Bull. Chem. Soc. Jpn., **64**, 1695—1697 (1991)

Synthesis and Characterization of Six-Membered Cyclometallated Complexes of 2-Bezylpyridine with Rhodium(III)

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(Received December 25, 1990)

Synopsis. 2-Benzylpyridine (Hpiph) is metallated with $RhCl_3 \cdot 3H_2O$ to give $[\{Rh(piph)Cl_2(Hpiph)\}_2] \cdot H_2O$ [piph=2-(2-picolyl)phenyl] in which piph is coordinated at phenyl-1-C and picolyl-N atoms. This complex reacts with tertiary phosphines (PR_3) such as PEt_3, PEt_2Ph, and PPh_3 to yield $[Rh(piph)Cl_2(PR_3)_2]$.

Considerable interest has developed concerning cyclometallated complexes owing to not only the direct activation of the carbon–hydrogen bonds with transition metal complexes,[1-3] but also the wide range of the utilization for organic synthesis,[4] optical resolution of organic compounds,[5] catalyst precursors,[6] and so on. Several articles have already been published concerning five-members-chelated organorhodium(III) complexes derived from nitrogen-containing ligands, such as 2-phenylpyridine,[7] benzo[*h*]quinoline,[7] azobenzenes,[8] aromatic oximes,[9] 1-phenylpyrazole,[10] and 8-methylquinoline.[11] However, six-membered cyclometallated complexes with rhodium(III) are very scarce.

We have studied six-membered cyclopalladated complexes of 2-benzylpyridine,[12] 2-benzoylpyridine,[13] and 2-neopentylpyridine.[14] Here, we will report the synthesis and characterization of new six-membered cyclometallated complexes of 2-benzylpyridine with rhodium(III).

Results and Discussion

When 2-benzylpyridine was heated with $RhCl_3 \cdot 3H_2O$ in 2-methoxyethanol at 80 °C, a yellow-brown complex, $[\{Rh(piph)Cl_2(Hpiph)\}_2] \cdot H_2O$ [piph=2-(2-picolyl)phenyl] (**1**) was formed in 45% yield. Complex **1** was so poorly soluble in organic solvents that NMR spectra of **1** could not be obtained. However, **1** was tentatively ascribed to a chloro-bridged dimeric structure on the basis of the elemental analysis and the poor solubility. Treatment of **1** with excess amounts of tertiary phosphines in refluxing dichloromethane afforded mononuclear complexes, $[Rh(piph)Cl_2(PR_3)_2]$ (**2a**, R=Et; **2b**, PR_3=PEt_2Ph; **2c**, R=Ph). The elemental analyses of **2a**—**c** were satisfactory. Their IR spectra showed a weak absorption near 1600 cm^{-1} and fairly strong bands near 1430 and 1485 cm^{-1}, ascribable to ν(C=N) of the pyridyl group and phosphine moieties, respectively, supporting the above formulations.

The $^{13}C\{^1H\}$ NMR spectrum of **2a** showed a double triplet at δ=145.4 ($^1J_{CRh}$=29.3 Hz, $^2J_{CP}$=17.6 Hz, RhC), disclosing clearly that direct metallation took place at one aromatic carbon of 2-benzylpyridine and that the metallated carbon was situated cis to the two phosphine ligands (Fig. 1). In general, a pyridyl nitrogen is coordinated easily to a trivalent rhodium atom.[7] Indeed, in the ^1H NMR spectrum of **2a**, pyridyl 6-H of the piph moiety resonates at a considerably lower field (at δ=10.33) than that (δ=8.56) of free 2-benzylpyridine, indicating the coordination of the pyridyl group. Accordingly, it is certain that the rhodium-bonded carbon (1-C), located ortho to the picolyl group, and the pyridyl nitrogen are coordinated together to the rhodium atom, forming a new six-membered chelate structure, piph-*C*^{1}, *N*-Rh, similarly to the cases of $\{Pd(piph)(CH_3CO_2)\}_2]$ and its related complexes.[12]

2-Benzylpyridine, in which the phenyl and the 2-pyridyl groups are separated by the methylene group, reacted with $RhCl_3 \cdot 3H_2O$ in the alcohlic solvent at ca. 80 °C to afford the dimeric complex, **1** containing one metallated piph unit per Rh atom. This bears analogy with the cyclometallated rhodium(III) complexes of 8-methyl-quinoline,[11] in which the methyl group was not involved apparently in the conjugate system of the quinoline moiety. It is noted that these are in sharp contrast with the other N-containing ligands, such as 2-phenylpyridine,[7] benzo[*h*]quinoline,[7] azobenzenes,[8] aromatic oximes,[9] and 1-phenylpyrazole,[10] each of which consists of a continuous conjugate system and reacted with $RhCl_3 \cdot 3H_2O$ in refluxing ethanol to give a dimeric complex containing two metallated C,N-chelate units per Rh atom.

