# Facile Oxidative Addition of C−Cl Bonds to New Neutral and Cationic Rhodium(I)-Bipyridine Complexes

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Neutral and cationic Rh(dmbpy) systems (dmbpy = 4,4′-dimethyl-2,2′-bipyridine) were synthesized starting from different metal precursors. [RhCl(dmbpy)(DMSO)] (**3**) was obtained either from the ethylene precursor [RhCl(dmbpy)($C_2H_4$)] (**1**) or directly from [$Rh_2Cl_2(COE)_4$] (COE = cyclooctene) in DMSO. The neutral isocyanide complex [RhCl(dmbpy){CNC($CH_3$)$_3$}] (**4**) was obtained by reaction of **1** with *tert*-butyl isocyanide. Reaction of dmbpy with [Rh(DMSO)$_4$]$PF_6$ gave the corresponding cationic complex [Rh(dmbpy)(DMSO)$_2$]$PF_6$ (**5**), and the cationic system [Rh(dmbpy){CNC($CH_3$)$_3$}$_2$]$BF_4$ (**6**) was prepared starting from [Rh(dmbpy)(HD)]$BF_4$ (**2**) (HD = 1,5-hexadiene). All of these complexes were found to activate the C–Cl bond in benzyl chloride leading to quantitative isolation of the corresponding $Rh^{III}$ complexes [$RhCl_2$($CH_2C_6H_5$)(dmbpy)(DMSO)] (**7**), [$RhCl_2$($CH_2C_6H_5$)(dmbpy){CNC($CH_3$)$_3$}] (**9**) [RhCl($CH_2$-$C_6H_5$)(dmbpy)(DMSO)$_2$]$PF_6$ (**10**) and [RhCl($CH_2C_6H_5$)-(dmbpy){CNC($CH_3$)$_3$}$_2$]$BF_4$ (**12**). Oxidative addition of dichloromethane by complexes **3** and **5** yielded the corresponding chloromethyl complexes [$RhCl_2$($CH_2Cl$)(dmbpy)(DMSO)] (**8**) and [RhCl($CH_2Cl$)(dmbpy)(DMSO)$_2$]$PF_6$ (**11**). The reactivity of **3** towards oxygen led to the isolation of the peroxo $Rh^{III}$ complex [RhCl($O_2$)(dmbpy)(DMSO)] (**13**). Complexes **6**, **8**, **9** and **12** were characterized by X-ray crystallography.


## Introduction

The use of transition metal catalysts that employ nitrogen-donor ligands is expanding rapidly.[1] The most widely used nitrogen ligand is the bidentate 2,2′-bipyridine unit.[2] $Rh^I$-bipyridine systems and closely related derivatives have been extensively investigated as catalysts in the hydrogenation and hydrogen-transfer reactions of olefins and ketones.[3] In this context, the cationic complex [Rh(bpy)(L)$_2$]X (X = $PF_6^-$, $BF_4^-$, $ClO_4^-$; bpy = 2,2′-bipyridine, L = acetone) is believed to be the active species in the hydrogenation of olefins.[4] Such complexes with labile additional ligands have never been isolated, the only known complexes of this type being with L = CO,[5] or with chelating ligands such as dienes[6] or bipyridine.[7] Furthermore, oxidative addition to neutral or cationic precursors of this type has never been studied in detail, the only example reported involving oxidative addition of methyl iodide to [Rh(bpy)(CO)X] (X = Cl, Br, I; bpy = 2,2′-bipyridine).[8]

The oxidative addition of carbon halides to low-valent metal complexes is involved in numerous industrially important catalytic cycles and has therefore attracted considerable academic interest. Of particular interest is the activation of the relatively inert C−Cl bond, which is more challenging than that of the C−Br and C−I bonds. Oxidative addition of C−Cl bonds, especially of dichloromethane, requires an electron-rich rhodium center. Relatively few examples of simple oxidative addition of dichloromethane to $Rh^I$ complexes have been reported. These systems incorporate mono- or polydentate phosphorous ligands,[9−11] mono- or polydentate nitrogen ligands,[12−14] sulfur macrocycles[15] or phosphorous-nitrogen hybrid ligands,[16−18] and in several cases the starting $Rh^I$ species were not isolated.[12,14,17,18]

Herein we report the synthesis, characterization and oxidative addition chemistry of new $Rh^I$ complexes with the bidentate ligand 4,4′-dimethyl-2,2′-bipyridine (dmbpy).[19] The nucleophilicity of the $Rh^I$ can be controlled by the choice of the additional ligands. We chose the loosely bound DMSO ligand and the relatively strongly bound *tert*-butyl isocyanide ligand for our study. The oxidative addition of dichloromethane at room temperature takes place in the complexes stabilized by additional DMSO ligands. Oxidative addition of the C−Cl bond of benzyl chloride is observed in all of these complexes. Reaction of the neutral $Rh^I$-(dmbpy)-DMSO complex with $O_2$ leads to the isolation of a stable peroxo-$Rh^{III}$ compound.

## Results and Discussion

### Synthesis of the $Rh^I$-dmbpy Complexes

The new complexes **1**−**6** were prepared from different precursors. The preparation of **1** was achieved following a

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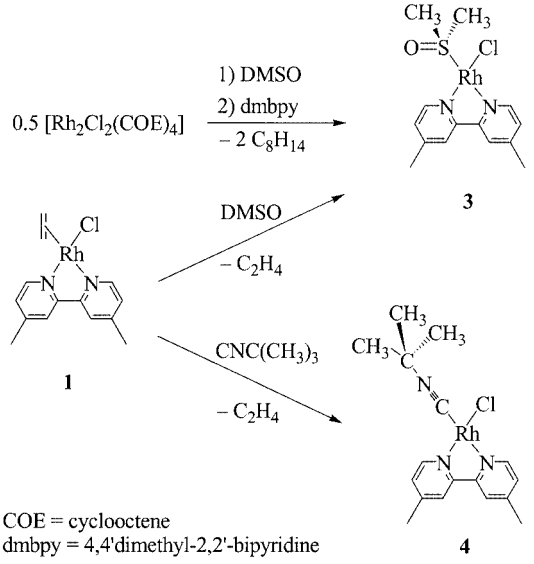
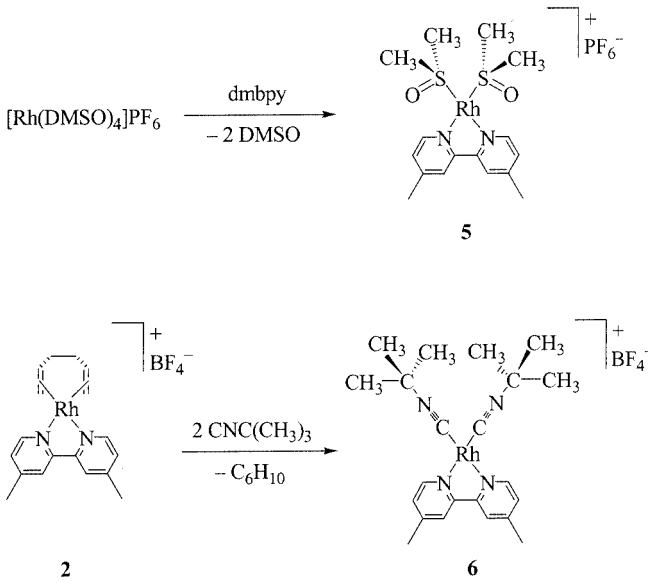
literature method published for the corresponding 2,2′-bipyridine complex.[20] Complex **1** was found to be moderately stable in a dichloromethane solution but decomposed immediately when dissolved in either acetonitrile, pyridine or methanol. Surprisingly, dissolution of **1** in DMSO resulted in quantitative formation of **3**, which was isolated by pouring the concentrated DMSO solution into a large excess of diethyl ether. Direct synthesis of **3** was achieved by treating a DMSO solution of the rhodium dimer $[Rh_2Cl_2(COE)_4]$ (COE = cyclooctene) with an equimolar amount of 4,4′-dimethyl-2,2′-bipyridine. Subsequent precipitation from diethyl ether gave **3** as a brick-red solid in high yield (Scheme 1).




