

Amine-Assisted C–Cl Bond Activation of Aryl Chlorides by a (Phebox)Rh-Chloro Complex

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Received March 7, 2008

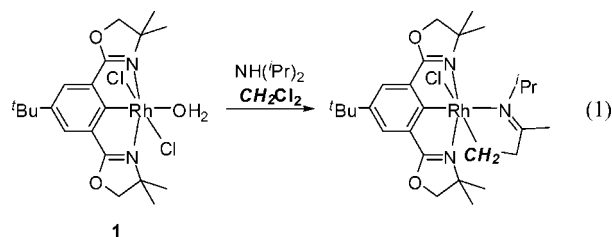
Summary: Oxidative addition of chlorobenzene and *p*-chlorotoluene by (Phebox)RhCl₂(H₂O) (**1**) in the presence of diisopropylamine was examined and was shown to produce the corresponding aryl complexes (Phebox)RhCl(Ar)(H₂O) in high yields via C–Cl bond cleavage. Reaction of **1** with chloropyridine in the presence of diisopropylamine provided a pyridinium rhodate complex.

Introduction

Oxidative addition of aryl halides to low-valent transition metal complexes is a common process to generate aryl complexes having a metal–carbon bond. Such a process is one of the most important steps in transition metal catalyzed reactions such as the Heck reaction and cross-coupling reaction.^{1,2} Utilization of an aryl chloride, which has the higher dissociation energy of a C–Cl bond compared with that of C–Br or C–I, has also been achieved in Pd-catalyzed arylation reactions.³ In comparison with the oxidative addition of an aryl halide to group 10 metals, examples for group 9 metal complexes such as Rh(I) and Ir(I) are still rare.^{4–9} Recent studies of the oxidative addition of Ar–Cl to Rh and Ir have been limited to RhCl₃(py)₃,⁵ (PCy₃)₂Rh(H)(Cl)₂,⁶ [(diimine)Rh(cod)],⁷ [(PPh₃)₃RhF],⁸ and (PNP)MX₂.⁹

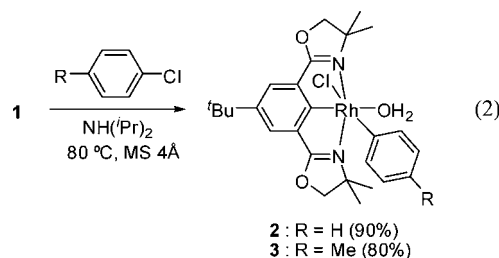
In this context, we have reported that (Phebox)Rh(Cl)₂(H₂O) [**1**; Phebox = bis(oxazolinyl)phenyl]¹⁰ exhibits high reactivity toward double C–Cl bond activation of CH₂Cl₂ in the presence

of NH(^{*i*}Pr)₂ and successive C–C bond formation between CH₂Cl₂ and NH(^{*i*}Pr)₂ to provide a azarhodacyclopentene complex (eq 1).^{11,12} In this reaction, the presence of the amine seems to be responsible for activation of an inactive Rh(III) complex to a (Phebox)Rh(I) species. We therefore envisioned that such a (Phebox)Rh(I) species may show a potential for C–Cl bond activation of aryl halides as well as CH₂Cl₂. Here we report a significant effect of amines to the reaction of **1** with aryl chlorides to provide aryl–Rh complexes.



Results and Discussion

Thermolysis of **1** in a neat solution of chlorobenzene with an excess amount of NH(^{*i*}Pr)₂ at 80 °C for 1 h resulted in the clean formation of a phenyl complex, (Phebox)Rh(Ph)Cl(H₂O) (**2**) (eq 2). Complex **2** was isolated in 90% yield after purification by column chromatography on silica gel. Similarly, reaction of **1** with *p*-chlorotoluene provided the *p*-tolyl complex (Phebox)Rh(*p*-CH₃C₆H₄)Cl(H₂O) (**3**) in 80% yield.



