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

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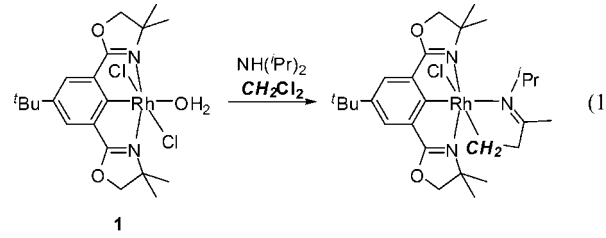
*Summary: Oxidative addition of chlorobenzene and p-chlorotoluene by (Phebox)RhCl$_2$(H$_2$O) (**1**) in the presence of diisopropylamine was examined and was shown to produce the corresponding aryl complexes (Phebox)RhCl(Ar)(H$_2$O) in high yields via C−Cl bond cleavage. Reaction of **1** with chloropyridine 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 RhCl$_3$(py)$_3$,[5] (PCy$_3$)$_2$Rh(H)(Cl)$_2$,[6] [(diiminate)Rh(cod)],[7] [(PPh$_3$)$_3$RhF],[8] and (PNP)MX$_2$.[9]

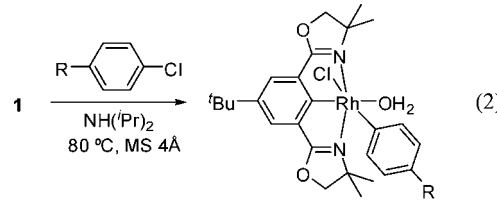
In this context, we have reported that (Phebox)Rh(Cl)$_2$(H$_2$O) [**1**; Phebox = bis(oxazolinyl)phenyl][10] exhibits high reactivity toward double C−Cl bond activation of CH$_2$Cl$_2$ in the presence of NH(*i*Pr)$_2$ and successive C−C bond formation between CH$_2$Cl$_2$ and NH(*i*Pr)$_2$ to provide 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 CH$_2$Cl$_2$. Here we report a significant effect of amines to the reaction of **1** with aryl chlorides to provide aryl-Rh complexes.



1 (1)

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(H$_2$O) (**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*-CH$_3$C$_6$H$_4$)Cl(H$_2$O) (**3**) in 80% yield.



2 : R = H (90%)
3 : R = Me (80%) (2)

Complexes **2** and **3** were characterized on the basis of ^{1}H and ^{13}C NMR and IR spectra. In the ^{13}C 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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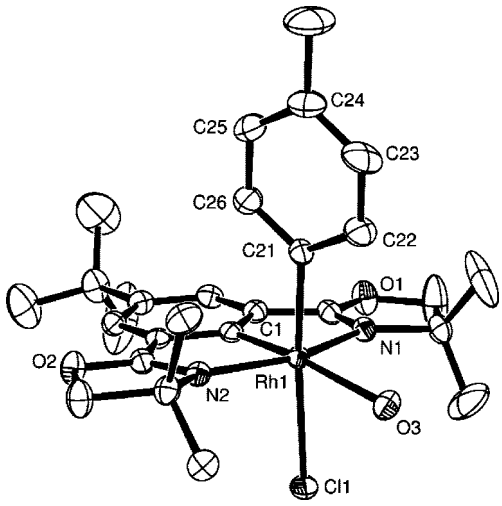
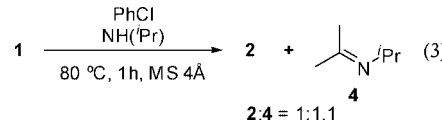


Figure 1. ORTEP diagram of **3** at the 50% probability level. Selected bond lengths (Å): Rh1−C1 1.909(4), Rh1−C21 2.028(5), Rh1−N1 2.078(4), Rh1−N2 2.067(4), Rh1−Cl1 2.5144(14), Rh1−O3 2.292(3).

