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Synthesis, Structure, and Reactivity of Rhodium Bipyridine Compounds: Formation of a Rh^{II} Hydrido Cluster and a Rh^{III} Peroxido Complex

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Treatment of $[Rh(\mu\text{-}Cl)(coe)_2]_2$ (coe = cyclooctene) with 4,4′-di-*tert*-butyl-2,2′-bipyridine (tbbpy) gives the bipyridine complex [Rh(Cl)(tbbpy)(coe)] (**1**). A subsequent reaction with dihydrogen results in the formation of the cluster $[\{Rh(Cl)(H)(tbbpy)\}]_4$ (**2**). The reaction of $[Rh(\mu\text{-}Cl)(coe)_2]_2$ with tbbpy in thf followed by the addition of CN*t*Bu affords [Rh(Cl)(tbbpy)(CN*t*Bu)] (**3**). The latter reacts with O_2 or $^{18}O_2$ to yield the peroxido complexes $[Rh(Cl)(O_2)(tbbpy)(CNtBu)]$ (**4a**) and $[Rh(Cl)(^{18}O_2)(tbbpy)\text{-}(CNtBu)]$ (**4b**), respectively. Complexes **1**–**4** were characterized by X-ray crystallography.

Introduction

An attractive substrate for transition-metal-mediated oxygenation or oxidation reactions is oxygen itself, as it is a cheap and environmentally benign reagent.[1] Peroxido complexes can play a key role in these processes.[1–3] We showed that they can be intermediates in the rhodium-mediated formation of peroxides, but they are also useful starting compounds for the formation of rhodium perborates and perboronates.[4,5] In addition they can be applied in the oxygenation of pinacolborane.[6] Tejel et al. found that ligands like cyclooctadiene can be oxygenated in the coordination sphere of rhodium.[7] The conversions proceed presumably via intermediate peroxido species.

A variety of Rh^{III} peroxido complexes have been reported in the literature, in some of which oxygen is bound reversibly.[8,9] Furthermore, rhodium complexes have also been described that might bind oxygen with no net change in the oxidation state of the metal.[10] By far, most of the rhodium peroxido complexes contain phosphane ligands in the coordination sphere of the metal. Because a free phosphane as well as a metal-bound phosphane are prone to oxygenation reactions, the corresponding peroxido complexes are less suitable as oxygenation catalysts.[6,11–15] It is therefore desirable to synthesize rhodium peroxido compounds that do not include any phosphanes as additional ligands. So far, only a limited number of these compounds have been reported, including complexes with N-heterocyclic carbene ligands.[10,13] Cationic rhodium peroxido complexes that contain tetradentate tri(2-pyridylmethyl)amine ligands have also been described.[14] Furthermore, a phosphane-free scorpionate peroxido rhodium complex is known, whereas Milstein et al. found that dioxygen reacts with a rhodium(I) dimethylbypyridine species to give the peroxido complex $[Rh(Cl)(O_2)(dmso)(dmbpy)]$ (dmso = dimethyl sulfoxide, dmbpy = 4,4′-dimethyl-2,2′-bipyridine).[16] For the latter compound, the exact configuration at the rhodium center has not been determined. Note that rhodium(I) bipyridine species are fairly rare and most of them are cationic.[16–19]

In this paper we report on the synthesis of new rhodium(I) bipyridine compounds, one of which serves as a useful starting compound for a rhodium(III) peroxido complex. The formation of an unusual rhodium hydride cluster has also been observed.

Results and Discussion

The reaction of $[Rh(\mu\text{-}Cl)(coe)_2]_2$ (coe = cyclooctene) with 4,4′-di-*tert*-butyl-2,2′bipyridine (tbbpy, 1 equiv.) in thf affords the intense-blue product [Rh(Cl)(tbbpy)(coe)] (**1**; Scheme 1). The ^1H NMR spectrum of **1** exhibits six resonances in the aromatic region, which can be assigned to the aromatic hydrogen atoms of the bipyridine ligand. Two singlets at 1.02 and 1.00 ppm reveal the *t*Bu groups and three signals at 4.84, 2.54, and 1.61 ppm were observed for the coordinated cyclooctene unit.

Dark-brown crystals of **1** were obtained from a C_6D_6 solution at 283 K. The molecular structure was determined by X-ray diffraction analysis at low temperature (Figure 1). Selected bond lengths and angles are summarized in Table 1. Complex **1** crystallizes in the space group $P\bar{1}$ with two independent molecules in the unit cell. The rhodium atom exhibits a square-planar coordination sphere. The Rh1–N1 bond to the bipyridine ligand in **1** [2.086(3) Å and 2.084(3) Å for two independent molecules in the unit cell]

