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Single and Double C–Cl-Activation of Methylene Chloride by P,N-ligand Coordinated Rhodium Complexes

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Abstract: The synthesis of Rh^{I} complexes with P-functionalized aminopyridine ligands is reported as well as the first simultaneous observation of a single and double activation of C–Cl bonds of methylene chloride affording both a dimeric Rh^{III} complex bearing terminal CH_2Cl groups in addition to a binuclear Rh^{III} complex with a bridging μ-CH_2 group. The structures of the oxidative addition products were obtained by X-ray diffraction studies and NMR experiments were performed to elucidate some aspects of the reaction pathway.

Keywords: C–Cl activation · NMR spectroscopy · P,N-ligand · rhodium · X-ray diffraction

Introduction

The oxidative addition of molecules containing a C–X bond (X = I, Br, Cl) to low-valent transition metals is of great academic and industrial interest as the resulting compounds are key intermediates in many catalytic cycles. Moreover, the activation of the C–X bond is often the rate determining step of the overall reaction, especially when X = Cl.[1] Therefore, a detailed knowledge of this oxidative addition step is of great interest.

The addition of CH_3X (X = I, Br, Cl), CH_2I_2, and CH_2Br_2 to various transition metal centers is well documented in the literature.[2] However, the activation of the relatively inert C–Cl bond (bond dissociation energy ≈ 338 kJ mol^{-1}),[3] especially in CH_2Cl_2, is more challenging than for C–Br or C–I bonds. Hence, fewer examples for the oxidative addition of CH_2Cl_2 under mild conditions have been reported so far. The most widely known reaction is the simple oxidative addition of one molecule of CH_2Cl_2 to electron-rich transition metal complexes stabilized by mono-[4,5,6] and polydentate[7] phosphorous ligands, mono-,[8] bi-,[9,10] and polydentate[11,12,13] nitrogen ligands, hybrid nitrogen-phosphorous ligands,[14,15,16] sulphur macrocycles,[17] and pyridine/phosphine functionalized NHCs[18,19] affording complexes with a terminal CH_2Cl group.

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The double activation of one molecule of CH_2Cl_2 to two distinct rhodium centers affording bridging μ-methylene complexes is rare, and has only been reported for the basic Rh^{I} complexes $[(dppe)Rh(\mu\text{-}Cl)]_2$[20] (dppe = 1,2-bis(diphenylphosphino)-ethane), $[(PR_3)_2Rh(\mu\text{-}Cl)]_2$ (R = Et, Ph_2Me),[21] as well as for the isocyanide complexes $[Rh(CN\mathit{t}Bu)(\mu\text{-}pz)]_2$[22] (Bu = butyl, pz = pyrazolate), $[Rh(CN\mathit{t}Bu)(\mu\text{-}S\mathit{t}Bu)]_2$,[23] *syn*-$[Rh(\mu\text{-}NH\{p\text{-}toluyl\})(CN\mathit{t}Bu)_2]_2$,[24] and *syn*-$[(cod)Rh(\mu\text{-}NH\{p\text{-}toluyl\})_2Rh(CN\mathit{t}Bu)_2]$[24] (cod = 1,5-cyclootadiene).

To date, the reaction conditions determining the formation of either the terminal or the bridging binding mode are still unknown. In light of the first discovery of the dimeric Rh^{III} complex containing a bridging μ-CH_2 group, Fryzuk et al. suggested that only basic and chelating ligands, such as dppe, could afford such compounds.[20] However, this assumption was refuted by Brunet et al. who performed detailed NMR experiments with monophosphine-containing complexes and showed that the formation of a μ-methylene species is not limited to binuclear Rh^{I} starting complexes stabilized by chelating phosphine ligands, but could also be obtained from mononuclear, as well as binuclear monophosphine-ligand complexes.[21]

Herein, we report on the synthesis of Rh^{I} complexes with P-functionalized aminopyridine ligands[25] and their potential for the activation of methylene chloride. For the first time, the formation of both a Rh^{III} complex bearing a terminal CH_2Cl group and a binuclear Rh^{III} complex with a bridging μ-CH_2 group are observed simultaneously. X-ray single crystal structures of the oxidative addition products are provided and NMR experiments are performed in order to elucidate some aspects of the reaction pathway.

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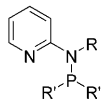
Results and Discussion

We recently reported a multi-gram synthesis protocol for the preparation of a variety of P,N-ligands and the preparation of their corresponding iridium complexes.[26] These ligands (see Scheme 1) were also used to stabilize rhodium

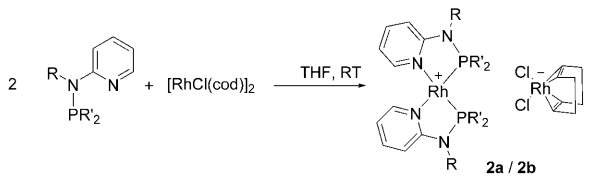


R = 2-pyridyl	R' = Ph	Py_2NPPh_2	**(1a)**
R = Me	R' = Ph	$PyMeNPPh_2$	**(1b)**
R = 2-pyridyl	R' = Cy	Py_2NPCy_2	**(1c)**
R = 2-pyridyl	R' = *t*Bu	$Py_2NP(tBu)_2$	**(1d)**
R = 2-pyridyl	R' = *i*Pr	$Py_2NP(iPr)_2$	**(1e)**

Scheme 1. Nomenclature of the P,N-ligands.

complexes and we discovered that in contrast to iridium, a rather unexpected chemistry takes place depending on the solvent as well as the nature of the P,N-ligand.

As previously reported,[27] two equivalents of P,N-ligand **1a** react with $[RhCl(cod)]_2$ in THF to form the ionic bimetallic Rh complex **2a** [$^{31}P\{^1H\}$ NMR, δ (CD_2Cl_2) = 126.9 ppm, J_{P-Rh} = 174.8 Hz] (Scheme 2). When this reaction is performed with P,N-ligand **1b**, a similar ionic Rh complex **2b** [$^{31}P\{^1H\}$ NMR, δ (CD_2Cl_2) = 128.4 ppm, J_{P-Rh} = 173.3 Hz] is obtained in quantitative yield as a yellow solid which is almost insoluble in THF, diethylether, and benzene but very soluble in chlorinated solvents such as CH_2Cl_2. The crystal structure of complex **2b** is shown in Figure 1.