Scheme 1. Synthesis of the neutral $Rh^I$ complexes **3** and **4**

The $^1H$ NMR spectrum of **3** showed six resonances in the aromatic region attributable to the nonequivalent parts of the ligand unit, one singlet at δ = 3.19 ppm for the coordinated DMSO (bound through the sulfur atom) and two singlets for the methyl groups of dmbpy at δ = 2.31 and 2.51 ppm . The corresponding neutral isocyanide complex **4** was synthesized in high yield by treating a suspension of **1** in THF with 1 equiv. of *tert*-butyl isocyanide as shown in Scheme 1. Starting with **3** and treating it with 1 equiv. of *tert*-butyl isocyanide led to a mixture of products. One of the by-products was isolated by precipitation from the solution mixture and identified by $^1H$ NMR spectroscopy to be the symmetrical species $[Rh(dmbpy)\{CNC(CH_3)_3\}_2]Cl$. This indicates that displacement of the DMSO molecule in **3** is much slower than that of ethylene leading to the displacement of the chloride and the formation of the more stable bis-isocyanide species. The $^1H$ NMR spectrum of **4** showed the expected peaks for the nonsymmetrical dmbpy ligand and a singlet at δ = 1.53 ppm for the coordinated *tert*-butyl isocyanide.

The corresponding cationic complexes, **5** and **6**, respectively, were also synthesized (Scheme 2). Compound **5** was obtained as a red solid after addition of dmbpy to a DMSO solution containing $[Rh(DMSO)_4]PF_6$.[21] As expected, the $^1H$ NMR spectrum in $[D_6]$DMSO showed only three peaks in the aromatic region for the ligand and one singlet for the two methyl groups of dmbpy. Complex **6** was obtained by treating a THF slurry of $[Rh(dmbpy)(HD)]BF_4$ (**2**) (HD = 1,5-hexadiene) with 2 equiv. of *tert*-butyl isocyanide. After precipitation from pentane, **6** was obtained as a deep-red solid. FT-IR spectroscopy, $^1H$ NMR spectroscopy and elemental analysis support its formulation, and the molecular structure of **6** was confirmed by an X-ray diffraction study of red single crystals obtained by slow evaporation of an acetone solution. An ORTEP drawing is shown in Figure 1 and the averages of selected bond lengths and angles are given in Table 1. The rhodium atom of complex **6** is located in the center of a square planar arrangement with the two




Scheme 2. Synthesis of the cationic $Rh^I$ complexes **5** and **6**

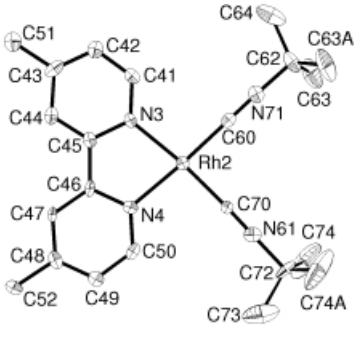



Figure 1. ORTEP drawing of a molecule of **6** (50% of probability); hydrogen atoms are omitted for clarity

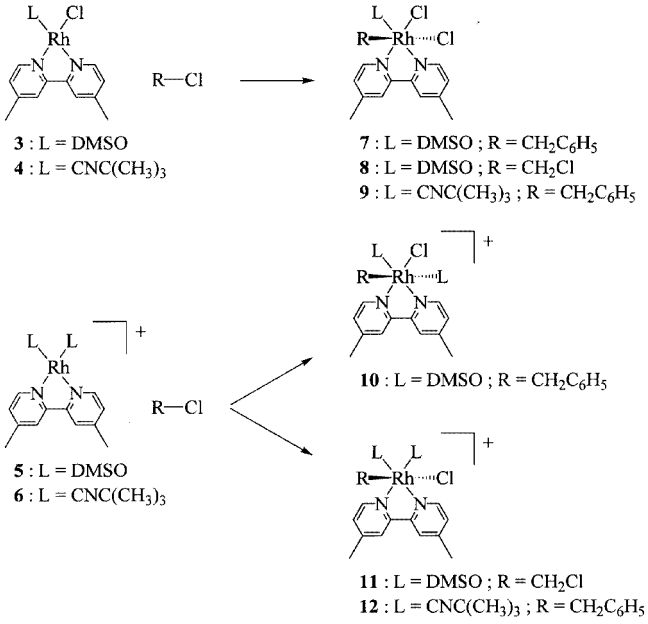
Table 1. Selected bond lengths (Å) and bond angles (°) for **6**

| | | | |
|---|---|---|---|
| Rh(2)−C(70) | 1.909(7) | Rh(2)−N(3) | 2.060(7) |
| Rh(2)−C(60) | 1.910(8) | Rh(2)−N(4) | 2.077(6) |
| C(70)−Rh(2)−C(60) | 87.5(4) | C(70)−Rh(2)−N(4) | 95.6(3) |
| C(70)−Rh(2)−N(3) | 174.5(3) | C(60)−Rh(2)−N(4) | 176.9(3) |
| C(60)−Rh(2)−N(3) | 97.9(3) | N(3)−Rh(2)−N(4) | 79.0(3) |

isocyanide ligands *trans* to the corresponding pyridine moieties of dmbpy.