Complexes **2** and **3** were characterized on the basis of ¹H and ¹³C NMR and IR spectra. In the ¹³C NMR spectra of **2** and **3**, the signals of the *ipso*-phenyl carbons were observed at δ 140.3 (*J*_{RhC} = 35.4 Hz) and 134.5 (*J*_{RhC} = 35.3 Hz), respectively. The molecular structure of **3** was confirmed by X-ray diffraction, which revealed the pseudo-octahedral geometry on the Rh atom (Figure 1). The tolyl ligand was coordinated to the Rh at the perpendicular position to the Phebox plane. The Rh–C_{tolyl} bond length of 2.028(5) Å was comparable to that of the related Phebox acetate complex

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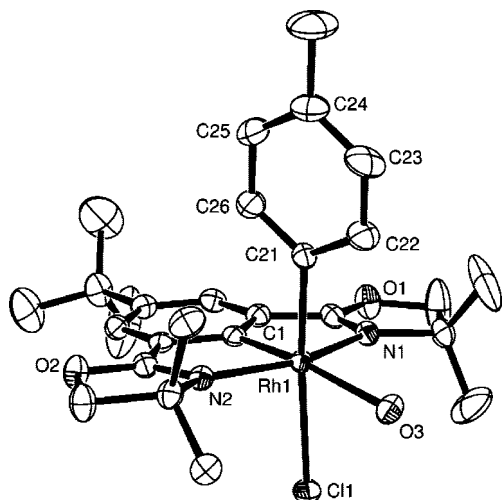


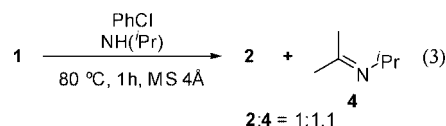
Figure 1. ORTEP diagram of **3** at the 50% probability level. Selected bond lengths (Å): Rh1–C1 1.909(4), Rh1–C21 2.028(5), Rh1–N1 2.078(4), Rh1–N2 2.067(4), Rh1–Cl1 2.5144(14), Rh1–O3 2.292(3).

(Phebox)Rh(Ph)(OAc) (2.005(2) Å).¹³ The Rh–Cl bond length of 2.5144(14) was significantly longer than those of (Phebox)-RhCl₂(H₂O) (Rh–Cl = 2.325(3), 2.331(3) Å)¹⁴ due to a *trans* influence of the tolyl group.

As we reported earlier, the Rh(III) dichloro complex (Phebox)Rh(Cl)₂(H₂O) did not react with chlorobenzene even at 120 °C for 40 h.¹³ Therefore, the presence of NH(^{*i*}Pr)₂ is essential to the C–Cl bond activation. In general, an electron-rich Rh(I) complex is active to the oxidative addition of a C–Cl bond.⁷ In the case of a Rh(III) complex, it is known that reductive elimination provides an active Rh(I) intermediate.^{9a,15}

To gain insight into the C–Cl bond activation by **1** with the amine, we checked the crude products on the reaction of **1** with chlorobenzene by ¹H NMR spectroscopy. Although other Rh complexes besides **2** were not detected, the formation of N(=CMe₂)(^{*i*}Pr) (**4**) as well as **2** was observed with the 2:4 ratio of 1:1.1 (eq 3).¹⁶ The formation of **4** is formally derived from dehydrogenation of NH(^{*i*}Pr)₂, involving deprotonation of the N–H bond and successive β-elimination.¹⁷ Such a dehydrogenation of an amine might afford a hydride intermediate, (Phebox)Rh(Cl)(H), that finally undergoes dehydrochlorination

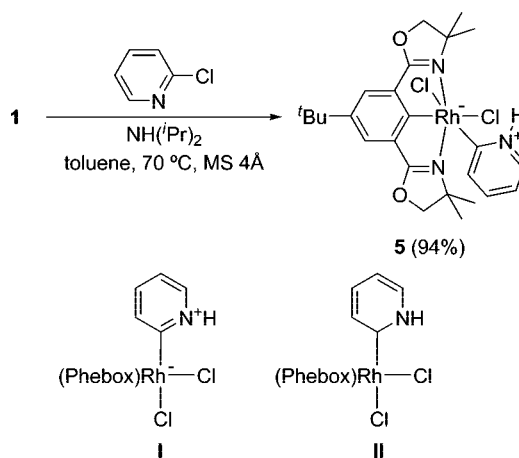
to generate (Phebox)Rh(I).¹⁸ Although we could not detect those intermediates, Ozerov and co-workers recently reported dehydrochlorination of (PNP)Rh(Cl)(H) with a base to provide the (PNP)Rh(I) complex.^{9c}



In contrast to NH(^{*i*}Pr)₂, NEt₃ is not a suitable reagent for C–Cl bond activation. Addition of NEt₃ instead of NH(^{*i*}Pr)₂ to a chlorobenzene solution of **1** at 80 °C for 1 h led to a decrease in the yield of **2** (35%).