Scheme 2. Formation of bimetallic ionic Rh complexes **2a** (R = 2-Py, R′ = Ph) and **2b** (R = Me, R′ = Ph).

However, the formation of this ionic bimetallic species seems to be highly dependent on the substituents at the phosphorus center, since only P,N-ligands carrying phenyl substituents (regardless of the amine substitution pattern) afford these ionic Rh complexes. When two equivalents of a P,N-ligand with cyclohexyl (**1c**), isopropyl (**1e**), or *tert*-butyl (**1d**) substituents are reacted with $[RhCl(cod)]_2$ in THF, no well-defined complexes can be obtained, but merely a mixture of unidentified products as observed by ^{31}P NMR spectroscopy.

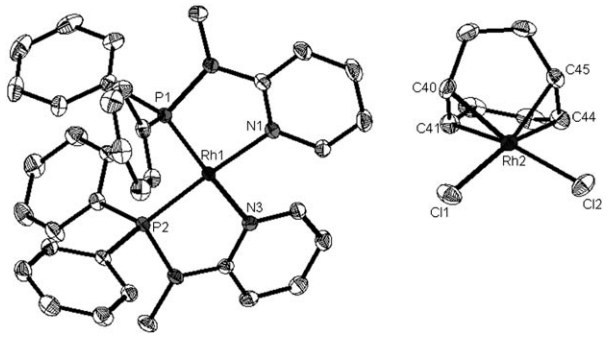


Figure 1. Molecular structure of $[(PyMeNPPh_2)_2Rh][RhCl_2(cod)]$ (**2b**). Hydrogen atoms and solvent molecules omitted for clarity; ellipsoids set to 40% probability level. Selected bond lengths [Å] and angles [°]: N1–Rh1 2.1274(19), N3–Rh1 2.1269(18), P1–Rh1 2.1809(6), P2–Rh1 2.1844(6), Cl1–Rh2 2.3797(7), Cl2–Rh2 2.3706(7), C40–Rh2 2.092(3), C41–Rh2 2.098(3), C45–Rh2 2.100(3), C44–Rh2 2.095(2), P1–Rh1–P2 99.90(2), N1–Rh1–P1 80.62(5), N3–Rh1–P2 81.07(5), N3–Rh1–N1 99.25(7), Cl2–Rh2–Cl1 91.19(3), C40–Rh2–Cl1 88.59(9), C41–Rh2–Cl1 92.29(9), C44–Rh2–Cl2 87.30(8), C45–Rh2–Cl2 92.39(7).

In order to elaborate a general method for the preparation of distinct Rh complexes with our P,N-ligands, we changed the solvent from THF to CH_2Cl_2 and were very pleased to find that well-defined complexes could be prepared with all ligands, except for **1a** and **1b** bearing phenyl substituents on the phosphorus atom. Dropwise addition of a solution of **1a** or **1b** in CH_2Cl_2 to a solution of $[RhCl(cod)]_2$ always affords a mixture of two compounds as determined by ^{31}P NMR spectroscopy. In the case of **1b**, the minor signal [$^{31}P\{^1H\}$ NMR, δ (CD_2Cl_2) = 128.2 ppm, J_{P-Rh} = 173.1 Hz] could be attributed to the bimetallic ionic Rh complex **2b**, whereas the major signal [$^{31}P\{^1H\}$ NMR, δ (CD_2Cl_2) = 105.5 ppm, J_{P-Rh} = 162.9 Hz] belonged to a yet unknown complex **5b**. However, after a few days, crystalline material had precipitated from the solution and a mixture of deep orange (major) (**3b**) and pale yellow (minor) (**4b**) crystals were obtained and both were analyzed by single crystal X-ray diffraction analysis. The molecular structures of **3b** and **4b** are shown in Figures 2 and 3, respectively.

The results of the single crystal analysis showed that the obtained crystals belonged to two distinct complexes in which the activation of C–Cl bonds had taken place. The activation of methylene chloride by Rh-complexes affording μ-methylene bridged bimetallic complexes[20–22] or dimeric Rh^{III} complexes with two activated molecules of CH_2Cl_2[19] has been reported before. However, the simultaneous formation of both compounds has to our knowledge not been described previously. In order to gain a better understanding of the reaction and determine the active species involved in the activation of methylene chloride, we performed

Abstract in German: Die Synthese von Rh^I Komplexen mit P-funktionalisierten Aminopyridinliganden und die erste gleichzeitige Beobachtung einer einfachen und doppelten C–Cl Bindungsaktivierung von Dichlormethan wird beschrieben. Diese Bindungsaktivierung führt sowohl zu einem dimeren Rh^{III} Komplex mit terminalen CH_2Cl Gruppen, als auch zu einem binuklearen Rh^{III} Komplex mit einer verbrückenden Methylengruppe. Die Strukturen der oxidativen Additionsprodukte wurden mittels Einkristalltröntgenstrukturanalyse charakterisiert. Außerdem wurden detaillierte NMR Experimente durchgeführt, um gewisse Aspekte des Reaktionsmechanismus aufzuklären.