(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)-$RhCl_2(H_2O)$ (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 $(Phebox)Rh(Cl)_2(H_2O)$ did not react with chlorobenzene even at 120 °C for 40 h.[13] Therefore, the presence of $NH(^iPr)_2$ 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]

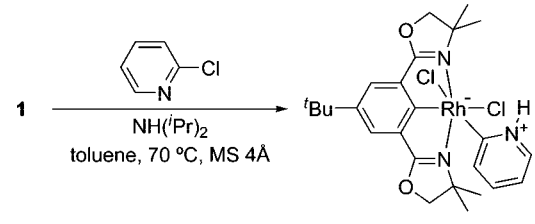
To gain insight into the C−Cl bond activation by **1** with the amine, we checked the crude products on the reaction of **1** with chlorobenzene by ^{1}H NMR spectroscopy. Although other Rh complexes besides **2** were not detected, the formation of $N(=CMe_2)(^iPr)$ (**4**) as well as **2** was observed with the **2**:**4** ratio of 1:1.1 (eq 3).[16] The formation of **4** is formally derived from dehydrogenation of $NH(^iPr)_2$, 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]

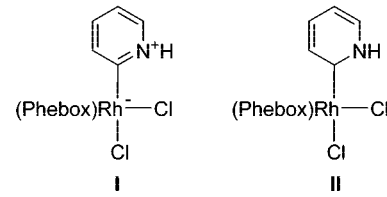


In contrast to $NH(^iPr)_2$, NEt_3 is not a suitable reagent for C−Cl bond activation. Addition of NEt_3 instead of $NH(^iPr)_2$ to a chlorobenzene solution of **1** at 80 °C for 1 h led to a decrease in the yield of **2** (35%).

It is interesting to note that an acetate analogue, $(Phebox)Rh(OAc)_2(H_2O)$, did not undergo C−Cl bond activation but did undergo C−H bond activation to produce the corresponding chlorophenyl complex $(Phebox)Rh(OAc)(C_6H_4Cl)$.[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 $NH(^iPr)_2$ in toluene at 70 °C to provide the rhodium complex **5** in 94% yield (eq 4). The ^{1}H NMR spectrum of **5** showed the low-field signal of the N−H proton at δ 15.8 (1H), which disappeared on treatment with D_2O. The IR spectrum of **5** also exhibited the ν_{NH} band at 3447 cm^{-1}. In the ^{13}C NMR spectrum, two low-field singals 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.





The molecular structure of **5** was confirmed by X-ray diffraction (Figure 2). The Phebox ligand and two chlorides are coordinated to the Rh atom. The C_5NH_5 ligand of **5** as observed in the tolyl ligand of **3** is bonded perpendicularly to the Phebox plane. The Rh−C bond lengths of 1.998(6) and 2.015(6) Å were comparable with those of **3**. The Rh−Cl bond length was also ca. 0.08 Å shorter than that of **3** probably due to weaker *trans* influence of the C_6H_5N ligand. The C_5NH_5 moiety of **5** is described to be a pyridinium rhodate (**I**).[19] Alternatively such

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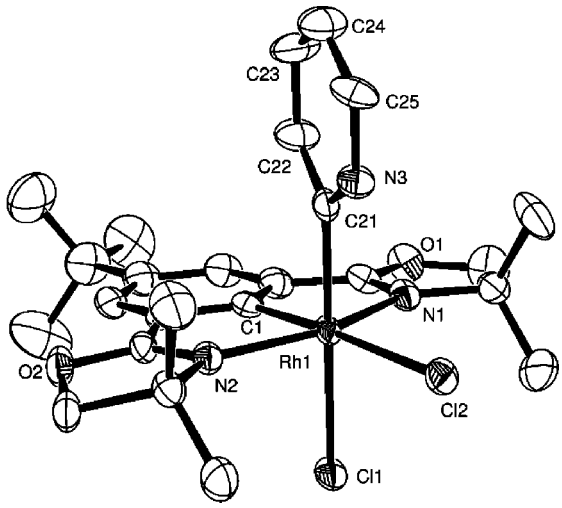

Figure 2. ORTEP diagram of **5** with 50% probability level ellipsoids. Selected bond lengths (Å): Rh1−C1 1.928(6), Rh1−C21 1.998(6), Rh1−N1 2.064(5), Rh1−N2 2.089(5), Rh1−Cl1 2.434317, Rh1−Cl2 2.4856(17); Rh2−C26 1.921(6), Rh2−C46 2.015(6), Rh2−N4 2.071(6), Rh2−N5 2.086(5), Rh2−Cl3 2.4384(17), Rh2−Cl4 2.4859(18).