It is interesting to note that an acetate analogue, (Phebox)Rh(OAc)₂(H₂O), did not undergo C–Cl bond activation but did undergo C–H bond activation to produce the corresponding chlorophenyl complex (Phebox)Rh(OAc)(C₆H₄Cl).¹³ Our results indicate that selectivity between C–Cl and C–H bonds of chloroarene can be controlled by the choice of ligand on the Rh center and a proper base.

Complex **1** also reacts with chloropyridine in the presence of NH(^{*i*}Pr)₂ in toluene at 70 °C to provide the rhodium complex **5** in 94% yield (eq 4). The ¹H NMR spectrum of **5** showed the low-field signal of the N–H proton at δ 15.8 (1H), which disappeared on treatment with D₂O. The IR spectrum of **5** also exhibited the ν_{NH} band at 3447 cm^{−1}. In the ¹³C NMR spectrum, two low-field singlets were observed at δ 184.3 (*J*_{RhC} = 38.3 Hz) and 185.5 (*J*_{RhC} = 25.7 Hz). In comparison with the Rh–C coupling constants of **2** and **3**, the signal at δ 184.3 is assigned to the pyridium carbon and the signal at δ 185.5 is assigned to the phenyl carbon in the Phebox ligand.



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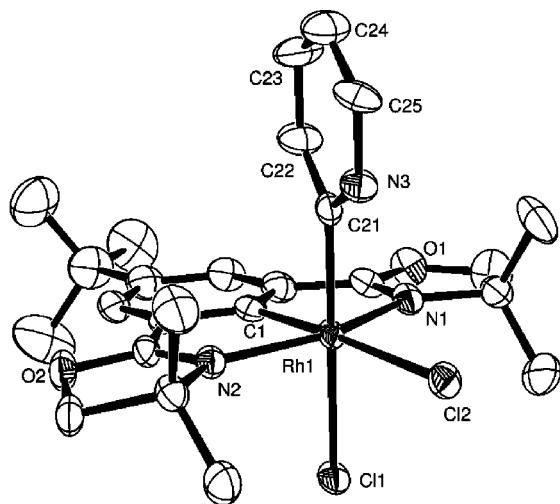


Figure 2. ORTEP diagram of **5** with 50% probability level ellipsoids. Selected bond lengths (Å): Rh1–C1 1.928(6), Rh1–C21 1.998(6), Rh1–N1 2.064(5), Rh1–N2 2.089(5), Rh1–Cl1 2.434(17), Rh1–Cl2 2.4856(17); Rh2–C26 1.921(6), Rh2–C46 2.015(6), Rh2–N4 2.071(6), Rh2–N5 2.086(5), Rh2–Cl3 2.4384(17), Rh2–Cl4 2.4859(18).

a pyridinium rhodate can be described as an N-heterocyclic carbene complex (**II**) or unstable pyridine tautomers.²⁰

In summary, we found a significant effect of amines on C–Cl bond activation of aryl chlorides by the Rh(III) complex to provide the corresponding aryl complexes. Formation of an equivalent amount of the imine **4** suggests that oxidation of amine promotes reduction of the inactive Rh(III) complex **1** to Rh(I) species. We envision that this method provides an alternative method for activation of an inactive Rh(III) complex.

Experimental Section

General Procedures. ¹H and ¹³C NMR spectra were obtained at 25 °C on a Varian Mercury 300 spectrometer. ¹H NMR chemical shifts are reported in δ units, in ppm relative to the singlet at 7.26 ppm for CDCl₃. ¹³C NMR spectra are reported in terms of chemical shift (δ, ppm) relative to the triplet at δ = 77.0 ppm for CDCl₃. Infrared spectra were recorded on a JASCO FT/IR-230 spectrometer. Mass spectra were recorded on a JEOL JMS-700. Elemental analyses were recorded on a Perkin-Elmer 2400II and a Yanaco MT-6. Column chromatography was performed with a silica gel column (Kanto Kagaku silica gel 60N). Complex **1** was prepared according to the literature.¹¹