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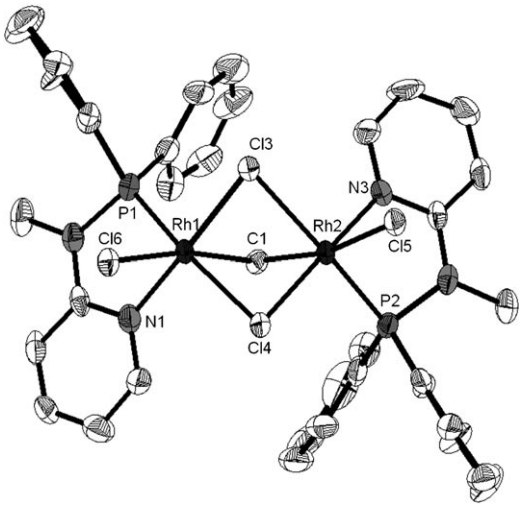


Figure 2. Molecular structure of $[(PyMeNPPh_2RhCl)_2(\mu\text{-}Cl)_2(\mu\text{-}CH_2)]$ (**3b**). Hydrogen atoms and solvent molecules omitted for clarity; ellipsoids set to 40% probability level. Selected bond lengths [Å] and angles [°]: C1–Rh2 2.036(10), C1–Rh1 2.041(9), N1–Rh1 2.017(9), N3–Rh2 2.040(8), P1–Rh1 2.169(3), P2–Rh2 2.174(3), Cl3–Rh1 2.358(3), Cl3–Rh2 2.514(3), Cl4–Rh2 2.378(2), Cl4–Rh1 2.550(3), Cl5–Rh2 2.503(3), Cl6–Rh1 2.531(2), Rh2–C1–Rh1 92.7(4), Cl5–Rh2–Cl3 86.72(8), Cl4–Rh2–Cl3 85.10(8), P2–Rh2–Cl5 98.63(9), N3–Rh2–Cl5 86.7(2), Cl4–Rh2–Cl5 95.55(9), Cl6–Rh1–Cl4 86.92(8), Cl3–Rh1–Cl4 84.72(9), Cl3–Rh1–Cl6 97.88(9), P1–Rh1–Cl6 99.17(9), N1–Rh1–Cl6 85.1(2).

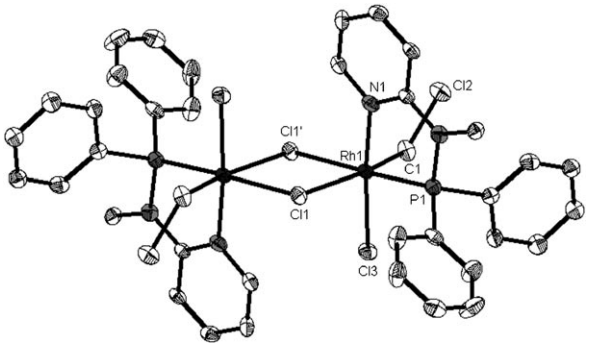


Figure 3. Molecular structure of $[\{PyMeNPPh_2Rh(CH_2Cl)Cl(\mu\text{-}Cl)\}_2]$ (**4b**). Hydrogen atoms and solvent molecules omitted for clarity; ellipsoids set to 40% probability level. Selected bond lengths [Å] and angles [°]: N1–Rh1 2.031(7), P1–Rh1 2.160(2), Cl1–Rh1 2.511(2), Cl1′–Rh1 2.468(2), Cl3–Rh1 2.318(2), C1–Rh1 2.010(8), C1–Cl2 1.801(9), P1–Rh1–Cl3 90.28(8), P1–Rh1–Cl1 101.22(8), P1–Rh1-Cl1' 178.19(9), N1–Rh1–P1 83.2(2), C1–Rh1–P1 91.6(3), N1–Rh1–Cl3 173.5(2), N1–Rh1–Cl1 89.0(2), N1–Rh1–Cl1' 95.9(2), C1–Rh1–N1 94.2(3), Cl3–Rh1–Cl1 92.13(7), Cl3–Rh1–Cl1' 90.56(8).

^{31}P NMR kinetic experiments with Ph_3PO as an internal standard (Figure 4).

As determined by these NMR experiments, the active species for the activation of methylene chloride is compound **5b**, whereas the bimetallic ionic complex **2b** does not react with CH_2Cl_2 and stays unchanged in the reaction mixture. Therefore, further attempts were made to prepare a pure sample of **5b** and suppress the formation of **2b**. However, the only way to suppress the formation of **2b** was to perform the reaction with an excess of Rh precursor, affording a 1:1 mixture of **5b** and unreacted starting material (Scheme 3). The information obtained from NMR experiments show that the Rh center in **5b** is coordinated by one

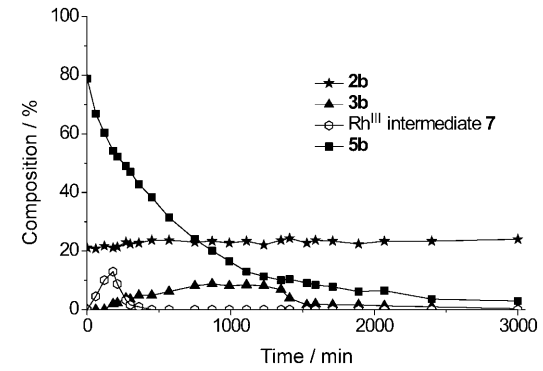
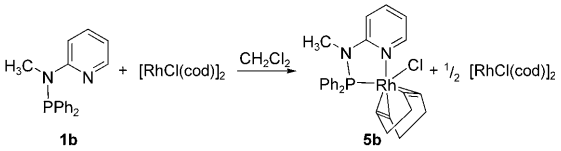


Figure 4. Time-resolved ^{31}P NMR experiment of the CH_2Cl_2 activation.



Scheme 3. Preparation of **5b** with an excess of Rh precursor.

molecule of ligand **1b** as well as one chelating molecule of cyclooctadiene, comparable to the already reported equivalent Ir complexes of this type.[26]

We therefore assumed that in solution, **5b** must be an equilibrium between a four- or fivefold-coordinated Rh^I complex which is highly reactive. A similar complex has been reported by Danopoulos et al., but a crystal structure analysis revealed that the pyridine moiety of the ligand does not coordinate to the metal center, reducing the coordination number to four.[19] Hence, we were interested in determining whether the pyridyl part in our P,N-ligands really coordinates to the metal center or not, since this is not obvious for complex **5b**. Use of ligand **1c** with two pyridyl groups in the molecule should, in the case of a pyridyl coordination to the transition metal center, lead to inequivalent and clearly distinguishable pyridyl rings in a ^1H NMR spectrum.

