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Reaction of a Rhodium(III) α-Chlorotolyl Complex with Water and Oxygen: Stable Rhodium Peroxo Compounds

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The reaction of the rhodium(III) α-chlorotolylcomplex [$RhCl_2(CHClPh)(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)$] (**1**) with H_2O and O_2 afforded the rhodium(III) chloride [$RhCl_3(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)$] (**11**), benzaldehyde, and H_2O_2 in 80−90% yield. This reaction proceeds via two reaction sequences. First, when O_2 is absent the hydride complex [$Rh(H)Cl_2(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)$] (**2**), benzaldehyde, and HCl are formed. Hydrolysis of the metal-bonded CHClPh fragment gives a short-lived CH(OH)Ph moiety, which then by *β*-H elimination of the hydroxyl group affords the products. Alternatively, a rhodium carbene type of intermediate might be involved. The subsequent reaction sequence probably proceeds via two separate pathways. In the first one the hydride **2** may insert O_2 to give a rhodium hydroperoxo species which converts with HCl to the Rh(III) complex **11** and H_2O_2. The second pathway appears to involve first the formation of the Rh(I) complex [$RhCl(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)$] (**8**) from the hydride **2** in H_2O, which subsequently reacts with O_2 to give the peroxo complex [$RhCl(O_2)(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)$] (**12**). The latter reacts with HCl to give the rhodium(III) chloride **11** and H_2O_2. Both pathways were investigated separately by employing the novel hydride **2** and peroxo **12** complexes, which have been prepared in high yields from the rhodium(I) complex **8** with HCl(DCl) and O_2, respectively. The hydride **2** has acidic character in H_2O and is conducting owing to dissociation to a small extent into HCl and the rhodium(I) complex **8**. This solution does react with O_2 in the presence of HCl to from **11** and 80−90% H_2O_2. The peroxo complex **12**, in which O_2 is side-on bonded, dissolves in H_2O to give the weakly basic [$RhCl(OOH)(OH_2)(C_5H_3N(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)$]$^+OH^-$ as two equilibrating isomeric forms which can be converted with HCl to **11** and about 90% H_2O_2. The peroxo complex **12** reacted with SO_2 to [$RhCl(SO_4)(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)$] (**15**) but not with CO, CO_2, and fumaronitrile in dichloromethane. These peroxo complexes are the first examples of rhodium peroxo complexes in which the O_2 is irreversibly bonded to the rhodium atom.

Introduction

Recently we reported novel strongly nucleophilic Rh(I) complexes of the type [$RhCl(2,6\text{-}(C(R^1){=}N{-}R^2)_2\text{-}C_5H_3N)$] ($R^1$ = H, R^2 = *i*-Pr, *t*-Bu, cyclohexyl, and *p*-anisyl; R^1 = Me, R^2 = *p*-anisyl and *i*-Pr) which are able to cleave C−Cl bonds of reagents such as dichloromethane, chloroform, benzyl chloride, and α,α-dichlorotoluene by oxidative addition.[1] Unexpectedly, a side reaction was found in the case of the rhodium(III) chloromethyl complexes [$RhCl_2(CH_2Cl)(2,6\text{-}(C(R^1){=}N{-}R^2)_2C_5H_3N)$] involving the formation of rhodium(III) chloride complexes [$RhCl_3(2,6\text{-}(C(R^1){=}N{-}R^2)_2C_5H_3N)$], owing to a reaction of the chloromethyl moiety with both water and oxygen. In the case of the rhodium(III) α-chlorotolyl complex [$RhCl_2(CHClPh)(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)$] (**1**) we were able to identify in a qualitative way benzaldehyde and H_2O_2 in addition to the rhodium(III) chloride.

In this context it is interesting to mention a study on the stability of a series of chloro(chloromethyl)palladium(II) complexes in $CDCl_3$ solution both in the absence and presence of air published by McCrindle et al.[2] Depending on the nature of the ligands it was found that the chloromethyl moiety could react in three ways: (i) to formaldehyde by oxidation; (ii) to ylide complexes by reaction with a sulfide ligand; (iii) coupling to ethene by reaction of two chloromethyl complexes to give ethene and chloropalladium complexes or to propene by reaction of ethene with a (chloromethyl)-palladium to give chloropalladium complexes. Related *trans*-mono(chloromethyl)platinum(II) complexes decompose in the presence of moisture to formaldehyde and platinum hydrides, which undergo subsequent conversion with HCl into dichlorides.[3] The intermediacy of metal−carbene intermediates has been proposed.[3] Van Leeuwen et al.[4] demonstrated some time ago for Pd and Pt complexes that a metal-bound dichloro- or trichloromethyl group may serve as a carbene precursor.

Reaction of [$RhCl(cyclooctene)_2]_2$ with the terdentate nitrogen ligand bis(4,4-dimethyloxazolin-2-yl)pyridine

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(pybox) in dichloromethane gave the chloromethyl complex [$RhCl_2(CH_2Cl)$(pybox)].[5] In this case the complex [$RhCl_3$(pybox)] has been found as a side product of the oxidative addition reaction with CH_2Cl_2. An one-electron oxidative addition mechanism was proposed to account for this observation although no evidence was presented.

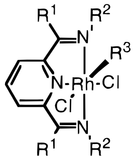
Our previous observations[1] in the context of these findings prompted us to study the reaction of **1** in H_2O with and without O_2 present with the aim to identify the intermediate steps in this reaction. To facilitate the identification of the intermediate steps the novel rhodium(III) hydride [$Rh(H)Cl_2(2,6\text{-}(C(R^1){=}N{-}R^2)_2C_5H_3N)$] ($R^1$ = Me, R^2 = *i*-Pr (**2**), R^1 = H, R^2 = *i*-Pr (**3**) and *t*-Bu (**4**)), the rhodium(III) deuteride [$Rh(D)Cl_2(2,6\text{-}(C(R^1){=}N{-}R^2)_2C_5H_3N)$] ($R^1$ = Me, R^2 = *i*-Pr (**5**), R^1 = H, R^2 = *i*-Pr (**6**), *t*-Bu (**7**)), and the new rhodium(III) peroxo complexes [$Rh(O_2)Cl(2,6\text{-}(C(R^1){=}N{-}R^2)_2C_5H_3N)$] ($R^1$ = Me, R^2 = *i*-Pr (**12**), R^1 = H, R^2 = *i*-Pr (**13**), *t*-Bu (**14**)) have been prepared and their reactivity studied.