Synthesis of 2. To a chlorobenzene solution (0.5 mL) of **1** (10.4 mg, 0.020 mmol) and 4 Å molecular sieves (100 mg) was added NH(Pr)₂ (56 μL, 0.40 mmol) under an argon atmosphere. After being stirred at 80 °C for 1 h, the mixture was filtered. The concentrated filtrate was purified by column chromatography on silica gel (hexane/ethyl acetate = 1:1) and then crystallized by slow vaporization from a solution of ethyl acetate/dichloromethane/hexane to give **2** (10.1 mg, 0.018 mmol, 90%). ¹H NMR (300 MHz, CDCl₃, rt): 1.25 (s, 6H, CH₃), 1.41 (s, 9H, C(CH₃)₃), 1.66 (s, 6H, CH₃), 1.71 (s, 2H, H₂O), 4.28 (d, *J*_{HH} = 8.4 Hz, 2H, CH₂), 4.45 (d, *J*_{HH} = 8.4 Hz, 2H, CH₂), 6.67–6.70 (m, 3H, C₆H₅), 6.86–6.92 (m, 2H, C₆H₅), 7.60 (s, 2H). ¹³C NMR (75 MHz, CDCl₃, rt): 27.0, 28.7, 31.7, 35.1, 66.6, 82.6, 122.1, 124.5, 125.5, 130.4, 136.6, 140.3 (d, *J*_{RhC} = 35.4 Hz), 145.8, 171.1 (d, *J*_{RhC} = 5.1 Hz), 186.4 (d,

*J*_{RhC} = 28.5 Hz). IR (KBr, cm^{−1}): 3311, 2965, 1624, 1563. Anal. Calcd for C₂₆H₃₄ClN₂O₃Rh: C, 55.67; H, 6.11; N, 4.99. Found: C, 55.60; H, 5.98; N, 4.80. HRMS (FAB): calcd for C₂₆H₃₂ClN₂O₂Rh [M − OH₂]⁺ 542.1207, found: 542.1199.

Synthesis of 3. To a *p*-chlorotoluene solution (0.5 mL) of **1** (26.0 mg, 0.050 mmol) and 4 Å molecular sieves (100 mg) was added NH(Pr)₂ (140 μL, 1.0 mmol). After being stirred at 80 °C for 3 h, the mixture was filtered. The concentrated filtrate was purified by column chromatography on silica gel (hexane/ethyl acetate = 1:4) to give **3** (23.2 mg, 0.040 mmol, 80%). ¹H NMR (300 MHz, CDCl₃, rt): 1.27 (s, 6H, CH₃), 1.40 (s, 9H, C(CH₃)₃), 1.65 (s, 6H, CH₃), 2.15 (s, 3H, CH₃), 2.18 (s, 2H, H₂O), 4.28 (d, *J*_{HH} = 8.4 Hz, 2H, CH₂), 4.45 (d, *J*_{HH} = 8.4 Hz, 2H, CH₂), 6.52 (d, *J*_{HH} = 8.0 Hz, 2H, C₆H₄), 6.73 (d, *J*_{HH} = 8.0 Hz, 2H, C₆H₄), 7.59 (s, 2H). ¹³C NMR (75 MHz, CDCl₃, rt): 20.4, 27.0, 28.8, 31.8, 35.2, 66.7, 82.7, 124.6, 126.6, 130.6, 131.4, 134.5 (d, *J*_{RhC} = 35.3 Hz), 136.2, 145.9, 171.3 (d, *J*_{RhC} = 5.7 Hz), 186.4 (d, *J*_{RhC} = 28.5 Hz). IR (KBr, cm^{−1}): 3324, 2961, 1622, 1586. Anal. Calcd for C₂₇H₃₆ClN₂O₃Rh: C, 56.40; H, 6.31; N, 4.87. Found: C, 56.27; H, 6.11; N, 4.56. HRMS (FAB): calcd for C₂₇H₃₄ClN₂O₂Rh [M − H₂O]⁺ 556.1364, found 556.1384.