Interestingly, in the case of the cyclohexyl ligand **1c**, when reacted with $[RhCl(cod)]_2$ in CH_2Cl_2, no byproducts similar to **2b** were formed and a sharp signal [$^{31}P\{^1H\}$ NMR, δ (CD_2Cl_2) = 125.8 ppm, J_{P-Rh} = 157.6 Hz] similar to **5b** was observed. The obtained complex **5c** was isolated in quantitative yields and extensively characterized by NMR spectroscopy and elemental analysis, which revealed a most likely fivefold-coordinated structure with a coordinated P,N-ligand as well as one coordinated cyclooctadiene unit and a chlorine atom in the molecule (Scheme 4). The ^1H NMR data shows the tight coordination of one pyridyl unit to the metal center (an exchange of the pyridyl rings is not observed) as well as an analogy of the olefinic $C-H_{cod}$ signals in **5c** to its

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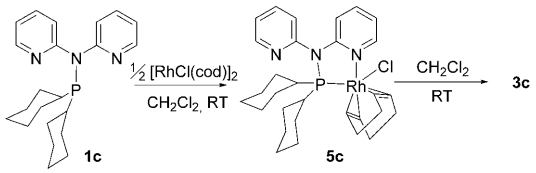


Scheme 4. Preparation of **5c** and reaction with CH_2Cl_2 affording μ-methylene complex **3c**.

corresponding fivefold-coordinated Ir complex.[26] Both complexes exhibit only one broad signal for all four olefinic C–H_{cod} protons at $\delta = 4.96$ and 3.90 ppm, respectively. However, all attempts to prepare single crystals suitable for X-ray analysis were unsuccessful since **5c** could only be prepared in methylene chloride, which also reacts with the latter, leading to the μ-methylene bridged complex **3c** (Figure 5).

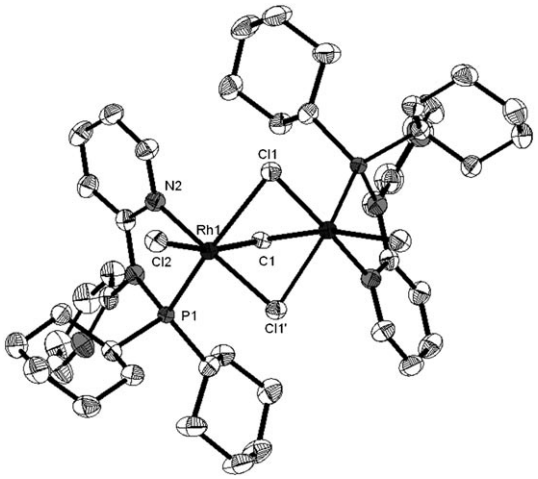


Figure 5. Molecular structure of $[(Py_2NPCy_2RhCl)_2(\mu\text{-}Cl)_2(\mu\text{-}CH_2]$ (**3c**). Hydrogen atoms and solvent molecules omitted for clarity; ellipsoids set to 40% probability level. Selected bond lengths [Å] and angles [°]: N2–Rh1 2.005(3), P1–Rh1 2.1853(11), C1–Rh1 2.023(4), Cl1–Rh1 2.6253(10), Cl1′–Rh1 2.3617(9), Cl2–Rh1 2.5143(10), N2–Rh1–P1 83.28(10), C1–Rh1–P1 90.54(9), N2–Rh1–Cl2 89.73(10), N2–Rh1–C1 89.52(13), P1–Rh1–Cl2 104.77(4), Cl2–Rh1–Cl1 85.78(3), Cl1′–Rh1–Cl2 95.41(3), Cl1 < C-Rh1-Cl1' 85.05(4).

Moreover, **5c** is much less reactive for the activation of C–Cl bonds than complex **5b** as determined by further time-resolved NMR experiments. In order to obtain a full conversion of **5c** into **3c** it takes about a month (Figure 6), whereas complex **5b** completely reacts with CH_2Cl_2 in less than 3 days.

Since we were unable to crystallize the active but unstable monomer, thought to be the fivefold-coordinated Rh complex **5c**, we performed an indirect experiment to determine its structural nature. We prepared **5c** by addition of ligand **1c** to a solution of $[RhCl(cod)]_2$ in CH_2Cl_2 and subsequently treated the resulting complex with $AgBF_4$ in order to remove the chlorine atom and obtain the stable fourfold-coordinated ionic complex **6c** (Scheme 5) which could easily

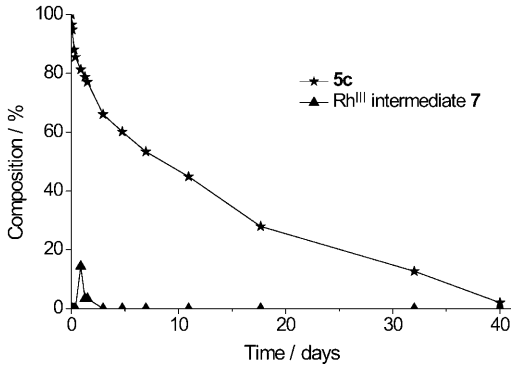
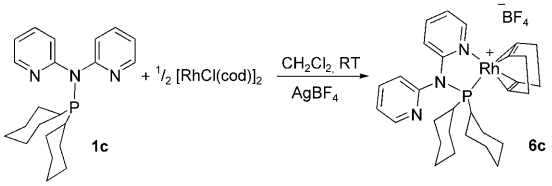


Figure 6. ^{31}P NMR experiment of the CH_2Cl_2 activation of **5c**.