Experimental Section

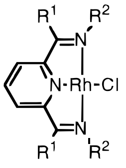
All experiments, including the experiments with oxygen, were carried out in a dry nitrogen atmosphere using standard Schlenk techniques at 298 K unless otherwise specified. Benzene, diethyl ether and hexane were distilled before use from sodium/benzophenone, and dichloromethane and chloroform, from calcium hydride. Molecular sieves (3 Å) were activated at 180 °C *in vacuo* for 24 h. Deuteriobenzene was dried over sodium and stored under nitrogen. Deuterated chlorinated solvents were dried with molecular sieves (3 Å) and stored under nitrogen. The ^1H NMR spectra were recorded on a Bruker AMX 300 MHz spectrometer. The spectra were indirectly referenced to TMS using residual solvent signals. Fast atom bombardment (FAB) mass spectrometry was carried out by the Institute for Mass Spectroscopy of the University of Amsterdam using a JEOL JMS SX/SX102A four-sector mass spectrometer, coupled to a JEOL MS-7000 data system. The samples were loaded in a matrix solution (nitrobenzyl alcohol) onto a stainless steel probe and bombarded with xenon atoms with an energy of 3 KeV. During the high-resolution FABMS measurements a resolving power of 5000 (10% valley definition) was used. CsI and/or glycerol was used to calibrate the mass spectrometer. Elemental analyses were carried out by our Institute. IR spectra were recorded on a Bio-Rad FTS-7 and a BIO-RAD FT IR FTS-60A spectrometer. Conductivity measurements were carried out with a Consort K720 conductometer. The pH measurements were carried out with a Metrohm digital pH-meter. Resonance Raman measurements were performed on a Dilor XY spectrophotometer, using a SP Model 2016 Ar^+ laser as excitation source. To avoid photodecomposition during the measurements the samples were spinned and the exciting laser beam was directed through a rotating prism. [$RhCl(C_2H_4)_2]_2$,[6] DCl gas,[7] the N−N−N nitrogen ligands $2,6\text{-}(C(R^1){=}N{-}R^2)C_5H_3N$ (R^1 = Me, R^2 = *i*-Pr, R^1 = H, R^2 = *i*-Pr, *t*-Bu), the rhodium(III) α-chlorotolyl complex [$RhCl_2(CHClPh)(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)$] (**1**), the square planar Rh(I) complexes [$RhCl(2,6\text{-}(C(R^1){=}N{-}R^2)_2C_5H_3N)$] ($R^1$ = Me, R^2 = *i*-Pr (**8**), R^1 = H, R^2 = *i*-Pr (**9**), *t*-Bu (**10**)) and the rhodium(III) chloride [$RhCl_3(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)$] (**11**) were prepared according to literature procedures.[1] Hoekloos oxygen 4.8 and Hoekloos HCl gas 2.5 were used. $N(Et_4)^+Cl^-$ was obtained from Aldrich.

The complexes studied have been collected in Table 1.

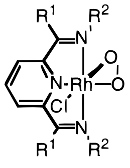
Table 1. Numbering of the Complexes and a Graphical Representation of the Complexes



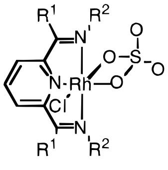
1–7, 11



8–10



12–14



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no.	R^1	R^2	R^3	no.	R^1	R^2	R^3
1	Me	*i*-Pr	CH(Cl)Ph	**8**[a]	Me	*i*-Pr	
2	Me	*i*-Pr	H	**9**[a]	H	*i*-Pr	
3	H	*i*-Pr	H	**10**[a]	H	*t*-Bu	
4	H	*t*-Bu	H	**11**[a]	Me	*i*-Pr	Cl
5	Me	*i*-Pr	D	**12**	Me	*i*-Pr	
6	H	*i*-Pr	D	**13**	H	*i*-Pr	
7	H	*t*-Bu	D	**14**	H	*t*-Bu	
				15	Me	*i*-Pr	

[a] See ref 1.

Conversion of [$RhCl_2(CHClPh)(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)$] (1) to [$Rh(H)Cl_2(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)$] (2) and Benzaldehyde in H_2O in the Absence of Oxygen. In 6 mL of degassed H_2O 0.0445 g of complex **1** (8.2×10^{-5} mol) was dissolved and heated to 353 K for 1 min. After the reaction mixture had cooled to room temperature, the volatile products were distilled off *in vacuo* giving a yellow powder of the hydride **2**. Yield: 0.0315 g (91%). The distillate, which had a pH of 2, was extracted with $CDCl_3$. ^1H NMR showed that the distillate contained benzaldehyde as was identified with an original sample. This experiment could also be carried out at RT (room temperature) for 1 h giving a virtually quantitative conversion to **2** and benzaldehyde.

When in a NMR tube 0.0045 g of complex **1** (8×10^{-6} mol) was dissolved in 0.5 mL of degassed D_2O, benzaldehyde, of which the carbonyl hydrogen atom was not deuterated, and the deuteride [$Rh(D)Cl_2(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)$] (**5**) were identified as the only products of the reaction. Also, the methyl group positioned on the imine carbon atom did not show deuterium incorporation.

Conversion of [$RhCl_2(CHClPh)(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)$] (1) to [$RhCl_3(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)$] (11), Benzaldehyde, and H_2O_2. In a NMR tube 0.0045 g of **1** (8×10^{-6} mol) was dissolved in 0.5 mL of D_2O and oxygen bubbled through at room temperature. Benzaldehyde, of which the carbonyl hydrogen atom was not deuterated, and **11** were identified as the only products of the reaction by ^1H NMR. The methyl group positioned on the imine carbon atom showed no deuterium incorporation. Benzoic acid, which might have been the oxidation product of benzaldehyde, was not observed by ^1H NMR.

Complex **1** (0.0028 g, 4.41×10^{-6} mol) was dissolved in H_2O, and O_2 was bubbled through at room temperature. The benzaldehyde was extracted with diethyl ether. The amount of H_2O_2 was determined by iodometry[8−10] which showed the formation of H_2O_2 in 80−90% yield. It was shown by a separate iodometric experiment that **11** did not interfere with the identification of H_2O_2. After the reaction no hydride **2** was present anymore, as the hydride itself was shown in a separate iodometric experiment to destroy the starch solution.

Study of the Reaction of the ligand $2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N$ with D_2O and with HCl(aq), respectively. The ligand $2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N$ (0.0023 g, 0.9×10^{-5} mol) was dissolved in 0.5 mL of D_2O, and subsequently within 10 min a ^1H NMR spectrum was recorded, which showed that the resonance of the methyl substituent on the imine carbon atom had disappeared indicating incorporation of deuterium.

A 3.0 mL volume of HCl (aq) (0.04 mol/L) was reacted with 0.0151 g of the ligand $2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N$ (6.2×10^{-5}

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mol) at reflux. After cooling to room temperature and evaporation of water *in vacuo,* white crystals of 2,6-diacetylpyridine were obtained as the hydrolysis product of 2,6-(C(Me)=N−*i*-Pr)$_2$C$_5$H$_3$N.