In the $^{13}C\{^1H\}$ NMR spectrum of **2a**, the methylene carbons of ethyl groups resonated as a triplet at δ=14.8 owing to virtual coupling with the two phosphorus atoms. Furthermore, the ^1H NMR spectrum of **2a** exhibited a quintet at δ=0.73 ascribable to the methyl protons, and its signal splitting was due to coupling with two vicinal methylene protons and virtual coupling with the two phosphorus atoms ($^3J_{HH}$=$^{3+5}J_{HP}$=7.3 Hz). These data imply unambiguously that the two phosphine

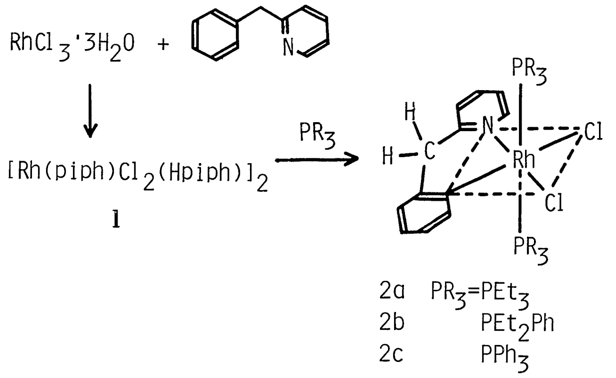

Fig. 1. The 2-(2-picolyl)phenyl-*C*^{1},*N*-rhodium(III) complexes.

ligands in **2a** are equivalent and located trans to each other, similarly to the case of [Rh(CH_2–C_9H_6N)X_2(PBu^n_3)$_2$] (C_9H_6N=8-quinolyl).[11]

In the ^{1}H NMR spectrum of **2a**, the picolyl methylene protons appeared as a singlet at δ=4.22, which showed no change in the range of +30—−60 °C. These facts indicate that the two methylene protons are equivalent and that the piph moiety is plain and situated in the same plane as the $RhCl_2$ moiety forms. In addition, the piph moiety is rigid and shows no inversion motion, in sharp contrast with the piph moiety in [Pd(piph)Cl{$C_5H_3N(Me)_2$-3.5}].[12] The rigid plain structure of the piph moiety in **2a** is due to steric effect of the two tertiary phosphine ligands, located above and below the central rhodium atom.

In the $^{13}C\{^1H\}$ NMR spectrum of **2b**, the signal patterns of the rhodium-bonded carbon and the methylene carbons of the ethyl groups are quite similar to those of the corresponding carbons in **2a**, indicating that **2b** has an analogous structure to **2a**. This is also supported by the facts that the ipso-carbons of the phosphine phenyl groups exhibited a triplet owing to virtual coupling ($^{1+3}J_{CP}$=7.3 Hz), and that the phosphine ortho-protons showed a quartet due to combination of virtual coupling and H–H coupling ($^{3+5}J_{HP}$=$^3J_{HH}$=7 Hz). Its ^{1}H NMR spectrum exhibited two quintets at δ=0.81 and 1.02 (each 6H, $^3J_{HH}$=$^{3+5}J_{HP}$=7.3 Hz, CH_3), one broad quartet at δ=2.06 (4H, $^3J_{HH}$=ca. 7 Hz, CH_2CH_3), and two multiplets at δ=2.50 and 2.77 (each 2H, $CH_AH_BCH_3$). Irradiation at the quintet at δ=0.81 converted the broad quartet into a broad singlet, whereas that at the quintet at δ=1.02 changed the two multiplets into two broad doublets [each, $^2J(H_AH_B)$=15.6 Hz]. These data imply that two ethyl groups in the PEt_2Ph ligand are unequivalent owing to the restriction of rotation of the PEt_2Ph ligands and that two methylene protons in one of the two ethyl groups are also nonequivalent. Furthermore, it is notable that $^{2+4}J_{HP}$ of the methylene protons in the PEt_2Ph ligands was too small to be detected. In fact, the corresponding $^2J_{HP}$ of methylene prontons in uncoordinated PEt_3 is very small (0.5 Hz).[15] However, the coupling constant of PEt_3 varies depending on the coordination. For example, [$PdBr_2(PEt_3)_2$] and [$PdBrPh(PEt_3)_2$] exhibited 4 Hz of $^{2+4}J_{HP}$ of the methylene protons.[16]