Scheme 5. In situ preparation of **5c** and subsequent treatment with 1 equiv of $AgBF_4$ affording stable ionic complex **6c**.

be crystallized and characterized by single crystal X-ray analysis (Figure 7). Complex **6c** is stable in CH_2Cl_2 and does not lead to an activation of the solvent. In the ^1H NMR spectrum, **6c** exhibits two separate sets of signals for the olefinic C–H_{cod} protons at $\delta = 5.55$ and 4.38 ppm whereas **5c** affords only one broad signal for all these protons at $\delta =$ 4.96 ppm. Even at a temperature of −20 °C, this broad signal does not resolve into two separate signal sets as observed for **6c**, which brings us to the conclusion that for the complexes of type **5** in solution, the chlorine atom is probably coordinating to the metal center and does not act as a dissociated counterion. Nevertheless, an equilibrium of five-

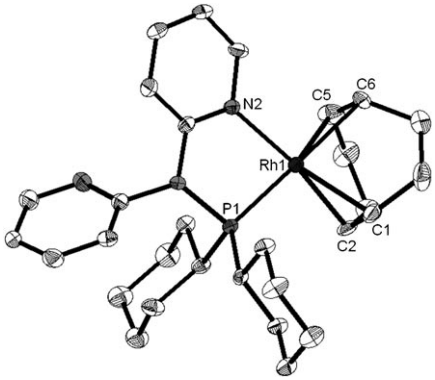


Figure 7. Molecular structure of $[Py_2NPCy_2)Rh(cod)]BF_4$ (**6c**). Hydrogen atoms, solvent molecules, and BF_4-anion omitted for clarity; ellipsoids set to 40% probability level. Selected bond lengths [Å] and angles [°]: P1–Rh1 2.2566(10), N2–Rh1 2.108(3), C1–C2 1.386(6), C2–Rh1 2.162(4), C5–C6 1.339(9), C5–Rh1 2.201(4), C6–Rh1 2.265(4), N2–Rh1–P1 81.58(9), C1–Rh1–C2 37.45(17), C5–Rh1–C6 34.8(2), P1–Rh1–C6 177.10(15), C1–Rh1–P1 100.73(12), C2–Rh1–P1 93.28(11), C5–Rh1–P1 147.56(18), N2–Rh1–P1 81.58(9), N2–Rh1–C5 95.62(16), N2–Rh1–C1 157.54(16), N2–Rh1–C2 164.83(15), N2–Rh1–C6 96.86(15).

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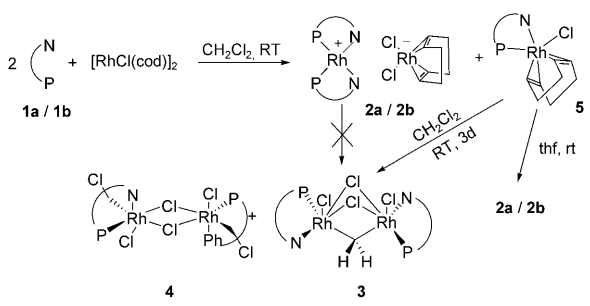
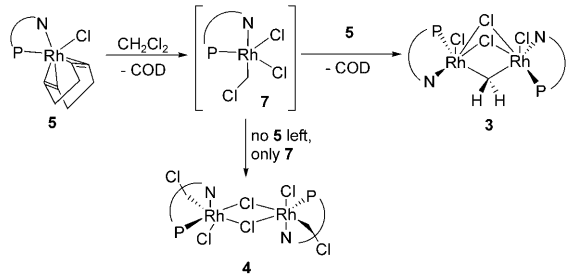
coordinated **5c** and a highly reactive three- or four-coordinated intermediate that results from temporary de-coordination of either the pyridyl or the cyclooctadiene unit from the metal center is possible, though we have no direct evidence for this.

Arising from the high activity of complex **5b** towards the oxidative addition of CH_2Cl_2, we focussed on this complex for further experiments. As mentioned above, the reaction of the P,N-ligands with $[RhCl(cod)]_2$ is highly dependent on the solvent. Therefore, we wanted to understand the formation of the bimetallic ionic complex **2b** and determine whether it results from the monomeric complex **5b** as well. An aliquot of isolated **5b** (containing 85% **5b**) was redissolved in a small quantity of THF and a yellow precipitate rapidly developed, which was washed twice with hexane, dried in vacuum and analyzed by NMR spectroscopy. The ^{31}P NMR signal $\delta = 128.4$ ppm ($J_{P-Rh} = 173.3$ Hz) corresponds exactly to complex **2b**. It seems that in polar donor solvents such as THF a quick rearrangement of the chlorine atom as well as a redistribution of the ligands occur, affording an equilibrium of different Rh species, which in the case of phenyl-substituted ligands **1a** and **1b**, is shifted towards the formation of the sparingly soluble (in THF) complexes **2a** and **2b**, respectively (Scheme 6). The latter are the thermodynamically stable species that precipitate from the solution and can only be redissolved in methylene chloride. However, **2a** and **2b** do not activate CH_2Cl_2, even upon heating of the reaction mixture and long reaction times (2 months).

Having determined the most likely fivefold-coordinated complexes of type **5** to be the active species for the activation of C–Cl bonds, we were furthermore interested to find out how both CH_2Cl_2 activation products **3** and **4** can form simultaneously. Scheme 7 depicts a possible reaction pathway that could be an explanation for the formation of both compounds based on our experimental findings. The NMR experiments in Figure 4 and Figure 6 exhibit the rapid formation of an uncharacterized intermediate **7** that might instantly react with a further equivalent of **5** to afford the μ-methylene bridged Rh complex **3**. Since the latter is almost insoluble it rapidly crystallizes from the solution as bright orange crystals. This reaction takes place as long as the concentration of compound **5** is sufficiently high to enable a quick reaction with intermediate **7**. At the end of the reaction when most of **5** has been consumed, the reactive and



Scheme 6. Preparation and reactivity of complexes **2a**/**b** and **5**.



Scheme 7. Suggested mechanism for the simultaneous formation of **3** and **4**.

unstable Rh^{III}-intermediate **7** dimerizes in order to obtain a stable octahedral coordination sphere, affording complex **4**. The latter is also poorly soluble in CH_2Cl_2 and crystallizes from the solution as a pale yellow solid.