Synthesis of [Rh(H)Cl$_2$(2,6-(C(R^1)=N−R^2)$_2$C$_5$H$_3$N)] [R^1 = Me, R^2 = *i*-Pr (2), R^1 = H, R^2 = *i*-Pr (3), *t*-Bu (4)] and [Rh(D)Cl$_2$(2,6-(C(R^1)=N−R^2)$_2$C$_5$H$_3$N)] [R^1 = Me, R^2 = *i*-Pr (5), R^1 = H, R^2 = *i*-Pr (6), *t*-Bu] (7). As an example the preparation of complex **3** is given. To a solution of 0.0356 g of [RhCl(C$_2$H$_4$)$_2$]$_2$ (0.9×10^{-4} mol) in 3 mL of benzene was added a solution of 0.0409 g of 2,6-(C(H)N−*i*-Pr)$_2$C$_5$H$_3$N (1.9×10^{-4} mol) in 3 mL of benzene. The resulting mixture was heated to reflux, and a green solution was obtained, which indicated that [RhCl(2,6-(C(H)=N−*i*-Pr)$_2$C$_5$H$_3$N)] (**9**) was formed.[1] Subsequently the solution was filtered and cooled to room temperature. Benzene was evaporated *in vacuo* and the residue washed with diethyl ether (3 × 3 mL) to remove excess free ligand giving a green powder. The green powder was dissolved in benzene, and HCl gas (or in the case of the complexes **5**−**7** DCl gas) was bubbled through the green solution giving an orange precipitate, which was filtered off, washed with hexanes (3 × 2 mL), and dried *in vacuo* giving [Rh(H)Cl$_2$(2,6-(C(H)=N−*i*-Pr)$_2$C$_5$H$_3$N)] (**3**) as an orange powder. Yield: 0.069 g (93%). Yields: **2**, 89%; **4**, 96%; **5**, 96%; **6**, 78%; **7**, 96%.

Elemental analyses did not give really satisfactory results owing to product instability and/or solvent incorporation. However, FAB measurements clearly established the composition of the formed products.

MS-FAB+ (obs *m/z*, *calc m/z*): **2** (C$_{15}$H$_{24}$Cl$_2$N$_3$Rh − H), 418.0361, *418.0317*; **3** (C$_{13}$H$_{20}$Cl$_2$N$_3$Rh − H), 390.0002, *390.0004*; **5** (C$_{15}$H$_{23}$Cl$_2$DN$_3$Rh − D), 418.0309, *418.0317*; **6** (C$_{13}$H$_{19}$Cl$_2$DN$_3$Rh − D), 389.9978, *390.0004*; **7** (C$_{15}$H$_{23}$Cl$_2$DN$_3$Rh + H): 421.0528, *421.0535*. For complex **4** no FAB$^+$ spectrum could be obtained.

IR KBr disk (Rh−H): **2**, 2039 cm^{-1}; **4**, 2082 cm^{-1}. IR (Rh−D): **5**, 1456 cm^{-1}; **7**, 1499 cm^{-1}. No IR data could be obtained for **3** and **6** owing to product instability in KBr.

Reaction of [RhCl(2,6-(C(Me)=N−*i*-Pr)$_2$C$_5$H$_3$N)] (8) with HCl(aq). To a solution of 0.0850 g of [RhCl(C$_2$H$_4$)$_2$]$_2$ (2.18×10^{-4} mol) in 6 mL of benzene was added a solution of 0.1073 g of the ligand 2,6-(C(Me)=N−*i*-Pr)$_2$C$_5$H$_3$N (4.37×10^{-4} mol) in 4 mL of benzene. The reaction mixture was heated to reflux for 5 min during which it turned green indicating that **8** was formed.[1] The reaction mixture was cooled to room temperature, and subsequently 20 mL of 0.1 M degassed HCl(aq) (20×10^{-4} mol) was added with vigorous stirring, yielding a two-phase system containing a colorless benzene and a yellow acidic water solution. The colorless benzene solution was decanted, after which water was evaporated *in vacuo* giving a yellow powder of [Rh(H)Cl$_2$(2,6-(C(Me)=N−*i*-Pr)$_2$C$_5$H$_3$N)] (**2**). The product was washed with diethyl ether (3 × 3 mL) and dried *in vacuo*. Yield: 0.12 g (65%).

Study of the Stability of [Rh(H)Cl$_2$(2,6-(C(Me)=N−*i*-Pr)$_2$C$_5$H$_3$N)] (2) in Water. In 1.0 mL of degassed water was dissolved 0.0034 g of the yellow complex **2** (0.8×10^{-5} mol) yielding a yellow solution, which was stable for at least 1 h. Subsequently water was evaporated *in vacuo* giving a black colored residue. Analysis of this residue with IR spectroscopy showed that it did not contain **2** as the IR spectrum had changed and the Rh−H band had disappeared, which is in contrast to the experiment above, as in the latter case the presence of HCl stabilizes **2**.

The yellow hydride **2** (0.0023 g, 0.5×10^{-5} mol) was dissolved in 6.0 mL of degassed water, and subsequently, the conductivity and the pH were measured. The solution had a pH of 4.5 (i.e. a pK_a of 5.9), indicating that about 4% dissociation of HCl had occurred, and showed a molar conductance of 168 Ω^{-1} cm^2 mol^{-1}, which indicated the formation of HCl.

Reaction of [RhCl(2,6-(C(Me)=N−*i*-Pr)$_2$C$_5$H$_3$N)] (8) with HCl and Oxygen. A green solution of 0.0365 g of complex **8** (0.95×10^{-4} mol) in 4 mL of benzene was added to a stirred solution of HCl in 10 mL of water (pH = 1.4, 4.0×10^{-4} mol). The benzene solution turned colorless and the water phase yellow, as the hydride **2** was formed. Subsequently, oxygen was bubbled through the two-phase system. The colorless benzene solution was decanted. The water solution contained the known yellow complex [RhCl$_3$(2,6-(C(Me)=N−*i*-Pr)$_2$C$_5$H$_3$N)] (**11**) and H$_2$O$_2$, as was identified with iodometry.

Bubbling oxygen gas through a solution of the rhodium hydride **2** (0.0032 g, 7.6×10^{-6} mol) in 10 mL of HCl(aq) (0.1 mol L^{-1}) for 3 min gave H$_2$O$_2$ in 80−90% yield, as indicated by iodometry.

A solution of 0.0024 g of complex **11** (0.52×10^{-5} mol) had a pH of 6.5 and a molar conductance of 18.2 Ω^{-1} cm^2 mol^{-1} in 6.0 mL of degassed water, indicating some Cl$^-$ dissociation.