### Oxidative Addition of C−Cl Bonds

When an acetone or DMSO solution of **3** was treated with benzyl chloride, an immediate color change from deep red to yellow took place. The $^1$H NMR spectrum showed clean oxidative addition of the C−Cl bond, and subsequent workup of the yellow solution gave complex **7** in high yield (Scheme 3). The benzylic $CH_2$ group is seen as two nonequivalent proton signals showing couplings with each other (6.8 Hz) and with the rhodium metal center (3.1 Hz). In the case of dichloromethane, oxidative addition was, as expected, much slower and took 15 h for completion, giving complex **8** in quantitative yield. Following the process by $^1$H NMR spectroscopy showed the appearance of two signals at δ = 4.31 ppm (dd, $J$ = 5.7, 3.0 Hz) and δ = 4.75 ppm (dd, $J$ = 5.7, 3.0 Hz) for the $CH_2Cl$ unit (Figure 2) together with a new set of peaks for the dmbpy unit. When the reaction was performed in [$D_6$]DMSO, minor amounts




Scheme 3. Reaction of the Rh$^{I}$ complexes **3**−**6** with R−Cl to yield the Rh$^{III}$ complexes **7**−**12**

(<10% by integration) of an isomeric species were also present. In this case, the ligand seems to be symmetrical with three signals in the aromatic region and one singlet for the methyl group of dmbpy. The chloromethyl moiety gives rise to one doublet at δ = 5.05 ppm (d, $J$ = 3.1 Hz). These data indicate a species with the two chloride ligands *trans* to the

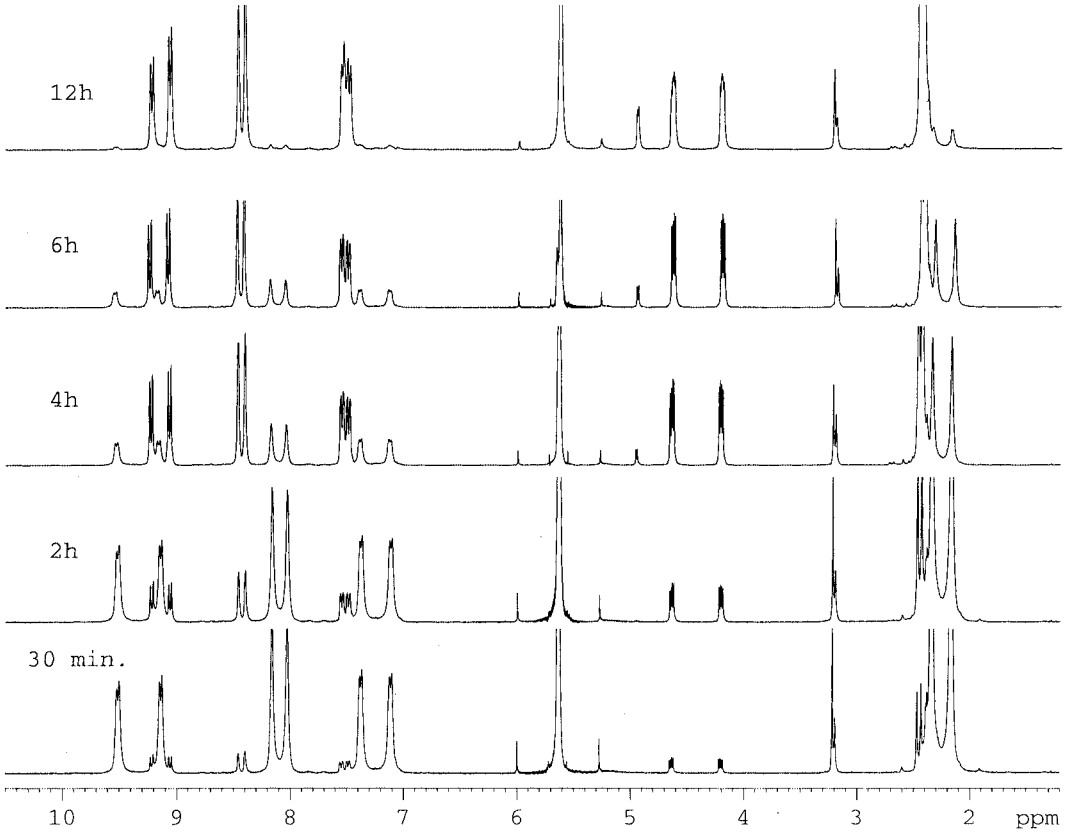



Figure 2. $^1$H NMR follow-up experiment of the reaction between **3** and dichloromethane in [$D_6$]DMSO

bipyridine moiety and with the chloromethyl group and the DMSO ligand axially arranged. This compound could be removed during workup due to its higher solubility in diethyl ether. It was not observed when the reaction was performed in acetone. Trying to obtain this compound in pure form, an NMR tube sample of **8** in [$D_6$]DMSO was heated at 80 °C for 2 h. Indeed, the $^1$H NMR spectrum showed 30% of this compound compared to **8** was formed.[22] Colorless single crystals of **8** suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a concentrated DMSO solution. The geometry around the rhodium atom in this complex is distorted octahedral (Figure 3). In the equatorial plane, a chloride atom, the two N atoms of dmbpy and the S atom of DMSO are coordinated to the rhodium atom. The chloromethyl ligand and the second chloride atom occupy the axial positions. As expected, the two chloride atoms show quite different bond lengths to rhodium, the one *trans* to the N atom being significantly shorter than the chloride *trans* to the chloromethyl moiety [Rh(1)−Cl(3) = 2.3528(7) and Rh(1)−Cl(3) = 2.4891(7)] (Table 2). The Rh(1)−C(4) distance of 2.046(2) Å is very close to the value reported recently for [$RhCl_2(CH_2Cl)$\{2,6-(CH=N*i*Pr)$_2$-$C_5H_3N$\}].[13] The C(4)−Cl(4) bond length of 1.811(3) Å is longer than those found for other metal chloromethyl complexes, indicating a slightly higher carbene character of **8** ($Rh=CH_2^+Cl^-$).