Conclusions

In summary, we have synthesized new rhodium complexes bearing P,N-ligands, that can activate up to two C–Cl bonds of methylene chloride and form μ-methylene bridged Rh^{III} complexes as well as dimeric Rh^{III} complexes with terminal chloromethyl groups. This is the first example of the simultaneous formation of both CH_2Cl_2 activation products. Furthermore, detailed NMR studies were carried out to determine the active species involved in the oxidative addition of the solvent and to gain a better understanding of its possible mechanistic pathway.

Experimental Section

All reactions and manipulations involving air-sensitive compounds were performed under dry argon, using standard Schlenk and glovebox techniques. Non-halogenated solvents were distilled over sodium benzophenone ketyl and halogenated solvents over P_2O_5. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried using molecular sieves, and distilled prior to use. All chemicals were purchased from commercial sources in purities >97% and used without further purification, unless stated otherwise in the synthetic procedure. NMR spectra were obtained using a Varian INOVA 300 or a Varian INOVA 400 spectrometer at 298 K unless stated otherwise. Chemical shifts are reported in ppm relative to the deuterated solvent. Elemental analyses were performed on a Vario elementar EL *III*. X-ray crystal structure analysis of all compounds was performed by using a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished using SIR97,[28] SHELXL-97[29] and WinGX.[30] CCDC 700638 (compound **3c**), CCDC 700639 (compound **3b**), CCDC 700640 (compound **2b**), CCDC 700641 (compound **4b**) and CCDC 700642 (compound **6c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

All P,N-ligands were prepared according to the literature procedure.[26]

*Synthesis of [(PyMeNPPh$_2$)$_2$Rh][RhCl$_2$(cod)] (**2b**):*

$[RhCl(cod)]_2$ (0.098 g, 0.20 mmol) was dissolved in THF (10 mL) and a solution of $PyMeNPPh_2$ (**1b**) (0.117 g, 0.40 mmol) in THF (5 mL) was slowly added at RT with vigorous stirring. Rapidly a yellow solid precipitated and the suspension was stirred overnight. Then, the solvent was

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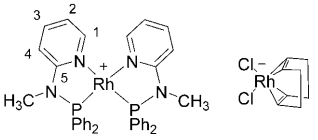
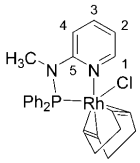


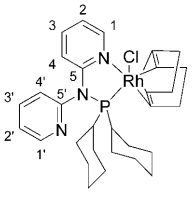
decanted, the solid washed twice with hexane (15 mL), and dried in vacuo, affording **2b** as a bright yellow solid (0.336 g, 87%). ^{1}H NMR (400 MHz, CD_2Cl_2, 296 K): δ = 8.30 (d, J = 5.5 Hz, 2H, H_1), 7.89 (t, J = 7.9 Hz, 2H, H_3), 7.36–7.26 (m, 12H, H_{Ph}), 7.19–7.10 (m, 8H, H_{Ph}), 7.06 (t, J = 5.9 Hz, 2H, H_2), 6.84 (d, J = 8.4 Hz, 2H, H_4), 4.10 (m, 4H, H_{CHcod}), 2.82 (t, J = 2.2 Hz, 6H, H_{CH3}), 2.39–2.28 (m, 4H, H_{CH_2cod}), 1.65–1.54 ppm (m, 4H, H_{CH_2cod}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 161.5 (ddd, J = 7.1, 7.1, 1.6 Hz, C_5), 149.9 (s, C_1), 140.6 (s, C_3), 132.9 (t, J = 6.9 Hz, $C_{o,\ Ph}$), 131.6 (s, $C_{p,\ Ph}$), 130.5 (ddd, J = 26.7, 22.9, 2.6 Hz, $C_{q,\ Ph}$), 129.0 (t, J = 5.5 Hz, $C_{m,\ Ph}$), 117.0 (s, C_2), 110.0 (t, J = 4.2 Hz, C_4), 76.8 (br, C_{CHcod}) 33.9 (t, J = 2.5 Hz, C_{CH3}), 31.6 ppm (s, C_{CH_2cod}). ^{31}P NMR (161 MHz, CD_2Cl_2): δ = 128.3 ppm (d, J = 173.4 Hz). elemental analysis: calcd (%) for $C_{44}H_{42}Cl_2N_4P_2Rh_2$: C 54.74, H 4.38, N 5.80; found: C 54.98, H 4.77, N 5.79.