Complex **2c** is scarcely soluble in organic solvents and the NMR data could not be obtained.

Experimental

2-Benzylpyridine was available from Tokyo Kasei Kogyo Co., Ltd. General procedures were described previously.[17]

Reaction of 2-Benzylpyridine with $RhCl_3\cdot 3H_2O$. A 2-methoxyethanol solution (20 cm^3) containing $RhCl_3\cdot 3H_2O$ (300 mg, 1.20 mmol) and 2-benzylpyridine (1.00 g, 6.0 mmol) was heated at 80 °C for 0.5 h. After cooling, the resulting products were filtered and the precipitates were washed with diethyl ether to give a pale yellow solid, [Rh(piph)Cl_2(Hpiph)]$_2\cdot H_2O$ (**1**). Yield 280 mg (45%). Mp 242—250 °C. IR (KBr) 760 (o-C_6H_4), 1020 (Py ring), 1480 (CH_2), 1560, 1605 (Py), and 3030 cm^{-1} (aromatic CH). Found: C, 55.49; H, 4.11; N, 5.26%. Calcd for $C_{24}H_{23}N_2Cl_2ORh$: C, 55.41; H, 4.26; N, 5.38%.

[Rh(piph)Cl_2(PEt_3)$_2$] (2a). A dichoromethane suspension (10 cm^3) containing **1** (100 mg, 0.10 mmol) and triethylphosphine (0.08 cm^3, 0.55 mmol) was refluxed for 1 h to afford a yellow solution. The yellow solution was evaporated to dryness under reduced pressure. The resulting solid was recrystallized from dichloromethane and hexane to yield lemon yellow powders, **2a**. Yield 41 mg (86%). Mp 207—212 °C, IR (KBr) 755 (o-C_6H_4), 1030 (Py ring), 1420 (PCH_2), 1450 (CH_2), 1570, 1600 (Py), 2890, 2940, 2970 (CH), and 3025 cm^{-1} (aromatic CH); ^{1}H NMR (CD_2Cl_2) **PEt_3:** δ=0.73 (18H, quintet, $^3J_{HH}$=$^{3+5}J_{HP}$=7.3 Hz, CH_3), 1.71 (12H, m, PCH_2); **pich:** δ=4.22 (2H, s, $PyCH_2$), 6.92 (1H, t, ^3J=7.3 Hz, CH), 6.95 (1H, d, ^3J=ca. 6.5 Hz, CH), 6.97 (1H, t, ^3J=7.0 Hz, CH), 7.20 (1H, dt, ^3J=7.3 Hz, ^4J=1.5 Hz, CH), 7.39 (1H, d, ^3J=7.0 Hz, CH), 7.75 (1H, dt, ^3J=7.3 Hz, ^4J=1.5 Hz, CH), 8.20 [1H, d, ^3J=7.3 Hz, 3-H(Py)], and 10.33 [1H, d, ^3J=6.0 Hz, 6-H(Py)]; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) **PEt_3:** δ=7.53 (s, CH_3), 14.79 (t, $^{1+3}J_{CP}$=12.7 Hz, PCH_2); **piph:** 49.45 (s, $PyCH_2$), 122.3 (s), 123.7 (s), 125.2 (s), 125.8 (s), 127.2 (s), 135.9 (s), 138.8 (s), 140.5 (s), 145.4 (dt, $^1J_{CRh}$=29.3 Hz, $^2J_{CP}$=17.6 Hz, Rh-C), 157.7 (s, quarternary C), and 161.0 (s, quarternary C). Found: C, 49.58; H, 6.81; N, 2.34%. Calcd for $C_{24}H_{30}NCl_2P_2Rh$: C, 49.84; H, 6.97; N, 2.42%.

