050, 2900, 2850, 1600, 1500, 745, 690: 345, 330 (terminal Pd-Cl).
4	905	3030, 2900, 2850, 1600, 1500, 750, 690; 1580, 1510 (Acac group), 1200 (H-C bending of Acac group).
6	910	3030, 2950, 2830, 1600, 1500, 750, 690; 1710 (ester).
7	910	3030, 2950, 2800, 1600, 1500, 745, 690; 960 (*trans* -CH=CH-).
8	910	3030, 2950, 2800, 1600, 1500, 750, 690; 1660 (-CO-CH=CH-), 960 (*trans* -CH=CH-).
9	910	3030, 2950, 2800, 1600, 1500, 750, 690, 1660 (-CO-CH=CH-), 960 (*trans* -CH=CH-).
10	910	3050, 2950, 2800, 1600, 1500, 745, 690; 1100, 1000 (Fc), 960 (*trans* -CH=CH-).
11	910	3020, 2900, 2800, 1600, 1500, 750, 690; 1620, 990 (-CH=CH$_2$).
12	910	3020, 2900, 2800, 1600, 1500, 750, 690; 1620, 965 (*trans* -CH=CH-).

Table 3. Properties and analysis of [π-1-(dimethylamenomethyl)cyclopentadienyl]-tetraphenylcyclobutadienecobalt(I) derivatives

Compound	
6	pale yellow crystals, mp 112—113 °C. Found: C, 76.71; H, 5.84; N, 2.13%. MS: *m/e* 609 (M$^+$). Calcd for $C_{39}H_{36}CoNO_2$: C, 76.83; H, 5.95; N, 2.29%; mol wt, 609.
7	pale yellow crystals, mp 86—88 °C. Found: C, 82.48; H, 5.86; N, 2.05%. MS: *m/e* 639 (M$^+$). Calcd for $C_{44}H_{38}CoN$: C, 82.61; H, 6.01; N, 2.18%; mol wt, 639.
8	pale yellow crystals, mp 109—111 °C. Found: C, 79.23; H, 5.88; N, 2.25%. MS: *m/e* 605 (M$^+$). Calcd for $C_{40}H_{36}CoNO$: C, 79.32; H, 5.99; N, 2.31%; mol wt, 605.
9	pale yellow crystales, mp 157—159 °C. Found: C, 80.61; H, 5.59; N, 1.88%. MS: *m/e* 667 (M$^+$). Calcd for $C_{45}H_{38}CoNO$: C, 80.79; H, 5.73; N, 2.09%; mol wt, 667.
10	reddish yellow crystals, mp 79—81 °C. Found: C, 76.87; H, 5.71; N, 1.73%. MS: *m/e* 747 (M$^+$). Calcd for $C_{48}H_{42}CoFeN$: C, 77.08; H, 5.67; N, 1.87%; mol wt, 747.
11	pale yellow crystals, mp 124—125 °C. Found: C, 80.90; H, 5.95; N, 2.33%. MS: *m/e* 563 (M$^+$). Calcd for $C_{38}H_{34}CoN$: C, 80.97; H, 6.07; N, 2.48%; mol wt, 536.
12	yellow crystals, mp 244—246 °C. Found: C, 80.77; H, 5.72; N, 2.45%; mol wt 1094 (in CHCl$_3$). Calcd for $C_{74}H_{64}Co_2N_2$: C, 80.86; H, 5.86; H, 2.54%; mol wt, 1099.

Experimental

Materials. All the melting points are uncorrected. [π-(Dimethylaminomethyl)cyclopentadienyl]tetraphenylcyclobutadienecobalt(I) (**1**) was prepared according to the method described by Rausch and Genetti.[13] Phenyl vinyl ketone[14] and vinylferrocene[15] were synthesized according to known procedures. The other olefins were obtained from commercial sources.

Measurements. The ^{1}H-NMR spectra were determined in CDCl$_3$ with a Hitachi R-22 spectrometer (90 MHz), using TMS as the internal standard (δ, ppm). The IR spectra were measured (4000—650 cm^{-1}) and Nujol mulls mounted on thin polythene windows (700—200 cm^{-1}) with Hitachi 215 and EPI-L spectrometers. The mass spectra were obtained on 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{[*π-1-(dimethylaminomethyl)cyclopentadienyl*-2C, N]*tetraphenylcyclobutadienecobalt(I)*}*dipalladium(II) (2).* A mixture of lithium tetrachloropalladate(II) (2.62 g, 10 mmol) and sodium acetate trihydrate (1.36 g, 10 mmol) in methanol (50 ml) was stirred for 30 min at room temperature. To the reaction mixture, a solution of **1** (5.37 g, 10 mmol) in methanol (100 ml) was added, and the mixture was stirred for 36 h at room temperature. The yellow precipitate which formed was filtered and washed successively with several portions of methanol and then ether. The solid (6.5 g, 96% yield) was insoluble in all common solvents; mp 208—210 °C (dec). Found: C, 60.68; H, 4.67; N, 2.02%. Calcd for $C_{64}H_{62}Cl_2Co_2N_2Pd_2$: C, 60.96; H, 4.95; N, 2.22%.

Chloro(triphenylphosphine{[*π-1-(dimethylaminomethyl)cyclopentadienyl*-2C,N]*tetraphenylcyclobutadienecobalt(I)*}*palladium(II) (3).* A mixture of the complex (5.0 g, 3.7 mmol) and triphenylphosphine (1.94 g, 7.4 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 (CHCl$_3$) gave triphenylphosphine derivative (**3**) (6.9 g, 99% yield); mp 235—237 °C (dec). Found: C, 67.33; H, 5.31; N, 1.71%; mol wt 884 (in CHCl$_3$). Calcd for $C_{50}H_{46}ClCoNPPd$: C, 67.27; H, 5.19; N, 1.55%; mol wt 892.