Synthesis of 5. To a toluene solution (2 mL) of **1** (26.0 mg, 0.0500 mmol), 2-chloropyridine (24 μL, 0.25 mmol), and 4 Å molecular sieves (200 mg) was added NH(Pr)₂ (140 μL, 1.0 mmol). After being stirred at 70 °C for 1 h, the mixture was filtered. The concentrated filtrate was purified by column chromatography on silica gel (CH₂Cl/MeOH = 8:1) to give **5** (27.4 mg, 0.047 mmol, 94%). ¹H NMR (300 MHz, CDCl₃, rt): 1.05 (s, 6H, CH₃), 1.41 (s, 9H, C(CH₃)₃), 1.77 (s, 6H, CH₃), 4.28 (d, *J*_{HH} = 8.1 Hz, 2H, CH₂), 4.46 (d, *J*_{HH} = 8.1 Hz, 2H, CH₂), 6.39 (d, *J*_{HH} = 8.4 Hz, 1H, C₅NH₅), 7.04 (t, *J*_{HH} = 6.0 Hz, 1H, C₅NH₅), 7.29 (d, *J*_{HH} = 8.1 Hz, 1H, C₅NH₅), 7.66 (s, 2H), 8.16 (d, *J*_{HH} = 8.1 Hz, 1H, C₅NH₅), 15.8 (brs, *w*_{1/2} = 27.1 Hz, 1H, NH). ¹³C NMR (75 MHz, CDCl₃, rt): 27.6, 27.9, 31.8, 35.1, 66.5, 82.5, 118.5, 125.0, 129.4, 136.2, 137.8, 138.0, 146.0, 169.6 (d, *J*_{RhC} = 5.1 Hz), 184.3 (d, *J*_{RhC} = 38.3 Hz), 185.5 (d, *J*_{RhC} = 25.7 Hz). IR (KBr, cm^{−1}): 3447 (NH), 2964, 1623, 1571. Anal. Calcd for C₂₅H₃₂Cl₂N₃O₂Rh: C, 51.74; H, 5.56; N, 7.24. Found: C, 51.35; H, 5.53; N, 6.83. HRMS (FAB): calcd for C₂₅H₃₂ClN₃O₂Rh [M]⁺: 544.1238, found 544.1254.

X-ray Analyses. Single crystals of **3** and **5** suitable for X-ray diffraction study were obtained from slow vaporization of a hexane/ethyl acetate/dichloromethane solution and hexane/ethyl acetate at room temperature, respectively. The diffraction data were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction was applied by using SADABS. The structure was solved by direct methods and refined by full-matrix least-squares on *F*² using SHELXTL. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data for **3**: C₂₇H₃₆ClN₂O₃Rh; *M*_r = 574.94; temperature 153 K; monoclinic, *P*2₁/c; *a* = 15.962(2) Å, *b* = 10.6524(14) Å, *c* = 17.215(2) Å, β = 114.013(2)°; *V* = 2673.9(6) Å³; *Z* = 4; ρ_{calcd} = 1.428 Mg/m³; μ = 0.769 mm^{−1}; reflections collected 18 678, independent reflections 6137 [*R*(int) = 0.0399]; data/restraints/parameters 6137/0/323; goodness-of-fit on *F*²: 1.081; final *R* indices [*I* > 2σ(*I*)] *R*1 = 0.0320, *wR*2 = 0.0803; *R* indices (all data) *R*1 = 0.0364, *wR*2 = 0.0834; largest diff peak/hole 1.223 and −0.314 e Å^{−3}. Crystallographic data for **5**: C₂₅H₃₂Cl₂N₃O₂Rh·1.5(CH₂Cl₂); *M*_r = 706.22; temperature 153 K; triclinic, *P*1̄; *a* = 13.364(4) Å, *b* = 15.834(5) Å, *c* = 16.154(5) Å, α = 105.268(7)°, β = 97.952(6)°, γ = 90.103(7)°; *V* = 3263.2(18) Å³; *Z* = 4; ρ_{calcd} = 1.438 Mg/m³; μ = 0.960 mm^{−1}; reflections collected 22 966, independent reflections 14 967 [*R*(int) = 0.0478]; data/restraints/parameters 14 967/1/682; goodness-of-fit on *F*²: 1.022; final *R* indices [*I* > 2σ(*I*)] *R*1 = 0.0697, *wR*2 = 0.1737; *R* indices (all

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data) $R1 = 0.1251$, $wR2 = 0.2041$; largest diff peak/hole 2.471 and $-1.618 \text{ e } \text{\AA}^{-3}$.

Acknowledgment. This research was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology, Japan (460:18065011, Concerto Catalyst), the Japan Society for

the Promotion of Science (18350049), G-COE in chemistry (Nagoya), and The Mitsubishi Foundation.

Supporting Information Available: Spectral data for **2**, **3**, and **5** and CIFs of **3** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM8002174