[Rh(piph)Cl_2(PEt_2Ph)$_2$]CH_2Cl_2 (2b). A dichloromethane suspension (10 cm^3) containing **1** (100 mg, 0.10 mmol) and diethylphenylphosphine (0.09 cm^3 0.50 mmol) was refluxed for 1.5 h to afford a reddish yellow solution. The solvent was removed under reduced pressure. The resulting solids were recrystallized from dichloromethane and diethyl ether to give a yellow solid, **2b**. Mp 207—214 °C; IR (KBr) 735 (o-C_6H_4), 1030 (Py ring), 1435 (PCH_2), 1455 (CH_2), 1490 (PC_6H_5), 1575, 1610 (Py), 2880, 2940, 2970 (CH), and 3050 cm^{-1} (aromatic CH). ^{1}H NMR (CD_2Cl_2) **PEt_2Ph**: δ=0.81 (6H, quintet, $^3J_{HH}$=$^{3+5}J_{HP}$=7.3 Hz, CH_3), 1.02 (6H, quintet, $^3J_{HH}$=$^{3+5}J_{HP}$=7.3 Hz, CH_3), 2.06 (4H, broad quartet, $^3J_{HH}$=ca. 7 Hz, CH_2), 2.50 (2H, m, CH_2), 2.77 (2H, m, CH_2), 6.81 (4H, t, ^3J=7.3 Hz, m-CH), 6.93 (4H, quartet, $^3J_{HH}$=$^{3+5}J_{HP}$=7 Hz, o-CH), ca. 6.9 (2H, overlapping, p-CH); **piph:** δ=3.55 (2H, s, CH_2), 6.36 (1H, d, ^3J=7.3 Hz, CH), 6.71 (1H, t, ^3J=7.3 Hz, CH), 6.9—7.05 (3H, overlapping, CH), 7.07 (1H, t, ^3J=6.9 Hz, CH), 8.42 [1H, d, ^3J=8.0 Hz, 3-H(Py)], and 9.93 [1H, d, ^3J=6.3 Hz, 6-H(Py)]; $^{13}C\{1H\}$ NMR (CD_2Cl_2) **PEt_2Ph**: δ=7.51 (2C, s, CH_3), 7.7 (2C, s, CH_3), 13.5 (2C, t, $^{1+3}J_{CP}$=13.7 Hz, CH_2), 14.5 (2C, t, $^{1+3}J_{CP}$=13.7 Hz, CH_2), 127.6 (4C, s, m-C), 128.9 (2C, s, p-C), 131.3 (4C, s, o-C), 132.7 (2C, t, $^{1+3}J_{CP}$=7 Hz, ipso-C); **piph:** δ=48.6 (s, CH_2), 122.3 (s), 123.9 (s), 124.8 (s), 127.2 (s), 136.1 (s), 137.3 (s), 140.7 (s), 145.3 (1C, dt, $^1J_{CRh}$=27 Hz, $^2J_{CP}$=15 Hz, RhC), 156.3 (s, quarternary C), and 159.0 (s, quarternary C). Found: C, 54.84; H, 6.03; N, 2.08%. Calcd for $C_{32}H_{40}NCl_2P_2Rh+CH_2Cl_2$: C, 54.75; H, 5.85; N, 1.98%.

[Rh(piph)Cl_2(PPh_3)$_2$] (2c). A dichloromethane suspension (15 cm^3) involving **1** (100 mg, 0.10 mmol) and triphenylphosphine (130 mg, 0.50 mmol) was refluxed for 2.5 h to yield an orange solution. The solution was evaporated to dryness under reduced pressure and the residue was washed with dichloromethane to give yellow powders, **2c**. Yield 35 mg, 20%. Mp 189—194 °C. IR (KBr) 745 (o-C_6H_4), 1090 (Py ring), 1435, 1485 (PC_6H_5), 1450 (CH_2), 1575, 1610 (Py), and 3050 cm^{-1} (aromatic CH). Found: C, 66.34; H, 4.82; N, 1.67%. Calcd for $C_{48}H_{40}NCl_2P_2Rh$: C, 65.91; H, 5.53; N, 1.60%.

The authors wish to express their thanks to Shoei Chemical Industry Inc. for its financial support to the present work.

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