*Synthesis of [PyMeNPPh$_2$RhCl(cod)] (**5b**):*



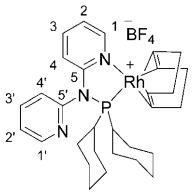
To a solution of $[RhCl(cod)]_2$ (0.148 g, 0.30 mmol) in CH_2Cl_2 (15 mL), a solution of $PyMeNPPh_2$ (**1b**) (0.088 g, 0.30 mmol) in CH_2Cl_2 (5 mL) was added dropwise under stirring. The reaction mixture was stirred for 15 min at room temperature and the solvent removed in vacuo. The residue was washed twice with hexane (15 mL) and dried in vacuo, affording a 1:1 mixture of the title compound and residual $[RhCl(cod)]_2$ in quantitative yields. ^{1}H NMR (400 MHz, CD_2Cl_2, 296 K): δ = 7.97 (t, J = 7.5 Hz, 1H, H_3), 7.80 (d, J = 5.9 Hz, 1H, H_1), 7.72–7.64 (m, 6H, H_{Ph}), 7.62–7.59 (m, 4H, H_{Ph}), 7.09 (t, J = 6.2 Hz, 1H, H_2), 7.06 (d, J = 8.8 Hz, 1H, H_4), 4.74 (s br, 4H, H_{CHcod}), 4.08 (s br, 4H, $H_{CH\text{-}[RhCl(cod)]_2}$), 2.94 (d, J = 5.1 Hz, 3H, H_{CH3}), 2.48–2.37 (m, 4H, $H_{CH_2[RhCl(cod)]_2}$), 2.37–2.26 (m, 8H, H_{CH_2cod}), 1.59 ppm (d, J = 7.7 Hz, 4H, $H_{CH_2[RhCl(cod)]_2}$). ^{13}C NMR (100 MHz, CD_2Cl_2, 296 K): δ = 162.6 (d, J = 18.0 Hz, C_5), 148.9 (s, C_1), 142.6 (s, C_3), 133.1 (d, J = 1.9 Hz, $C_{p,\ Ph}$), 132.9 (d, J = 13.5 Hz, $C_{o,\ Ph}$), 130.1 (d, J = 10.9, $C_{m,\ Ph}$), 128.1 (dd, J = 51.5, 1.9 Hz, $C_{q,\ Ph}$), 117.8 (s, C_2), 111.4 (d, J = 8.1 Hz, C_4), 77.1 (br, C_{CHcod}+$C_{CH[RhCl(cod)]_2}$), 34.4 (d, J = 5.2 Hz, C_{CH3}), 31.5 (s, C_{CH_2cod}), 30.4 ppm (s, $C_{CH_2[RhCl(cod)]_2}$). ^{31}P NMR (162 MHz, CD_2Cl_2, 296 K): δ = 106.0 ppm (d, J = 166.8 Hz). No elemental analysis owing to the mixture of compounds.

*Synthesis of [Py$_2$NPCy$_2$Rh(cod)Cl] (**5c**):*



To a solution of $[RhCl(cod)]_2$ (0.098 g, 0.20 mmol) in CH_2Cl_2 (10 mL) was slowly added a solution of Py_2NPCy_2 (**1c**) (0.147 g, 0.40 mmol) in CH_2Cl_2 (2 mL). The solution was stirred for 10 min at RT and subsequently the solvent was removed in vacuo. The residue was washed with hexane (2× 10 mL) and dried in vacuo, affording the title compound as an orange solid (0.230 g, 92%). ^{1}H NMR (400 MHz, CD_2Cl_2, 296 K): δ = 8.64 (s, 1H, H_1), 8.01 (t, J = 6.6 Hz, 1H, H_3), 7.74 (d, J = 4.0 Hz, 1H, $H_{1'}$), 7.66 (t, J = 6.3 Hz, 1H, $H_{3'}$), 7.51 (t, J = 4.8 Hz, 1H, H_2), 7.27 (d, J = 7.3 Hz, 1H, H_4), 7.03 (t, J = 5.9 Hz, 1H, $H_{2'}$), 6.33 (d, J = 8.1 Hz, 1H, $H_{4'}$), 4.96 (br, 4H, H_{CHcod}), 2.54 (br, 5H, H_{CH_Cy}+H_{CH_2cod}), 2.43–2.30 (m, 5H, H_{CH_Cy}+H_{CH_2cod}), 2.12–1.94 (m, 2H, $H_{CH_2\_Cy}$), 1.90–1.81 (m, 3H, $H_{CH_2\_Cy}$), 1.78–1.56 (m, 5H, $H_{CH_2\_Cy}$), 1.36–0.79 ppm (m, 10H, $H_{CH_2\_Cy}$). ^{13}C NMR (100 MHz, CD_2Cl_2, 296 K): δ = 164.2 (d, J = 14.5 Hz, C_5), 152.7 (s, $C_{5'}$), 151.1 (s, C_1), 148.2 (s, $C_{1'}$), 141.7 (s, $C_{3'}$), 140.6 (s, C_3), 125.0 (s, C_2), 124.2 (s, C_4), 118.2 (s, $C_{2'}$), 112.3 (d, J = 4.5 Hz, $C_{4'}$), 110.0 (br, $C_{CHcod/trans-P}$), 79.8 (br, $C_{CHcod/cis-P}$), 40.3 (m, $C_{CH\ Cy}$), 37.0 (m, C_{CH_Cy}), 31.5 (m, C_{CH_2cod}), 31.3–29.5 (m, C_{CH_2cod}), 28.9–27.5 (m, $C_{CH_2\_Cy}$), 27.3–26.7 (m, $C_{CH_2\_Cy}$), 26.3 ppm (d, J = 0.7 Hz, $C_{CH_2\_Cy}$). ^{31}P NMR (162 MHz, CD_2Cl_2, 296 K): δ = 125.8 ppm (d, J = 157.2 Hz). elemental analysis: calcd (%) for $C_{30}H_{42}ClN_3PRh \times 0.5\ CH_2Cl_2$: C 55.80, H 6.60, N 6.40; found: C 55.70, H 6.50, N 6.47.