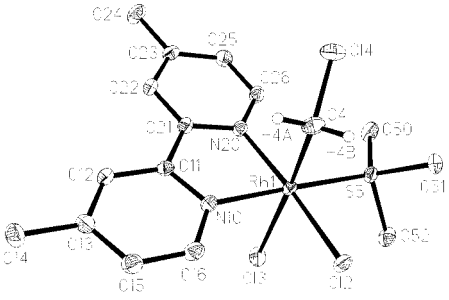



Figure 3. ORTEP drawing of a molecule of **8** (50% of probability); hydrogen atoms (except Rh−$Ch_2$Cl) are omitted for clarity

Table 2. Selected bond lengths (Å) and bond angles (°) for **8**

| | | | |
|---|---|---|---|
| Rh(1)−C(4) | 2.046(2) | Rh(1)−S(5) | 2.2870(7) |
| Rh(1)−N(20) | 2.0526(19) | Rh(1)−Cl(2) | 2.3528(7) |
| Rh(1)−N(10) | 2.0678(19) | Rh(1)−Cl(3) | 2.4891(7) |
| | | | |
| C(4)−Rh(1)−N(20) | 89.92(9) | N(10)−Rh(1)−Cl(2) | 93.79(5) |
| C(4)−Rh(1)−N(10) | 89.78(9) | S(5)−Rh(1)−Cl(2) | 86.46(2) |
| N(20)−Rh(1)−N(10) | 79.19(7) | C(4)−Rh(1)−Cl(3) | 175.50(8) |
| C(4)−Rh(1)−S(5) | 92.71(8) | N(20)−Rh(1)−Cl(3) | 89.58(6) |
| N(20)−Rh(1)−S(5) | 100.68(6) | N(10)−Rh(1)−Cl(3) | 85.74(5) |
| N(10)−Rh(1)−S(5) | 177.51(5) | S(5)−Rh(1)−Cl(3) | 91.78(2) |
| C(4)−Rh(1)−Cl(2) | 87.08(8) | Cl(2)−Rh(1)−Cl(3) | 92.88(4) |
| N(20)−Rh(1)−Cl(2) | 172.38(5) | | |

The reactivity of the corresponding *tert*-butyl isocyanide complex **4** towards C−Cl bonds was checked next. As expected, complex **4** is much less reactive due to significantly higher backbonding from the rhodium center to the *tert*-butyl isocyanide ligand and the resulting lower nucleophilicity of the metal center. Treating a deep-red acetone solution of **4** with benzyl chloride for 12 h at room temperature led to a color change to yellow. The $^1$H NMR spectrum showed that clean oxidative addition took place also in this case, leading to quantitative isolation of complex **9**. In contrast, oxidative addition of dichloromethane to complex **4** did not occur at room temperature. Even after stirring a solution of **4** with excess $CH_2Cl_2$ for several days the starting complex was recovered unchanged. The crystal structure of [$RhCl_2(CH_2C_6H_5)$(dmbpy)\{$CNC(CH_3)_3$\}] (**9**) has been determined (Figure 4) and found to adopt an octahedral geometry. In the equatorial plane, the rhodium center is bound to the dmbpy, the *tert*-butyl isocyanide and to one of the chloride atoms. The benzylic moiety together with the second chloride atom adopt the apical positions. As in the case of **8**, the Rh−Cl bond length of the chloride *trans* to the pyridine of dmbpy is significantly shorter than the one *trans* to the benzyl moiety [Rh(1)−Cl(3) = 2.3573(10) and Rh(1)−Cl(2) = 2.5391(9), respectively] (Table 3).

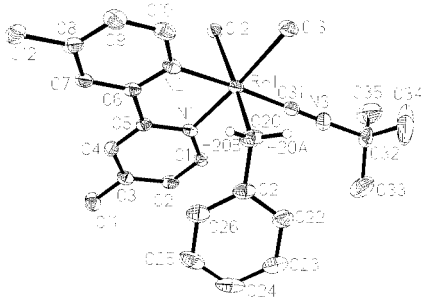



Figure 4. ORTEP drawing of a molecule of **9** (50% of probability); hydrogen atoms (except Rh−$Ch_2$R) are omitted for clarity

Table 3. Selected bond lengths (Å) and bond angles (°) for **9**

| | | | |
|---|---|---|---|
| Rh(1)−C(31) | 1.943(4) | Rh(1)−C(20) | 2.100(4) |
| Rh(1)−N(1) | 2.023(3) | Rh(1)−Cl(3) | 2.3573(10) |
| Rh(1)−N(2) | 2.070(3) | Rh(1)−Cl(2) | 2.5391(9) |
| | | | |
| C(31)−Rh(1)−N(1) | 98.11(13) | N(2)−Rh(1)−Cl(3) | 95.57(8) |
| C(31)−Rh(1)−N(2) | 176.73(13) | C(20)−Rh(1)−Cl(3) | 86.42(11) |
| N(1)−Rh(1)−N(2) | 79.50(11) | C(31)−Rh(1)−Cl(2) | 94.09(11) |
| C(31)−Rh(1)−C(20) | 88.59(16) | N(1)−Rh(1)−Cl(2) | 84.55(8) |
| N(1)−Rh(1)−C(20) | 94.04(13) | N(2)−Rh(1)−Cl(2) | 87.93(8) |
| N(2)−Rh(1)−C(20) | 89.35(14) | C(20)−Rh(1)−Cl(2) | 177.12(12) |
| C(31)−Rh(1)−Cl(3) | 86.84(11) | Cl(3)−Rh(1)−Cl(2) | 94.76(3) |
| N(1)−Rh(1)−Cl(3) | 175.04(8) | | |

The cationic complexes **5** and **6** also undergo oxidative addition of the C−Cl bond of benzyl chloride (Scheme 3). In both cases, oxidative addition occurred somewhat slower than for the corresponding neutral complexes, leading to the cationic $Rh^{III}$ complexes **10** and **12**, respectively. Surprisingly, the benzyl methylene group in **10** shows formation of the asymmetrical species with one DMSO molecule *trans* to the benzyl methylene, giving rise to two doublets of doublets for the methylene group. Oxidative addition to complex **6** does lead to the expected symmetrical species with the methylene group appearing as one doublet at δ = 3.12 ppm, the doublet signal arising from coupling to the

rhodium center. Slow diffusion of diethyl ether into an acetone solution of **12** led to colorless crystals suitable for X-ray diffraction. As shown in Figure 5, compound **12** adopts the expected octahedral arrangement around the metal center. The bond lengths between the rhodium atom and the *tert*-butyl isocyanide and dmbpy ligands are very close to the values observed in the starting complex **6** with marginally longer Rh(1)−C(40) and Rh(1)−C(30) bond lengths (Table 4). As observed in the neutral systems, also in the cationic case the DMSO stabilized complex **5** oxidatively added dichloromethane due to its higher nucleophilicity. Reaction of **5** with excess $CH_2Cl_2$ resulted in a gradual color change from deep-red to yellow when left standing at room temperature for two days and gave the symmetrical complex **11** in high yield (Scheme 3).