Synthesis of [RhCl(O$_2$)(2,6-(C(R^1)=N−R^2)$_2$C$_5$H$_3$N)] (R^1 = Me, R^2 = *i*-Pr (12), R^1 = H, R^2 = *i*-Pr (13), *t*-Bu (14)). A representative preparation is given for complex **13**. A solution of 0.0928 g of [RhCl(C$_2$H$_4$)$_2$]$_2$ (2.4×10^{-4} mol) in 3 mL of benzene was added to a solution of 0.1040 g of the ligand 2,6-(C(H)N-*i*-Pr)$_2$C$_5$H$_3$N (4.8×10^{-4} mol) in 3 mL of benzene. The resulting solution was heated to reflux yielding a green solution owing to the formation of [RhCl(2,6-(C(H)N-*i*-Pr)$_2$-C$_5$H$_3$N)] (**9**).[1] Subsequently the solution was cooled to room temperature and oxygen was bubbled through giving a brown suspension. The solid material was centrifuged off, washed with hexane (3 × 3mL), and dried *in vacuo* giving the product **13** as a yellow brown powder. Yield: 0.0831 g (49%). Yields: **12**, 49%; **14**, 67%.

Anal. Calcd for C$_{13}$H$_{19}$ClN$_3$O$_2$Rh (**13**): C, 39.36; H, 4.89; N, 10.36. Found: C, 40.28; H, 4.94; N, 10.84. Elemental analyses of **12** and **14** did not give satisfactory results, because the remaining solvent molecules could not be removed effectively. However, FAB measurement established clearly the composition of the formed products.

MS-FAB+ (obs *m/z*, *calc m/z*): **12** (C$_{15}$H$_{23}$O$_2$N$_3$ClRh + H), 416.0544, *416.0604*; **13** (C$_{13}$H$_{19}$O$_2$N$_3$ClRh + H), 388.0264, *388.0291*; **14** (C$_{15}$H$_{23}$ClN$_3$O$_2$Rh + H), 416.0591, *416.0604*.

We have carried out Raman measurements of the peroxo complexes **12** and **13** in a KNO$_3$ pellet with excitation wavelengths of 514.5, 488.0, and 457.9 nm, respectively. At lower excitation wavelengths, a band at 857 cm^{-1} in the case of **12** and at 879 cm^{-1} in the case of **13** with increasing intensity appeared, which is tentatively assigned to the ν(O−O) stretching frequency in accord with literature values.[11] No stretching frequency for ν(O-O) of complex **14** could be obtained, because of decomposition.

Reaction of Peroxo Complex 12 with HCl(aq). The peroxo complex **12** (0.0101 g, 2.4×10^{-5} mol) was dissolved in 3 mL of H$_2$O. Subsequently 2.3 mL of HCl(aq) (0.04 mol/L, 9.2×10^{-5} mol) was added. The solvent was evaporated *in vacuo* yielding a yellow powder which was extracted with dichloromethane. Dichloromethane was evaporated *in vacuo* yielding virtually quantitatively the complex **11**.

When the peroxo complex **12** (0.0030 g, 7.2×10^{-6} mol) was dissolved in HCl(aq), H$_2$O$_2$ was formed in 88% yield as shown by iodometry.

Reaction of [RhCl(2,6-(C(Me)N−*i*-Pr)$_2$C$_5$H$_3$N)] (8) with (Et$_4$)N$^+$Cl$^-$. In a NMR tube 0.0079 g of complex **8** (2.0×10^{-5} mol) and 0.0063 g of tetraethylammonium chloride (3.8×10^{-5} mol) were dissolved in 0.5 mL of deuterioacetone. A ^{1}H NMR spectrum of the mixture showed that no reaction had occurred. When instead of deuterioacetone D$_2$O was used as solvent, also no reaction was observed.

Study of the Stability of [RhCl(O$_2$)(2,6-(C(Me)N−*i*-Pr)$_2$C$_5$H$_3$N)] (12) in D$_2$O. In a NMR tube 0.0039 g of the peroxo complex **12** (9.3×10^{-6} mol) was dissolved in 0.46 mL of D$_2$O (2.0×10^{-2} mol/L) and subsequently a ^{1}H NMR spectrum recorded. Two species were observed in a ratio of 1.1:1.0 as concluded from the intensities of the H(5) signals of the nitrogen ligand. The solution was diluted to 4.4×10^{-3} mol/L, and a second ^{1}H NMR spectrum was recorded. Again

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[11] Allen, H.; Hill, O.; Tew, D. G. *Comprehensive coordination chemistry*; Pergamon: Oxford, U.K., 1987; Vol. 2, p 314 and references therein.

two species were observed, but now in a ratio of 1.0:2.3, which is in accord with the formation of two equilibrating species. After evaporation of D_2O the remaining yellow solid was dissolved in CD_2Cl_2. ^1H NMR of this solution showed that the peroxo complex **12** had not decomposed in D_2O and also that incorporation of deuterium into the ligand had not taken place.

A solution of 0.0026 g of the peroxo complex **12** (0.62×10^{-5} mol) in 6.0 mL of degassed water had a pH of 10 (i.e. a pK_b of 5) and a molar conductance of 24 Ω^{-1} cm^2 mol^{-1}.

Reaction of [RhCl(O$_2$)(2,6-(C(Me)N−*i*-Pr)$_2$C$_5$H$_3$N)] (12) in CH$_2$Cl$_2$ with *p*-Cresol, *p*-Chlorophenol, and *p*-Cyanophenol. To a brown-yellow solution of 0.0153 g of the rhodium(III) peroxo complex **12** (3.7×10^{-5} mol) in 3 mL of CH_2Cl_2 was added 0.0040 g of *p*-cresol (3.7×10^{-5} mol) at room temperature. After 1 min, a sample of the reaction mixture was taken and analyzed with ^1H NMR. No reaction had taken place as indicated by the ^1H NMR spectrum. However, when *p*-chlorophenol or *p*-cyanophenol was used, a reaction occurred, but the products could not be characterized.

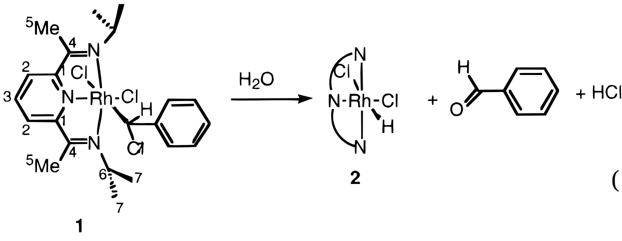
Reaction of [RhCl(O$_2$)(2,6-(C(Me)N−*i*-Pr)$_2$C$_5$H$_3$N)] (12) with SO$_2$, CO$_2$, CO, and Fumaronitrile in CD$_2$Cl$_2$. The peroxo complex **12** (0.0020 g, 4.8×10^{-6} mol) was dissolved in 0.5 mL of CD_2Cl_2. Subsequently, SO_2 gas was bubbled through the solution for 1 min at room temperature. Instantaneously [RhCl(SO$_4$)(2,6-(C(Me)N−*i*-Pr)$_2$C$_5$H$_3$N)] (**15**) was formed in quantitative yield as was concluded by ^1H NMR. The ^1H NMR spectrum of **15** was recorded before the complex had precipitated from the dichloromethane solution, which took 30 min.