*Synthesis of [Py$_2$NPCy$_2$Rh(cod)] BF$_4$ (**6c**):*



To a solution of $[RhCl(cod)]_2$ (0.148 g, 0.30 mmol) in CH_2Cl_2 (10 mL) was slowly added a solution of Py_2NPCy_2 (**1c**) (0.220 g, 0.60 mmol) in CH_2Cl_2 (4 mL). The solution was stirred for 10 min at RT and subsequently a solution of $AgBF_4$ (0.123 g, 0.63 mmol) in acetone (1 mL) was added. After stirring for 30 min, the white precipitate (AgCl) was filtered over a glass frit filled with Celite (2 cm). The frit was washed with CH_2Cl_2 (2×10 mL). The solvent was removed in vacuo, the yellow solid washed with hexane (1× 20 mL) and dried in vacuo (0.340 g, 85%). ^{1}H NMR (400 MHz, CD_2Cl_2, 296 K): δ = 8.67 (d, J = 2.6 Hz, 1H, H_1), 7.99 (t, J = 7.3 Hz, 1H, H_3), 7.71–7.69 (m, 2H, $H_{1'}$+$H_{3'}$), 7.50 (t, J = 5.1 Hz, 1H, H_2), 7.26 (d, J = 7.7 Hz, 1H, H_4), 6.97 (t, J = 6.0 Hz, 1H, $H_{2'}$), 6.31 (d, J = 8.8 Hz, 1H, $H_{4'}$), 5.55 (s br, 2H, H_{CHcod}), 4.38 (s_br, 2H, H_{CHcod}), 2.88–2.40 (m, 7H, H_{CH_Cy}+H_{CH_2cod}), 2.38–2.24 (m, 3H, H_{CH_2cod}), 2.19–0.60 ppm (m, 20H, $H_{CH_2\_Cy}$). ^{13}C NMR (100 MHz, CD_2Cl_2, 296 K): δ = 164.6 (d, J = 15.5 Hz, C_5), 152.8 (s, $C_{5'}$), 151.3 (s, C_1), 148.0 (s, $C_{1'}$), 141.8 (s, $C_{3'}$), 140.6 (s, C_3), 125.2 (s, C_2), 124.4 (s, C_4), 118.1 (s, $C_{2'}$), 112.6 (s, $C_{4'}$), 108.3–107.6 (m, C_{CHcod}), 80.8–78.7 (m, C_{CHcod}), 78.3–76.2 (m, C_{CHcod}), 41.2–39.3 (m, C_{CH_Cy}), 37.8–36.1 (m, C_{CH_Cy}), 33.6–32.0 (m, C_{CH_2cod}), 30.2 (s, C_{CH_2cod}), 29.3–27.8 (m, C_{CH_2cod}+$C_{CH_2\_Cy}$), 27.5–27.0 (m, $C_{CH_2\_Cy}$), 26.5 ppm (m, $C_{CH_2\_Cy}$). ^{31}P NMR (162 MHz, CD_2Cl_2, 296 K): δ = 126.0 ppm (d, J = 157.7 Hz). ^{19}F NMR (376 MHz, CD_2Cl_2, 296 K): δ = −153.7 ppm. elemental analysis: calcd (%) for $C_{30}H_{42}N_3PRhBF_4$: C 54.15, H 6.36, N 6.32; found: C 53.60, H 6.57, N 5.94.

General Procedure for the Activation of CH_2Cl_2 with P,N-Rhodium Complexes

$[RhCl(cod)]_2$ (1.0 equiv) was dissolved in 0.4 mL of CH_2Cl_2 and a solution of P,N-ligand (2.0 equiv) in 0.2 mL CH_2Cl_2 was added dropwise at RT with stirring. The orange solution was left for several days until crystallization was complete. The supernatant solution was decanted, the crystalline material washed twice with CH_2Cl_2 and dried in vacuum.

Owing to the poor solubility of the CH_2Cl_2 activation compounds **3b**, **4b**, and **3c** in common solvents, no NMR-characterization could be obtained. Since the CH_2Cl_2 activation with **5b** is too fast, no pure sample of the μ-methylene complex **3b** and the dimeric chloromethyl complex **4b** could be isolated for elemental analysis. However, the reaction with ligand **1c** is slow enough to be able to obtain a pure sample of μ-methylene compound **5c** for elemental analysis by aborting the reaction after only a few days and washing the crystalline material with CH_2Cl_2. Elemental analysis: calcd (%) for $C_{45}H_{62}Cl_4N_6P_2Rh_2 \times 1\ CH_2Cl_2$: C 46.76, H 5.46, N 7.11; found: C 46.43, H 5.39, N 7.08.

Crystallographic parameters for all analyzed compounds are presented in Table 1.

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Table 1. Crystal parameters for all analyzed compounds.

Compound	**2b**	**3b**	**4b**	**3c**	**6c**
Formula	$C_{44}H_{46}Cl_2N_4P_2Rh_2 \times 0.5$ THF	$C_{37}H_{36}Cl_4N_4P_2Rh_2 \times 3$ CH_2Cl_2	$C_{38}H_{38}Cl_4N_4P_2Rh_2$	$C_{45}H_{62}Cl_4N_6P_2Rh_2 \times 3$ CH_2Cl_2	$C_{30}H_{42}BF_4N_3PRh$
Crystal system	triclinic	triclinic	triclinic	monoclinic	orthorhombic
Space group	*P*1	*P*1	*P*1	*C*2/*c*	*Pna*2(1)
a [Å]	9.5610(6)	10.8080(12)	9.1840(11)	18.4140(6)	18.5830(10)
b [Å]	14.2130(8)	11.1800(11)	10.8320(12)	11.3250(6)	10.6640(5)
c [Å]	16.0760(10)	20.693(2)	12.4680(15)	27.5170(14)	14.6970(8)
α [°]	77.014(5)	100.962(8)	96.882(9)	90.00	90.00
β [°]	83.227(5)	99.008(8)	100.357(9)	96.664(4)	90.00
γ [°]	87.635(5)	92.987(8)	101.756(9)	90.00	90.00
V [Å^3]	2113.6(2)	2415.8(4)	1178.7(2)	5699.6(5)	2912.5(3)
Crystal size [mm]	$0.68 \times 0.68 \times 0.61$	$0.29 \times 0.13 \times 0.12$	$0.26 \times 0.17 \times 0.11$	$0.34 \times 0.15 \times 0.11$	$0.39 \times 0.18 \times 0.16$
$\rho_{calcd.}$ [g cm^{-3}]	1.577	1.651	1.453	1.584	1.517
μ [mm^{-1}] (Mo-K_α)	1.023	1.337	1.137	1.143	0.693
T [K]	173(2)	173(2)	133(2)	191(2)	133(2)
θ range [°]	1.31–26.11	1.86–25.93	1.69–26.08	1.49–26.07	1.39–26.14
No. of unique refl.	7979	9095	4435	5377	5497
No. of obsd. refl. [$I>2\sigma(I)$]	7537	4622	3514	4360	4889
No. of parameters	534	525	236	422	361
wR_2 (all data)	0.0693	0.1788	0.1777	0.1019	0.0818
R value [$I>2\sigma(I)$]	0.0264	0.0673	0.0649	0.0427	0.0346

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