Acetylacetonato{[*π-1-(dimethylaminomethyl)cyclopentadienyl*-2C, N]*tetraphenylcyclobutadienecobalt(I)*}*palladium(II) (4).* A suspension of the complex **2** (0.80 g, 0.6 mmol) and thallium(I) acetylacetonate (0.33 g, 1.2 mmol) in benzene (20 ml) was stirred for 24 h at room temperature. The filtrate was evaporated *in vacuo*, and the residue was purified by column chromatography on silica gel ($CHCl_3$) and gave the acetylacetonate derivative (**4**) (0.7 g, 80% yield); mp 219—221 °C (dec). Found: C, 64.15; H, 5.62; N, 2.17%; mol wt 686 (in $CHCl_3$). Calcd for $C_{37}H_{38}CoNO_2Pd$: C, 64.03; H, 5.51; N, 2.01%; mol wt 694.

*Reduction of Complex **2** with Lithium Aluminum Hydride.* Lithium aluminum hydride (0.08 g, 2 mmol) in dry ether (50 ml) was slowly added to a solution of the complex **2** (2.52 g, 2 mmol) in dry THF (50 ml). The resulting black mixture was stirred at 50 °C for 8 h; then water (20 ml) was added with cooling. The ether layer was washed with water and dried over anhydrous $MgSO_4$. After the removal of the solvent, **1** was obtained as yellowish needles from benzene–cyclohexane; mp 189—190 °C (lit,[13] mp 189—190 °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 (0.035 g) was conducted under the same conditions as in the preceeding experiment. After recrystallization from benzene–cyclohexane, the product (mp 189—191 °C) was identified as [π-1-(dimethylaminomethyl)cyclopentadienyl-2-*d*]tetraphenylcyclobutadienecobalt(I) (**5**) on the basis of the following evidence; ^{1}H-NMR ($CDCl_3$): δ 2.23 (s, 6H, $-N(C\underline{H}_3)_2$), 2.71 (s, 2H, $-C\underline{H}_2-$), 4.63 (s, 3H, Cp-$\underline{H}$), 7.10—7.65 ppm (m, 20H, Ar-$\underline{H}$). MS: *m/e* 538 (M^+). Found: C, 80.16; H, 6.01; N, 2.45%. Calcd for$C_{36}H_{31}$-CoDN: C, 80.27; H, 6.19; N, 2.60%; mol wt, 538.

*Carbonylation of Complex **3** in Ethanol.* In an autoclave, a suspension of the complex **3** (2.0 g, 2.1 mmol) in ethanol (80 ml) was stirred for 24 h at 100 °C under carbon monoxide pressure of 50 atm. The reaction mixture was filtered to remove precipitated palladium, and the filtrate was evaporated *in vacuo*. The residue was dissolved in $CHCl_3$ and column chromatographed on silica gel to afford [π-1-(dimethylaminomethyl)-2-ethoxycarbonylcyclopentadienyl]-tetraphenylcyclobutadienecobalt(I) (**6**): mp 112—113 °C, (0.41 g, 42% yield). The structure of **6** has been confirmed by elemental analysis and ^{1}H-NMR, IR, and mass spectra (Tables 1, 2, and 3).

*General Procedure for the Reaction of Complex **2** with Olefins.* In a closed vessel, a mixture of the complex **2** (1.26 g, 1 mmol), 3 mmol of olefin (styrene, methyl vinyl ketone, phenyl vinyl ketone, and vinylferrocene) and triethylamine (0.20 g, 2 mmol) in toluene (50 ml) was stirred for 8 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 $CHCl_3$ which had been washed with brine, and dried over anhydrous $MgSO_4$. After removal of the solvent, purification of the crude product by column chromatography (silica gel–$CHCl_3$) gave [π-1-(dimethylaminomethyl)-2-styrylcyclopentadienyl]tetraphenylcyclobutadienecobalt(I) (**7**), [π-1-(dimethylaminomethyl)-2-(2-acetylvinyl)cyclopentadienyl]-tetraphenylcyclobutadienecobalt(I) (**8**), [π-1-(dimethylaminomethyl)-2-(2-benzoylvinyl)cyclopentadienyl]tetraphenylcyclobutadienecobalt(I) (**9**), and [π-1-(dimethylaminomethyl)-2-(2-ferrocenylvinyl)cyclopentadienyl]tetraphenylcyclobutadienecobalt(I) (**10**) in 30, 45, 57, and 40% yields, respectively.

In the case of the reaction with ethylene, a suspension of the complex **2** (2.52 g, 2 mmol) in triethylamine (30 ml) was stirred for 20 h at 100 °C under ethylene pressure of 50 atm in an autoclave. The crude products were purified by column chromatography on silica gel. First elution with $CHCl_3$ and recrystallization from benzene–cyclohexane afforded pale yellow crystals (78% yield), which were identified to [π-1-(dimethylaminomethyl)-2-vinylcyclopentadienyl]tetraphenylcyclobutadienecobalt(I) (**11**). Further elution with $CHCl_3$ and recrystallization from benzene-cyclohexane afforded yellow crystals, which were identified as μ-{bis[π-2-(dimethylaminomethyl)cyclopentadienyl] ethylene}-bis[tetraphenylcyclobutadienecobalt(I)] (**12**) (1.5% yield). The structure of the compounds (**7**—**12**) has been confirmed by elemental analysis and the ^{1}H-NMR, IR, and mass spectra (Tables 1, 2, and 3).

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