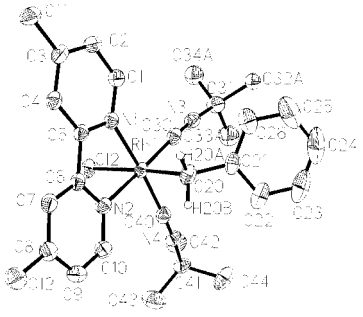


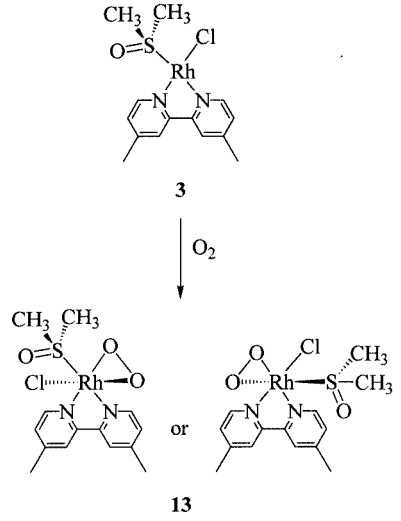
Figure 5. ORTEP drawing of a molecule of **12** (50% of probability); hydrogen atoms (except Rh−$Ch_2$R) are omitted for clarity

Table 4. Selected bond lengths (Å) and bond angles (°) for **12**

| | | | |
|---|---|---|---|
| Rh(1)−C(40) | 1.939(4) | Rh(1)−N(2) | 2.066(3) |
| Rh(1)−C(30) | 1.939(4) | Rh(1)−C(20) | 2.098(3) |
| Rh(1)−N(1) | 2.065(3) | Rh(1)−Cl(2) | 2.4928(10) |
| C(40)−Rh(1)−C(30) | 84.80(15) | N(1)−Rh(1)−C(20) | 90.36(13) |
| C(40)−Rh(1)−N(1) | 175.67(13) | N(2)−Rh(1)−C(20) | 84.42(13) |
| C(30)−Rh(1)−N(1) | 97.93(13) | C(40)−Rh(1)−Cl(2) | 86.09(11) |
| C(40)−Rh(1)−N(2) | 97.87(13) | C(30)−Rh(1)−Cl(2) | 88.75(11) |
| C(30)−Rh(1)−N(2) | 176.95(12) | N(1)−Rh(1)−Cl(2) | 90.60(8) |
| N(1)−Rh(1)−N(2) | 79.49(11) | N(2)−Rh(1)−Cl(2) | 92.89(8) |
| C(40)−Rh(1)−C(20) | 92.81(15) | C(20)−Rh(1)−Cl(2) | 176.93(11) |
| C(30)−Rh(1)−C(20) | 94.01(15) | | |

### Oxidative Addition of Oxygen to 3

When a deep-red DMSO or acetone solution of **3** was treated with 1 equiv. or excess $O_2$, an immediate color change to yellow occurred. The product was identified as being the peroxo complex $[RhCl_2(O_2)(dmbpy)(DMSO)]$ (**13**) based on elemental analysis and the appearance of an IR band at $\tilde{\nu} = 870\ cm^{-1}$ for the peroxo ligand (Scheme 4). The $^1H$ NMR spectrum showed shifts for all the protons relative to the peaks observed for the starting complex **3**. As expected, the biggest difference is seen in one of the protons in the α-position to the nitrogen of the dmbpy ligand, the pyridine moiety being substantially more shielded by the presence of the oxygen atom *trans* to it. However, we could not determine whether the DMSO ligand or the chloride occupy the position *trans* to the second oxygen atom. With respect to the properties of **13**, we should note that $O_2$ is bonded strongly and did not dissociate under vacuum or by bubbling $N_2$ through a solution of **13**.[23] Complexes **4** and **5** also add oxygen and a detailed investigation of the reactivity of these complexes will be published in due course.




Scheme 4. Reaction of complex **3** with $O_2$ giving the peroxo complex **13**

## Summary

New neutral and cationic rhodium complexes bearing the chelating 4,4′-dimethyl-2,2′-bipyridine (dmbpy) ligand and additional DMSO or *tert*-butyl isocyanide ligands were synthesized in high yield starting from various $Rh^I$ precursors. These complexes underwent oxidative addition of the C−Cl bond of benzyl chloride at room temperature. The complexes bearing the additional DMSO ligands were shown to be more nucleophilic at the rhodium center and underwent C−Cl oxidative addition of dichloromethane. In addition, the oxidative addition of $O_2$ to one of the $Rh^I$ complexes led to the quantitative isolation of a stable $Rh^{III}$ peroxo species.

## Experimental Section

**General Procedures:** All experiments were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glove box equipped with a MO 40-2 inert gas purifier. All solvents were reagent grade or better. All non-deuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under argon atmosphere. Deuterated solvents were used as received. All the solvents were degassed with argon and kept in the glove box over molecular sieves. Commercially available reagents were used as received. The complexes $[Rh_2Cl_2(COE)_4]$,[24] $[Rh_2Cl_2(C_2H_4)_4]$,[25] and $[Rh(DMSO)_4]PF_6$ [21] were prepared according to literature procedures.

$^1H$ NMR spectra were recorded at 250 MHz on a Bruker AMX-250 NMR spectrometer or on a Bruker AMX-400 NMR spectro-

meter. Chemical shifts are reported in ppm downfield from tetramethylsilane and are referenced to the residual hydrogen signal of the deuterated solvents (δ = 2.04 ppm, acetone; δ = 2.49 ppm, DMSO; δ = 5.32 ppm, dichloromethane). Abbreviations used in the description of NMR spectroscopic data are as follows: br., broad; s, singlet; d, doublet; t, triplet; m, multiplet. Elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, 45470 Mülheim, Germany.

**Synthesis of [RhCl(dmbpy)($C_2H_4$)] (1):** [$Rh_2Cl_2(C_2H_4)_4$] (241 mg, 0.620 mmol) was dissolved in toluene (35 mL) and filtered, affording an orange solution. 4,4′-dimethyl-2,2′-bipyridine (205 mg, 1.115 mmol) was dissolved in toluene (8 mL) and added dropwise. The color of the solution turned from orange to violet. Stirring at room temperature for 2 h resulted in the formation of a violet precipitate which was filtered off, washed with toluene and dried in vacuo. Yield: 346 mg, 89%. $^1$H NMR (250 MHz, $CD_2Cl_2$, 298 K): δ = 2.27 (s, 3 H), 2.53 (s, 3 H), 3.62 (s, 4 H), 7.00 (d, *J* = 5.1 Hz, 1 H), 7.21 (d, *J* = 5.9 Hz, 1 H), 7.39 (d, *J* = 5.6 Hz, 1 H), 7.63 (s, 1 H), 7.84 (s, 1 H), 9.06 (d, *J* = 5.6 Hz, 1 H) ppm. $C_{14}H_{16}ClN_2Rh$ (350.7): C 47.95, H 4.60, N 7.99; found C 47.99, H 4.78, N 7.78.