No reaction occurred between the peroxo complex **15** and CO, CO_2 and fumaronitrile in CD_2Cl_2.

FAB$^+$ (obs *m/z*, *calc m/z*): **15** ($C_{15}H_{23}ClN_3O_4RhS$ + H), 480.0231, *480.0224*.

Results

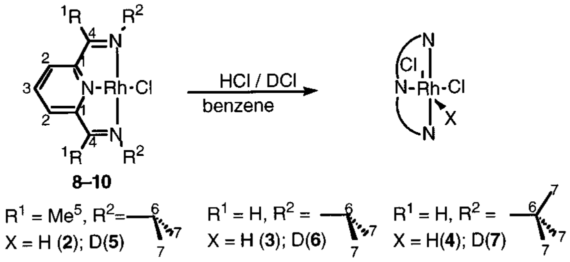
The reaction of the Rh(III) α-chlorotolyl complexes [RhCl$_2$(CHClPh)(2,6-(C(R^1)=N−R^2)$_2$C$_5$H$_3$N)] (R^1 = Me, R^2 = *i*-Pr (**1**), R^1 = H, R^2 = *i*-Pr and *t*-Bu) with H_2O in the absence or presence of oxygen could be studied most conveniently for complex **1**, because the reaction products could be isolated most easily. In the absence of oxygen complex **1** reacted with H_2O within 1 min at 353 K, or within 1 h at RT, to yield the hydride [Rh(H)Cl$_2$(2,6-(C(Me)=N−*i*-Pr)$_2$C$_5$H$_3$N)] (**2**), benzaldehyde, and HCl. In D_2O the metal deuteride [Rh(D)Cl$_2$(2,6-(C(Me)=N−*i*-Pr)$_2$C$_5$H$_3$N)] (**5**) was produced and DCl, but no incorporation of deuterium occurred in benzaldehyde nor did it occur in the N−N−N nitrogen ligand, indicating terdentate coordination during the course of the reaction (reaction 1). It should be noted that deuterium incorporation does occur rapidly when the free ligand is treated with D_2O. Furthermore, diacetylpyridine is formed when the free ligand is reacted with HCl(aq).



(1)

In order to investigate the properties of the above rhodium hydride (deuteride), the hydrides (deuterides) [Rh(X)Cl$_2$(2,6-(C(R^1)=N−R^2)$_2$C$_5$H$_3$N)] (X = H, R^1 = Me, R^2 = *i*-Pr (**2**), R^1 = H, R^2 = *i*-Pr (**3**), *t*-Bu (**4**) and X = D, R^1 = Me, R^2 = *i*-Pr (**5**), R^1 = H, R^2 = *i*-Pr (**6**) and *t*-Bu (**7**)) were prepared with gaseous HCl and DCl respectively (Scheme 1). The rhodium hydride **2** was also prepared with aqueous HCl. The hydrides (deuterides) are relatively unstable as they decomposed slowly even under a N_2 atmosphere. The rhodium hydrides and deuterides did not dissolve in benzene or toluene. In $CHCl_3$, CH_2Cl_2, CH_3OH, and CH_3CN the hydride **2** decomposed slowly but not in H_2O. IR spectra of the solid-state compounds in KBr showed the presence of metal−hydride and metal−deuteride stretching frequencies in the ranges 2039−2082 cm^{-1} and 1456−1499 cm^{-1}, respectively (see Experimental Section). The ratio of ν(Rh−H)/ν(Rh−D) is about 1.4 as would be expected.[12]

Scheme 1. Reaction of Complexes 8−10 with HCl or DCl To Yield the Rhodium(III) Hydride Complexes 2−4 and the Rhodium(III) Deuteride Complexes 5−7, Respectively



Owing to the instability of the complexes **2**−**7** ^{13}C spectra could not be measured, while for **2** a ^1H NMR spectra could be recorded in D_2O (Table 2), which showed that the N−N−N nitrogen ligand is terdentate bonded to Rh(III). We have observed that the difference between the chemical shifts of the H(2) *meta*-hydrogen atom and the H(3) *para*-hydrogen atom ($\Delta\delta$(H(3)−H(2))), which is 0.21 ppm for complex **2**, is a very good diagnostic parameter to distinguish between Rh(III) and Rh(I) complexes, as $\Delta\delta$(H(3)−H(2)) lies in the range of 0.1−0.3 ppm for Rh(III) and in the range of 0.5−1.2 ppm for Rh(I) complexes[1] (Table 2). The imine methyl group H(5) could not be deuterated in D_2O again indicating that the ligand coordinates as a terdentate. Unfortunately, the metal-bonded hydride could not be observed in D_2O owing to H/D exchange. As in the ^1H NMR spectra of the hydride **2**, the Me substituents of the *i*-Pr group are magnetically equivalent, and the H atom might be located at the equatorial position. However, in view of the stereochemistry of previously reported octahedral hydride complexes formed by addition of HX to square planar d^8-complexes,[13] it seems more likely that the H atom is located at one of the axial positions as designated in Scheme 1. The magnetic equivalence of the Me substituents of the *i*-Pr groups is then probably due to fast exchange of the hydride atom in D_2O. The occurrence of this exchange is very likely, as complex **2** is a conductor in H_2O with acidic properties (pK_a of 5.9). Therefore, this takes place via the formation of a small amount of HCl and of the Rh(I) complex **8**, which are in rapid equilibrium with the hydride **2** in H_2O. In addition one might also imagine the formation of anions of the type [RhCl$_2$(2,6-(C(Me)=N−*i*-Pr)$_2$C$_5$H$_3$N)]$^-$. However, treatment of **8** with N(Et$_4$)$^+$Cl$^-$ in either D_2O or deuterioacetone showed no evidence for these five-coordinate Rh(I) anions. The hydride **2** could be recovered by evaporation of water from the solution but only when some HCl was present. The absence of

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[12] Crabtree, R. G. *Encyclopedia of Inorganic Chemistry*; John Wiley & Sons: Chichester, U.K., 1994; Vol. 3, p 1392.

[13] Atwood, J. D. In *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole Publishing Co.: Monterey, CA, 1985; p 163.