a pyridiunium 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 chorides 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. ^{1}H and ^{13}C NMR spectra were obtained at 25 °C on a Varian Mercury 300 spectrometer. ^{1}H NMR chemical shifts are reported in δ units, in ppm relative to the singlet at 7.26 ppm for $CDCl_3$. ^{13}C NMR spectra are reported in terms of chemical shift (δ, ppm) relative to the triplet at δ = 77.0 ppm for $CDCl_3$. 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 Yanoco 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 $NH(^iPr)_2$ (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/dichlorometane/hexane to give **2** (10.1 mg, 0.018 mmol, 90%). ^{1}H NMR (300 MHz, $CDCl_3$, rt): 1.25 (s, 6H, CH_3), 1.41 (s, 9H, C(CH_3)$_3$), 1.66 (s, 6H, CH_3), 1.71 (s, 2H, H_2O), 4.28 (d, J_{HH} = 8.4 Hz, 2H, CH_2), 4.45 (d, J_{HH} = 8.4 Hz, 2H, CH_2), 6.67−6.70 (m, 3H, C$_6H_5$), 6.86−6.92 (m, 2H, C$_6H_5$), 7.60 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 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 $C_{26}H_{34}ClN_2O_3Rh$: C, 55.67; H, 6.11; N, 4.99. Found: C, 55.60; H, 5.98; N, 4.80. HRMS (FAB): calcd for $C_{26}H_{32}ClN_2O_2Rh$ [M − OH$_2$]$^+$ 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 $NH(^iPr)_2$ (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%). ^{1}H NMR (300 MHz, $CDCl_3$, rt): 1.27 (s, 6H, CH_3), 1.40 (s, 9H, C(CH_3)$_3$), 1.65 (s, 6H, CH_3), 2.15 (s, 3H, CH_3), 2.18 (s, 2H, H_2O), 4.28 (d, J_{HH} = 8.4 Hz, 2H, CH_2), 4.45 (d, J_{HH} = 8.4 Hz, 2H, CH_2), 6.52 (d, J_{HH} = 8.0 Hz, 2H, C$_6H_4$), 6.73 (d, J_{HH} = 8.0 Hz, 2H, C$_6H_4$), 7.59 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 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 $C_{27}H_{36}ClN_2O_3Rh$: C, 56.40; H, 6.31; N, 4.87. Found: C, 56.27; H, 6.11; N, 4.56. HRMS (FAB): calcd for $C_{27}H_{34}ClN_2O_2Rh$ [M − H$_2$O]$^+$ 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 $NH(^iPr)_2$ (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 (CH_3Cl/MeOH = 8:1) to give **5** (27.4 mg, 0.047 mmol, 94%). ^{1}H NMR (300 MHz, $CDCl_3$, rt): 1.05 (s, 6H, CH_3), 1.41 (s, 9H, C(CH_3)$_3$), 1.77 (s, 6H, CH_3), 4.28 (d, J_{HH} = 8.1 Hz, 2H, CH_2), 4.46 (d, J_{HH} = 8.1 Hz, 2H, CH_2), 6.39 (d, J_{HH} = 8.4 Hz, 1H, C$_5$NH_5), 7.04 (t, J_{HH} = 6.0 Hz, 1H, C$_5$NH_5), 7.29 (d, J_{HH} = 8.1 Hz, 1H, C$_5$NH_5), 7.66 (s, 2H), 8.16 (d, J_{HH} = 8.1 Hz, 1H, C$_5$NH_5), 15.8 (brs, $w_{1/2}$ = 27.1 Hz, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$, 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 $C_{25}H_{32}Cl_2N_3O_2Rh$: C, 51.74; H, 5.56; N, 7.24. Found: C, 51.35; H, 5.53; N, 6.83. HRMS (FAB): calcd for $C_{25}H_{32}ClN_3O_2Rh$ [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**: $C_{27}H_{36}ClN_2O_3Rh$; M_r = 574.94; temperature 153 K; monoclinic, $P2_1/c$; a = 15.962(2) Å, b = 10.6524(14) Å, c = 17.215(2) Å, β = 114.013(2)°; V = 2673.9(6) Å^3; Z = 4; ρ_{calcd} = 1.428 Mg/m^3; 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 [$I > 2\sigma(I)$] R1 = 0.0320, wR2 = 0.0803; R indices (all data) R1 = 0.0364, wR2 = 0.0834; largest diff peak/hole 1.223 and −0.314 e Å^{-3}. Crystallographic data for **5**: $C_{25}H_{32}Cl_2N_3O_2Rh \cdot 1.5(CH_2Cl_2)$; M_r = 706.22; temperature 153 K; triclinic, $P\bar{1}$; 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) Å^3; Z = 4; ρ_{calcd} = 1.438 Mg/m^3; 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 [$I > 2\sigma(I)$] R1 = 0.0697, wR2 = 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 e $Å^{-3}$.

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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.

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