**Synthesis of [Rh(dmbpy)(HD)]$BF_4$ (2):** A suspension of [$Rh_2Cl_2(COE)_4$] (140 mg, 0.196 mmol) in MeOH (7 mL) was treated with excess 1,5-hexadiene (1.1 mL) and the yellow suspension was stirred at room temperature for 1.5 h. Addition of a solution of 4,4′-dimethyl-2,2′-bipyridine (72 mg, 0.392 mmol) in dichloromethane (4 mL) resulted in a color change to deep red. After stirring the solution at room temperature for 1 h, a solution of $AgBF_4$ (76 mg, 0.392 mmol) in dichloromethane (4 mL) was added dropwise and the solution was stirred at room temperature for another hour. Filtration, followed by concentration of the red solution to 6 mL and addition of diethyl ether led to the precipitation of a red solid which was filtered, washed with additional diethyl ether and dried in vacuo. Yield: 173 mg, 97%. $^1$H NMR (250 MHz, $CD_2Cl_2$, 298 K): δ = 1.94 (m, 2 H), 2.54 (m, 2 H), 2.61 (s, 6 H), 3.00 (d, *J* = 13.9 Hz, 2 H), 3.59 (d, *J* = 7.7 Hz, 2 H), 4.78 (m, 2 H), 7.47 (d, *J* = 5.7 Hz, 2 H), 7.66 (d, *J* = 5.8 Hz, 2 H), 8.15 (s, 2 H) ppm. $C_{18}H_{22}BF_4N_2Rh$ (456.1): C 47.40, H 4.87, N 6.14; found C 47.36, H 4.79, N 6.08.

**Synthesis of [RhCl(dmbpy)(DMSO)] (3):** [$Rh_2Cl_2(COE)_4$] (494 mg, 0.692 mmol, COE = cyclooctene) was dissolved in DMSO (16 mL) and the deep-orange solution was stirred at room temperature for 30 min. 4,4′-Dimethyl-2,2′-bipyridine (255 mg, 1.384 mmol) was then added as a solid in small portions resulting in a color change to deep red. The solution was stirred for 3 h at room temperature and then poured into diethyl ether (450 mL). The resulting brick-red solid was carefully decanted, washed with diethyl ether and pentane and dried in vacuo. Yield: 460 mg, 83%. $^1$H NMR (250 MHz, [$D_6$]acetone, 298 K): δ = 2.31 (s, 3 H), 2.51 (s, 3 H), 3.19 (s, 6 H), 7.16 (d, *J* = 6.0 Hz, 1 H), 7.45 (d, *J* = 5.8 Hz, 1 H), 8.03 (s, 1 H), 8.18 (s, 1 H), 9.46 (d, *J* = 5.7 Hz, 1 H), 9.83 (d, *J* = 6.0 Hz, 1 H) ppm. $C_{14}H_{18}ClN_2ORhS$ (400.7): C 41.96, H 4.53, N 6.99; found C 41.78, H 4.46, N 7.06.

**Synthesis of [RhCl(dmbpy){CNC($CH_3$)$_3$}] (4):** A solution of *tert*-butyl isocyanide (40 mg, 0.486 mmol) in THF (10 mL) was added dropwise to a violet slurry of **1** (170 mg, 0.486 mmol) in THF (14 mL). The resulting green-brown solution was stirred at room temperature for 2 h. Concentration of the THF solution to 10 mL and addition of diethyl ether (40 mL) caused the precipitation of a green-brown solid which was washed with diethyl ether and dried in vacuo. Yield: 162 mg, 83%. $^1$H NMR (250 MHz, [$D_6$]acetone, 298 K): δ = 1.53 (s, 9 H), 2.23 (s, 3 H), 2.49 (s, 3 H), 7.10 (d, *J* = 5.9 Hz, 1 H), 7.46 (d, *J* = 5.7 Hz, 1 H), 7.98 (s, 1 H), 8.14 (s, 1 H), 8.85 (d, *J* = 5.6 Hz, 1 H), 9.37 (d, *J* = 5.7 Hz, 1 H) ppm. $C_{17}H_{21}ClN_3Rh$ (405.7): C 50.32, H 5.22, N 10.36; found C 50.21, H 5.29, N 10.26.

**Synthesis of [Rh(dmbpy)(DMSO)$_2$]$PF_6$ (5):** [$Rh(DMSO)_4$]$PF_6$ (65 mg, 0.115 mmol) and dmbpy (21 mg, 0.115 mmol) were dissolved in 4 mL DMSO and the resulting deep-red solution was stirred at room temperature for 2 h. The solution was then poured into diethyl ether (150 mL) and the brick-red precipitate was decanted, washed with additional diethyl ether and dried in vacuo. Yield: 61 mg, 90%. $^1$H NMR (250 MHz, [$D_6$]DMSO, 298 K): δ = 2.52 (s, 6 H), 7.52 (d, *J* = 5.9 Hz, 2 H), 8.41 (s, 2 H), 8.70 (d, *J* = 5.8 Hz, 2 H) ppm. $C_{16}H_{24}F_6N_2O_2PRhS_2$ (588.4): C 32.66, H 4.11, N 4.76; found C 32.78, H 4.18, N 4.71.

**Synthesis of [Rh(dmbpy){CNC($CH_3$)$_3$}$_2$]$BF_4$ (6):** A THF (3 mL) solution of *tert*-butyl isocyanide (33 mg, 0.401 mmol) was added dropwise to a red suspension of **2** (87 mg, 0.191 mmol) in THF (6 mL). The suspension was left stirring at room temperature for 2 h during which time the color turned deep-red with precipitation of a deep-red solid. Concentration to 3 mL, addition of pentane and subsequent washings with additional pentane afforded a deep-red solid which was dried in vacuo. Yield: 91 mg, 88%. $^1$H NMR (250 MHz, [$D_6$]acetone, 298 K): δ = 1.62 (s, 18 H), 2.55 (s, 6 H), 7.56 (d, *J* = 5.6 Hz, 2 H), 8.39 (s, 2 H), 8.67 (d, *J* = 5.5 Hz, 2 H) ppm. $C_{22}H_{30}BF_4N_4Rh$ (540.2): C 48.91, H 5.60, N 10.37; found C 48.76, H 5.52, N 10.27.