Table 2. ^{1}H NMR Data (ppm) of the Complexes 2, 8, and 11, 12−15[a]

no.	ox	H(2)	H(3)	Δδ	H(4)/H(5)	H(6)	H(7)
2[b]	III	8.09 (d, 2H)	8.30 (t, 1H)	0.21	2.68 (s, 6H)	4.49 (sp, 2H)	1.35 (d, 12H)
8[a,b]	I	7.61 (br, 2H)	8.10 (br, 1H)	0.49	2.33 (br s, 6H)	4.55 (sp, 2H)	1.36 (d, 12H)
11[c,d]	III	7.95 (d, 2H)	8.22 (t, 1H)	0.27	2.72 (s, 6H)	4.4 (br, 2H)	1.65 (br d, 12H)
11[b,d]	III	8.36 (d, 2H)	8.49 (t, 1H)	0.13	2.94 (s, 6H)	4.64 (sp, 2H)	1.54 (d, 12H)
12[c]	III	7.92 (d, 2H)	8.05 (t, 1H)	0.13	2.67 (s, 6H)	4.26 (sp, 2H)	1.76 (d, 6H), 1.26 (d. 6H)
12[c,e]	III	7.95 (d, 2H)	8.10 (t, 1H)	0.15	2.65 (s, 6H)	4.18 (sp, 2H)	1.68 (d, 6H), 1.11 (d, 6H)
12[b]	III	8.44−8.21[f]	(multi, 3H)	≤0.23	2.86 and 2.84[g]	4.57 (multi, 2H)	1.51−1.47 (multi, 12H)
13[c]	III	7.93 (d, 2H)	8.01 (t, 1H)	0.08	8.08(2.7)[h] (d, 2H)	4.01 (sp, 2H)	1.52 (d, 6H), 1.44 (d, 6H)
14[c]	III	7.94 (d, 2H)	8.06 (t, 1H)	0.12	8.00(3.1)[h] (d, 2H)		1.54 (s, 18H)
15[c]	III	8.00 (d, 2H)	8.28 (t, 1H)	0.28	2.87 (s, 6H)	4.77 (sp, 2H)	1.75 (d, 6H), 1.58 (d, 6H)

[a] The ^{1}H NMR spectra were recorded at room temperature, unless otherwise specified, with 300.13 MHz. Abbreviations: ox = oxidation state, $\Delta\delta = (\delta H(3) - \delta H(2))$, s = singlet, d = doublet, t = triplet, sp = septet, multi = multiplet, br = broad. [b] Measured in D_2O. [c] Measured in CD_2Cl_2. [d] The values have been taken from ref 1. [e] $T = 183$ K. [f] H(2) and H(3) show overlap. [g] Two singlets with a total intensity of 6H. [h] $^3J(Rh-H)$ in Hz.

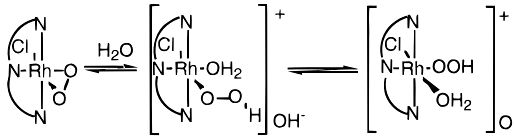
HCl caused the formation of a blackish material, which could not be characterized, but which was definitely not a hydride.

When we now turn to the second reaction sequence, i.e. the further reaction with O_2, we observed that the Rh(I) complex **8**, dissolved in benzene, reacted with HCl to give the hydride **2** and then with O_2 and HCl to give the trichloride [$RhCl_3$(2,6-(C(Me)=N−*i*-Pr)$_2C_5H_3N$)] (**11**). Treatment of **2** dissolved in HCl(aq) with O_2 yielded the trichloride **11** and 80−90% H_2O_2.

In order to find out if we could reverse the order of addition of HCl and O_2 to the Rh(I) complex **8**, we prepared the new compounds [Rh(O_2)Cl(2,6-(C(Me)=N−*i*-Pr)$_2C_5H_3N$)] (R^1 = Me, R^2 = *i*-Pr (**12**), R^1 = H, R^2 = *i*-Pr (**13**), *t*-Bu (**14**)). We have carried out Raman measurements of the peroxo complexes **12**−**14** in a KNO_3 pellet with excitation wavelengths of 514.5, 488.0, and 457.9 nm, respectively. At lower excitation wavelengths, a band at 857 cm^{-1} in the case of **12** and a band at 879 cm^{-1} in the case of **13** with increasing intensity appeared, which are tentatively assigned to the ν(O−O) stretching frequency in accord with literature values for peroxo groups.[11,14] Complex **14** decomposed in the laser beam during the Raman measurements. The complexes are soluble in H_2O, slightly soluble in $CHCl_3$, CH_2Cl_2, and CH_3CN, but insoluble in benzene and hexanes. The ^{13}C spectra could not be measured owing to the low solubility, but the ^{1}H NMR spectra of the rhodium(III) peroxo complexes in CD_2Cl_2 indicate the presence of Rh(III) species in view of the characteristic H(2) and H(3) chemical shifts of the nitrogen N−N−N ligand (Table 2). The Me groups on each *i*-Pr group are diastereotopic showing that the configuration is similar to that of e.g. $(Ph_3P)_2(CO)Ir(O_2)I$,[15] as one O atom must be in the equatorial plane and the other close to one of the axial positions, while the Cl atom is at the other axial position.

It should be noted that for **12** there are no changes in the ^{1}H NMR in CD_2Cl_2 of the N−N−N nitrogen ligand in the range 183−293 K indicating that there is no equilibrium between ter- and bidentate-bonded isomers as observed for [$RhCl_2(R^3)$(2,6-(C(Me)=N−*i*-Pr)$_2C_5H_3N$)] (R^3 = Cl, CH_2Cl, $CHCl_2$, CHClPh).[1] With respect to its properties we should note that O_2 is strongly bonded, as it did not dissociate under vacuum or by bubbling N_2 through a CD_2Cl_2 or H_2O solution.

Interestingly, the ^{1}H NMR of complex **12** in D_2O shows the presence of two species that are clearly different from the single species observed in CD_2Cl_2. Both species in D_2O contain the N−N−N ligand bonded as a terdentate ligand to Rh(III) (Table 2). When D_2O was evaporated and the residue dissolved in CD_2Cl_2, it could be clearly established that the peroxo complex **12** had been recovered quantitatively and unchanged. This shows that the two isomers in D_2O solution must have metal-bonded O_2-containing moieties. Rather illuminating is that a solution of **12** in H_2O with a concentration of 1.0×10^{-3} mol L^{-1} has a pH of 10 (i.e. a pK_b of 5), while the solution is to some extent conducting (see Experimental Section). The basicity of the solution points to the formation of OH^-, while the solubility in H_2O of **12** indicates H_2O coordination. We therefore, tentatively formulate the two equilibrating species as two isomers with composition [RhCl(OOH)(H_2O)(2,6-(C(Me)=N−*i*-Pr)$_2C_5H_3N$)]$^+OH^-$ (reaction 2).