**Reaction of 3 with Benzyl Chloride. Formation of [$RhCl_2$-($CH_2C_6H_5$)(dmbpy)(DMSO)] (7):** Complex **3** (70 mg, 0.175 mmol) was dissolved in an acetone/DMSO (3:1 mL) mixture and stirred at room temperature for 30 min giving a deep-red solution. Addition of benzyl chloride (44 mg, 0.348 mmol) led to an immediate color change to yellow. Leaving the solution at room temperature for 1 h resulted in the formation of a yellow precipitate which was carefully decanted, washed with diethyl ether and dried in vacuo. Yield: 77 mg, 84%. $^1$H NMR (250 MHz, [$D_6$]DMSO, 298 K): δ = 2.39 (s, 3 H), 2.48 (s, 3 H), 3.51 (dd, *J* = 6.8 Hz and 3.0 Hz, 1 H), 4.02 (dd, *J* = 6.8 Hz and 3.1 Hz, 1 H), 6.17 (d, *J* = 6.9 Hz, 2 H), 6.50 (dd, *J* = 7.5 Hz, 2 H), 6.70 (dd, *J* = 7.3 Hz, 1 H), 7.42 (d, *J* = 5.0 Hz, 1 H), 7.52 (d, *J* = 5.0 Hz, 1 H), 8.01 (s, 1 H), 8.18 (s, 1 H), 9.12 (d, *J* = 5.9 Hz, 1 H), 9.41 (d, *J* = 5.7 Hz, 1 H) ppm. $C_{21}H_{25}Cl_2N_2ORhS$ (527.3): C 47.83, H 4.78, N 5.31; found C 47.35, H 4.76, N 5.22.

**Reaction of 3 with Dichloromethane. Formation of [$RhCl_2$-($CH_2Cl$)(dmbpy)(DMSO)] (8):** Complex **3** (80 mg, 0.200 mmol) was dissolved in DMSO (2 mL) and five drops of $CH_2Cl_2$ were added. Leaving the solution at room temperature for one day led to the formation of pale yellow crystals. Addition of diethyl ether and subsequent washing with additional diethyl ether gave an off-white solid which was dried in vacuo. Yield: 82 mg, 85%. $^1$H NMR (250 MHz, [$D_6$]DMSO, 298 K): δ = 2.53 (s, 3 H), 2.57 (s, 3 H), 4.31 (dd, *J* = 5.7 Hz and 3.0 Hz, 1 H), 4.75 (dd, *J* = 5.7 Hz and 3.0 Hz, 1 H), 7.60 (d, *J* = 5.0 Hz, 1 H), 7.65 (d, *J* = 5.0 Hz, 1 H), 8.51 (s, 1 H), 8.57 (s, 1 H), 9.17 (d, *J* = 5.9 Hz, 1 H), 9.33 (d, *J* = 6.0 Hz, 1 H) ppm. $C_{15}H_{20}Cl_3N_2ORhS$ (485.7): C 37.10, H 4.15, N 5.77; found C 37.27, H 4.06, N 5.71.

**Reaction of 4 with Benzyl Chloride. Formation of [$RhCl_2$-($CH_2C_6H_5$)(dmbpy){CNC($CH_3$)$_3$}] (9):** Complex **4** (28 mg, 0.069 mmol) was dissolved in acetone (3 mL) giving a green-black solution. Addition of benzyl chloride (17 mg, 0.138 mmol) resulted in a color change to pale yellow after one day at room temperature.

Addition of diethyl ether led to the precipitation of an off-white solid which was washed with additional diethyl ether and dried in vacuo. Yield: 33 mg, 89%. $^1$H NMR (250 MHz, [D$_6$]acetone, 298 K): δ = 1.61 (s, 9 H), 2.42 (s, 3 H), 2.48 (s, 3 H), 3.00 (dd, *J* = 7.8 Hz and 3.2 Hz, 1 H), 3.70 (dd, *J* = 7.8 Hz and 3.0 Hz, 1 H), 6.54 (m, 2 H), 6.73 (m, 3 H), 7.25 (d, *J* = 5.8 Hz, 1 H), 7.48 (d, *J* = 5.7 Hz, 1 H), 8.25 (br. s, 2 H), 8.31 (d, *J* = 5.9 Hz, 1 H), 9.35 (d, *J* = 5.7 Hz, 1 H) ppm. $C_{24}H_{28}Cl_2N_3Rh$ (532.3): C 54.15, H 5.31, N 7.89; found C 54.04, H 5.15, N 7.93.

**Reaction of 5 with Benzyl Chloride. Formation of [RhCl(CH$_2$C$_6$H$_5$)(dmbpy)(DMSO)$_2$]PF$_6$ (10):** Complex **5** (70 mg, 0.119 mmol) was dissolved in DMSO (2 mL) and stirred at room temperature for 30 min giving a deep-red solution. Upon addition of benzyl chloride (30 mg, 0.238 mmol) the solution turned yellow. After 12 h at room temperature, the solution was poured into diethyl ether (17 mL) and the resulting yellow precipitate was washed with additional diethyl ether and dried in vacuo. Yield: 77 mg, 91%. $^1$H NMR (250 MHz, [D$_6$]DMSO, 298 K): δ = 2.44 (br. d, 6 H), 3.59 (dd, *J* = 6.8 Hz and 2.9 Hz, 1 H), 4.19 (dd, *J* = 6.8 Hz and 3.2 Hz, 1 H), 6.28 (d, *J* = 7.4 Hz, 2 H), 6.50 (dd, *J* = 7.5 Hz, 2 H), 6.74 (dd, *J* = 7.3 Hz, 1 H), 8.16 (s, 1 H), 8.26 (s, 1 H), 8.82 (br. s, 2 H), 9.09 (d, *J* = 5.9 Hz, 1 H), 9.30 (d, *J* = 5.9 Hz, 1 H) ppm. $C_{23}H_{31}ClF_6N_2O_2PRhS_2$ (715.0): C 38.64, H 4.37, N 3.92; found C 38.20, H 4.80, N 4.82.

**Reaction of 5 with Dichloromethane. Formation of [RhCl(CH$_2$Cl)(dmbpy)(DMSO)$_2$]PF$_6$ (11):** Complex **5** (80 mg, 0.136 mmol) was dissolved in DMSO (2 mL) and an excess of $CH_2Cl_2$ (five drops) was added. After two days at room temperature a pale yellow solution was formed. Addition of diethyl ether and subsequent washing with diethyl ether gave an off-white solid which was dried in vacuo. Yield: 71 mg, 78%. $^1$H NMR (250 MHz, [D$_6$]DMSO, 298 K): δ = 2.59 (s, 6 H), 3.44 (br. d, 2 H), 7.66 (d, *J* = 6.0 Hz, 2 H), 7.87 (d, *J* = 6.0 Hz, 2 H), 8.89 (s, 2 H) ppm. $C_{17}H_{26}Cl_2F_6N_2O_2PRhS_2$ (673.3): C 30.33, H 3.90, N 4.16; found C 32.70, H 3.73, N 5.15.

**Reaction of 6 with Benzyl Chloride. Formation of [RhCl(CH$_2$C$_6$H$_5$)(dmbpy){CNC(CH$_3$)$_3$}$_2$]BF$_4$ (12):** A deep-red acetone solution (10 mL) of **6** (60 mg, 0.111 mmol) was treated with benzyl chloride (28 mg, 0.222 mmol). The color turned to orange within 1 h and leaving the solution overnight led to the precipitation of a yellow solid. Addition of diethyl ether and subsequent washing with diethyl ether gave a yellow powder which was dried in vacuo. Yield: 64 mg, 86%. $^1$H NMR (250 MHz, [D$_6$]DMSO, 298 K): δ = 1.58 (s, 18 H), 2.57 (s, 6 H), 3.12 (d, *J* = 2.6 Hz, 2 H), 6.77 (m, 2 H), 7.00 (m, 3 H), 7.63 (d, *J* = 5.8 Hz, 2 H), 8.54 (d, *J* = 5.7 Hz, 2 H), 8.59 (s, 2 H) ppm. $C_{29}H_{37}BClF_4N_4Rh$ (666.8): C 52.24, H 5.60, N 8.40; found C 52.10, H 5.58, N 8.38.

**Reaction of 3 with Oxygen. Formation of [RhCl$_2$(O$_2$)(dmbpy)(DMSO)] (13):** A red DMSO solution (2 mL) of **3** (30 mg, 0.075 mmol) was treated with an equimolar amount of $O_2$ (1.7 mL). The solution turned yellow immediately and after 3 h at room temperature, it was poured into diethyl ether (17 mL). The pale-yellow precipitate was filtered, washed with diethyl ether and dried in vacuo. Yield: 30 mg, 93%. $^1$H NMR (250 MHz, [D$_6$]acetone, 298 K): δ = 2.59 (s, 3 H), 2.62 (s, 3 H), 3.39 (s, 6 H), 7.53 (d, *J* = 5.9 Hz, 1 H), 7.58 (d, *J* = 5.6 Hz, 1 H), 8.38 (s, 1 H), 8.42 (s, 1 H), 8.57 (d, *J* = 5.6 Hz, 1 H), 9.56 (d, *J* = 5.5 Hz, 1 H) ppm. FT-IR (nujol): $\tilde{\nu}$ = 870 (O−O) cm$^{-1}$. $C_{14}H_{18}ClN_2O_3RhS$ (432.7): C 38.86, H 4.20, N 6.47; found C 38.30, H 4.26, N 6.55.

**X-ray Crystal Structure Determination of 6, 8, 9 and 12:** A single crystal of **6**, **8**, **9** or **12** were mounted on the nylon loop and flash frozen in a nitrogen stream at 120 K. Data were collected on a Nonius Kappa-CCD diffractometer mounted on a FR590 generator equipped with a sealed tube with Mo-$K_\alpha$ radiation (λ = 0.71073Å) and a graphite monochromator. The four structures were solved by direct methods with SHELXS-97 and refined by full-matrix least-squares techniques with SHELXL-97 based on $F^2$.[26]

**Complex 6:** $C_{22}H_{30}N_4Rh{\cdot}BF_4$, orange needles, 0.2 × 0.03 × 0.03 mm$^3$, orthorhombic, $Pmc2_1$ (No. 20), *a* = 6.861(1), *b* = 16.516(3), *c* = 21.825(4) Å, *V* = 2473.1(9) Å$^3$, *Z* = 4, fw = 540.22, $D_c$ = 1.451 Mg/m$^3$, μ = 0.736 mm$^{-1}$. The final cycle of refinement based on $F^2$ gave an agreement factor *R* = 0.0252 for data with $I > 2\sigma(I)$ and *R* = 0.0294 for all data (2214 reflections) with a goodness-of-fit of 0.987. Idealized hydrogen atoms were placed and refined in a riding mode.

**Complex 8:** $C_{15}H_{20}Cl_3N_2OSRh$, yellow, thin parallelogram, 0.30 × 0.10 × 0.02 mm$^3$, monoclinic, $P2_1/c$ (No. 14), *a* = 7.5840(15), *b* = 10.636(2), *c* = 23.216(5) Å, β = 99.28(3)°, *V* = 1848.2(6) Å$^3$, *Z* = 4, fw = 485.65, $D_c$ = 1.745 Mg/m$^3$, μ = 1.474 mm$^{-1}$. The final cycle of refinement based on $F^2$ gave an agreement factor *R* = 0.027 for data with $I > 2\sigma(I)$ and *R* = 0.040 for all data (4219 reflections) with a goodness-of-fit of 1.030. Idealized hydrogen atoms were placed and refined in a riding mode. Two hydrogen atoms on C4 were found and refined manually.

**Complex 9:** $C_{24}H_{28}N_3Cl_2Rh{\cdot}1/2(C_3H_6O){\cdot}H_2O$, yellow, bipyramidal prisms, 0.05 × 0.05 × 0.05 mm$^3$, tetragonal, $I4_1/a$ (No. 88), *a* = *b* = 20.722(3), *c* = 26.090(5) Å, *V* = 11203(3) Å$^3$, *Z* = 16, fw = 579.36, $D_c$ = 1.374 Mg/m$^3$, μ = 0.824 mm$^{-1}$. The final cycle of refinement based on $F^2$ gave an agreement factor *R* = 0.0362 for data with $I > 2\sigma(I)$ and *R* = 0.0508 for all data (4291 reflections) with a goodness-of-fit of 1.054. Idealized hydrogen atoms were placed and refined in riding mode The acetone is disordered with 1/2 a molecule per asymmetric unit.

**Complex 12:** $C_{29}H_{37}N_4ClRh{\cdot}C_3H_6O{\cdot}BF_4$, colorless, prisms, 0.3 × 0.3 × 0.3 mm$^3$, monoclinic, $P2_1/n$ (No. 14), *a* = 12.623(3), *b* = 21.262(4), *c* = 14.011(3) Å, β = 105.84(3)°, *V* = 3617.7(13) Å$^3$, *Z* = 4, fw = 724.87, $D_c$ = 1.331 Mg/m$^3$, μ = 0.596 mm$^{-1}$. The final cycle of refinement based on $F^2$ gave an agreement factor *R* = 0.0491 for data with $I > 2\sigma(I)$ and *R* = 0.0596 for all data (7146 reflections) with a goodness-of-fit of 1.035. Idealized hydrogen atoms were placed and refined in a riding mode. C32, C33 and C34 (one *tert*-butyl group) and the $BF_4$ are partially disordered and modeled with two alternative positions.

CCDC-176695 (**9**), -176696 (**12**), -176697 (**6**), and -176698 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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