12

(2)

The two isomers (reaction 2) probably differ by the relative positions of the OOH and of the coordinated H_2O molecule, as either the equatorial or the axial O atom of the O_2 ligand may be protonated. Further evidence for this formulation is obtained from the fact that treatment of this H_2O solution with HCl afforded in virtually quantitative yield (90%) the rhodium(III) chloride complex **11** and H_2O_2. It is to be expected that in a H_2O solution hydrogen bridging will occur between solvent water, metal-coordinated water, and hydroxyl anions. It is therefore not surprising that the isomer ratio is concentration dependent (see Experimental Section). We have made strong attempts to identify the two isomers with IR spectroscopy in a Nujol water mixture and in THF containing a small amount of water and also in pure water, but we were not successful. It might be possible that one of these two species occurring in H_2O is in fact the same species as found in CD_2Cl_2, since the ^{1}H NMR shift might be strongly solvent dependent.

Finally it should be noted that the trichloride **11**, when dissolved in water, is only slightly conducting and is neither basic nor acidic (see Experimental Section).

Discussion

Previously, we reported that the reaction of [RhCl(2,6-(C(Me)=N−*i*-Pr)$_2C_5H_3N$)] with CH_2Cl_2, $CHCl_3$,

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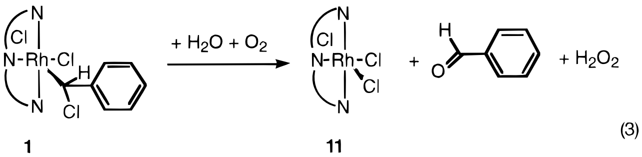
(14) Gubelmann, M. H.; Williams, A. F. *Struct. Bonding (Berlin)* **1983**, *55*, 2 and references therein.

(15) McGinnety, J. A.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 2243.

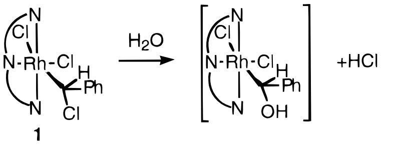
$PhCH_2Cl$, $PhCHCl_2$, and Cl_2 led to the facile formation of $[RhCl_2(R^3)(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)]$ ($R^3 = CH_2Cl$, $CHCl_2$, CH_2Ph, CHClPh (**1**) and Cl (**11**)).[1] Sometimes irreproducible amounts of **11** were observed as side products in the synthesis of the products with $R^3 = CH_2Cl$ and $CHCl_2$. It was soon discovered that the formation of the trichloride **11** was caused by the presence of O_2 and H_2O. We further found that, when the α-chlorotolyl complex **1** in H_2O was on purpose treated with O_2, the trichloride **11**, H_2O_2, and benzaldehyde were formed.[1] Our present investigations have now shown that the reaction (reaction 3) proceeds in two consecutive reaction sequences.



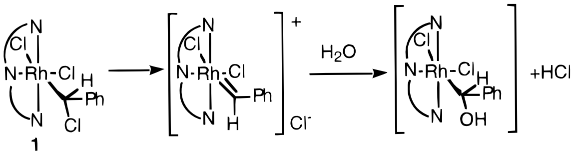
(3)

The first sequence (reaction 1) involves the reaction of the α-chlorotolyl complex **1** with H_2O which produces the rhodium hydride **2**, benzaldehyde, and HCl.

The first step (reaction 4) in this first sequence is likely the hydrolysis of the C−Cl bond, which is expected to be weak as indicated by the long C−Cl bond length in the X-ray structures of $[RhCl_2(CH_2Cl)(2,6\text{-}(C(H){=}N{-}R^2)_2C_5H_3N)]$ ($R^2 = i$-Pr, cyclohexyl).[1] In both cases the Rh−C bond is relatively short and as a resonance form one could imagine a rhodium−carbene type of bonding i.e. $[Rh{=}C(H)_2]Cl^-$ in analogy to other metal chloroalkyl complexes.[4,16] One may therefore also imagine a second alternative, as proposed by McCrindle et al.[3] for the hydrolysis of *trans*-$(PEt_3)_2Pt(CH_2Cl)Cl$, which involves the intermediacy of a metal−carbene species (reaction 5).

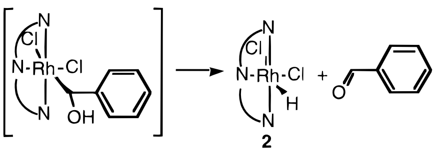


(4)



(5)

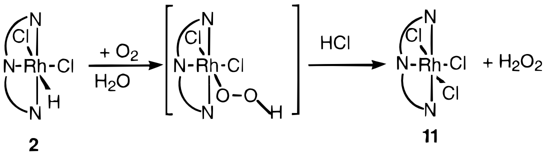
The nonobserved intermediate $[RhCl_2(CH(OH)Ph)(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)]$ (reactions 4 and 5) in aqueous HCl may undergo now a β-H elimination (reaction 6).[17] The necessary accessible coordination position is likely provided by substitution of Cl^- by H_2O, although dissociation of one imine N-atom cannot be excluded. This step (reaction 6) is analogous to the one proposed for the formation of formaldehyde and *trans*-$(PEt_3)_2Pt(H)Cl$ from *trans*-$(PEt_3)_2Pt(CH_2OH)Cl$.[3]



(6)

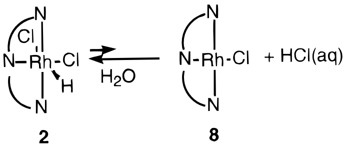
When the reaction of the chlorotolyl complex **1** was carried out in D_2O, the deuteride **5** and DCl were obtained together with nondeuterated benzaldehyde. Also, the N−N−N ligand was not deuterated indicating that the β-H elimination indeed proceeds via an easily available coordination site created by substitution of an equatorial Cl^- by H_2O rather than by N-dissociation of an imine side arm, as in the latter case incorporation of deuterium would be likely, as for the free ligand the incorporation of deuterium is a fast reaction (see Experimental Section).

The subsequent second reaction sequence might take two different routes, which could be studied separately, as it was possible to prepare the rhodium(III) hydride **2** and the rhodium(III) peroxo complex **12** from the square planar complex **8** with HCl (Scheme 1) and O_2, respectively. The first pathway may involve insertion of O_2 in the Rh−H bond of **2** to give $[RhCl_2(OOH)(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)]$, which is then converted with HCl in H_2O to the rhodium(III) chloride **11** and H_2O_2 (reaction 7).



(7)

There is ample evidence in the literature that O_2 insertion in metal−hydride bonds does occur.[18,19] However, we have also to take into account that in H_2O the hydride **2** behaves as a weak acid owing to dissociation of HCl. This dissociation is reversible, but some excess of HCl is needed to recover the hydride unchanged by evaporation of H_2O. It seems logical that in H_2O the Cl^- *trans* to the hydride dissociates and is substituted by H_2O with concomitant dissociation of H^+ and formation of the Rh(I) complex **8**. As the solution is weakly acidic and no Rh(I) complexes, which are badly soluble, deposit from the solution, the equilibrium must lie far to the left (reaction 8) and is expected to be fast on the NMR time scale. Also the chemical shifts of the N−N−N ligand of complex **2** in D_2O are characteristic of a Rh(III) complex (Table 2).



(8)

Another possible equilibrium is reaction 9. This type of equilibrium although certainly not excluded could not be confirmed, as treatment of **8** with $[NEt_4]Cl$ did not lead to observable $[RhCl_2(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)]^-$ anions. This equilibrium may well exist but must also be positioned very much to the left.

However, even if **8** or $[RhCl_2(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)]^-$ anions are present in only small amounts, addition of O_2 to these Rh(I) compounds will occur and

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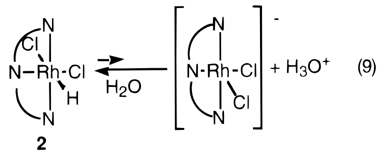
(16) Friedrich, H. B.; Moss, J. R. *Adv. Organomet. Chem.* **1991**, *33*, 235.

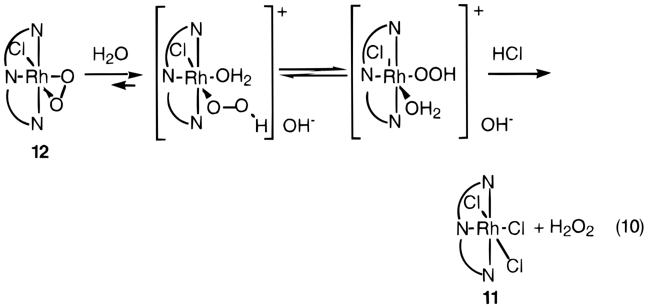
(17) Steinborn, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 401 and references therein.

(18) Carmona, D.; Lamata, M. P.; Ferrer, J.; Modrego, J.; Perales, M.; Lahoz, F. J.; Atencio, R.; Oro, L. A. *J. Chem. Soc., Chem. Commun.* **1994**, 575.

(19) Mimoun, H. *Comprehensive coordination chemistry*; Pergamon Press: New York, 1987; p 318 and references therein.



will drive reactions 8 and/or 9 to the right. This second pathway, which involves in fact first the formation of the rhodium(III) peroxo complex **12**, is indeed a real possibility, as demonstrated by the reaction of the square planar complexes **8**−**10** with O_2 which gives in high yields **12**−**14**, respectively. Treatment of **12** with aqueous HCl subsequently afforded the rhodium(III) chloride compound **11** and H_2O_2 in 80−90% yield (reaction 10).



In reaction 10 we have incorporated the findings that in water the dioxygen complex **12** occurs in two isomeric forms which are clearly different from the starting peroxo complex in CD_2Cl_2 or in the solid state. Two equilibrating isomers with a composition $[RhCl(OOH)(H_2O)(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)]^+OH^-$ are tentatively proposed. It should be noted that whether we make the peroxo complex react first with H_2O and then with HCl or directly with aqueous HCl does not make any difference at all for the formation of H_2O_2.

Also in the literature[14,20−23] there is sufficient evidence for the formation of MOOH species from peroxo complexes and subsequent conversion to H_2O_2. The virtually quantitative formation of H_2O_2 from the peroxo complex **12** is comparable to what is produced in reaction 3. Therefore, reaction 3 may proceed via a pathway involving the intermediacy of the peroxo complex **12** (reaction 10) in addition to a pathway proceeding via insertion of O_2 in the Rh−H bond of complex **2** (reaction 7).

As MOOH species have been prepared by reaction of $(PPh_3)_2PtO_2$ with HOR (R = Ph),[20] it has also been attempted to protonate the rhodium(III) peroxo **12** with *p*-cresol, *p*-chlorophenol, and *p*-cyanophenol. However, *p*-cresol did not react, while the other two phenols produced uncharacterizable products.

Finally, some attention will now be paid to some spectroscopic properties of the novel hydride (deuteride) rhodium complexes **2**−**7**. The hydrides are rather unstable and therefore difficult to investigate. Clearly, the Rh−H and Rh−D stretching frequencies decrease appreciably when R^1 = H and R^2 = *t*-Bu are substituted by R^1 = Me and R^2 = *i*-Pr, *i.e.* from 2082 to 2039 cm^{-1} and from 1499 to 1456 cm^{-1}, respectively (Experimental Section). It would appear that the Rh-H(D) bond is strongly influenced by electron donation from the three N-atoms of the nitrogen ligand. As the Rh−H(D) bond strength appears to decrease with increasing electron donation of the nitrogen ligand, it seems that in the solid state the hydride has hydridic character.[12]

Finally, it is interesting to note that very few peroxo complexes of rhodium have been reported,[11,19,22,24−31] while no peroxo complexes are known of Rh(III) containing terdentate bonded nitrogen ligands. In the case of $(Ph_3P)_2(CO)RhCl$ singlet oxygen had to be used to make an unstable peroxo compound,[28] while reversible dioxygen carriers have been reported in the case of *e.g.* rhodium iminophosphine complexes.[27] The dioxygen complexes reported by us appear to be unusually stable toward dissociation of O_2, as bubbling through N_2 gas or the employment of low pressures did not cause O_2 loss. This stability must be ascribed to the strong electron-donating properties of the N−N−N nitrogen ligands.[1] Such influence of electron-donating ligands on the stability of the metal−peroxo bond has been mentioned before.[32,33] Also, we wish to stress that, as far as we are aware, these rhodium peroxo compounds are the first examples in which O_2 is irreversible bonded to rhodium, while reversible O_2 binding is typical of rhodium complexes.[31 34]

In agreement with other work involving Rh complexes,[14,19,35,36] we find that the peroxo complex **12** reacts with SO_2 to give $[Rh(SO_4)Cl(2,6\text{-}(C(Me){=}N{-}i\text{-}Pr)_2C_5H_3N)]$ (**15**), but not with substrates such as CO, CO_2, and fumaronitrile in CD_2Cl_2. Complex **15** contains a terdentate bonded N−N−N nitrogen ligand and a SO_4 ligand which coordinates as a bidentate with one O atom in the equatorial position and a second O atom in the axial position, as shown by the diastereotopic methyl substituents on both *i*-Pr groups.

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