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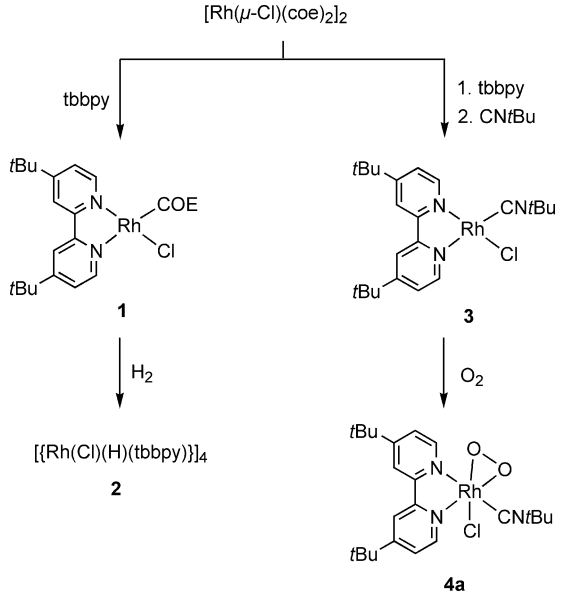

Scheme 1. Synthesis and reactivity of rhodium bipyridine compounds.

is identical to the rhodium nitrogen bonds lengths in [Rh(dmbpy)(CN*t*Bu)$_2$]Cl [2.060(7) and 2.077(6) Å].[16] The Rh1–N2 bond in **1** [2.016(3) Å] is shorter, possibly because of a push–pull interaction that leads to a transfer of electron density from the π-donor chlorido ligand to the bipyridine ligand, which is a π acceptor.

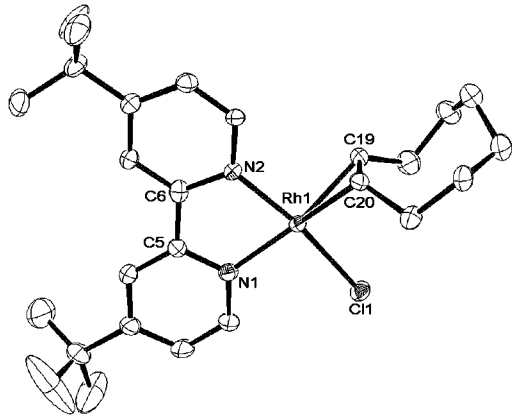

Figure 1. An ORTEP diagram of **1**. Ellipsoids are drawn at the 50% probability level; only one of the two independent molecules is depicted.

The reaction of cyclooctadiene complex **1** with dioxygen led only to a product mixture, which could not be identified further. Note that Tejel et al. found that a cyclooctadiene ligand can be oxygenated at rhodium.[7] To elucidate the ability of **1** towards oxidative addition reactions,[16] we became interested in its reactivity towards H_2. Rhodium bipyridine complexes have been applied as hydrogenation catalysts.[17] A reversible oxidative addition of H_2 at cationic rhodium bipyridine complexes has also been reported.[19]

Table 1. Selected bond lengths [Å] and angles [°] in **1**.[a]

Rh1–Cl1	2.3481(11) [2.3585(11)]	Rh1–N1	2.086(3) [2.084(3)]
Rh1–C19	2.123(4) [2.115(4)]	Rh1–N2	2.016(3) [2.018(3)]
Rh1–C20	2.135(4) [2.124(4)]	C19–C20	1.400(5) [1.386(5)]
Cl1–Rh1–N1	91.81(9) [91.88(9)]	N1–Rh1–N2	79.36(14) [79.11(13)]
Cl1–Rh1–C20	96.34(11) [96.82(10)]	Cl1–Rh1–N2	170.93(10) [170.73(10)]
N2–Rh1–C20	92.65(14) [92.33(14)]	N1–Rh1–C20	157.79(14) [155.56(14)]

[a] The corresponding data of the second independent molecule are given in square brackets.

On treatment of a solution of [Rh(Cl)(tbbpy)(coe)] (**1**) with dihydrogen, the cluster compound [{Rh(Cl)(H)(tbbpy)}]$_4$ (**2**) is furnished (Scheme 1). Compound **2** was characterized by its spectroscopic data. IR spectra do not reveal any terminal Rh–H vibration. Strong background fluorescence frustrated the acquisition of Raman data (Nd:YAG 1064 nm). The ^{1}H NMR spectrum of **2** reveals three signals for the hydrogen atoms at the heteroaryl ligand. A doublet at 10.63 ppm ($^3J_{H,H}$ = 6.1 Hz) can be attributed to the protons H-6 and H-6′. The spectrum also shows a signal that is of higher order at –20.29 ppm for the four hydrido ligands, compatible with either equivalent hydrides or a fluxional structure (Figure 2). Low-temperature NMR spectroscopy did not lead to a significant change in the shape of the signal. The longitudinal T_1 spin lattice relaxation times for the hydrides were determined by ^{1}H NMR spectroscopy in a [D$_8$]thf solution between 193 and 263 K. All data indicate the presence of hydrido ligands bound in a classical mode.[20] The T_1 at 203 K is 1150 ms at 400 MHz.

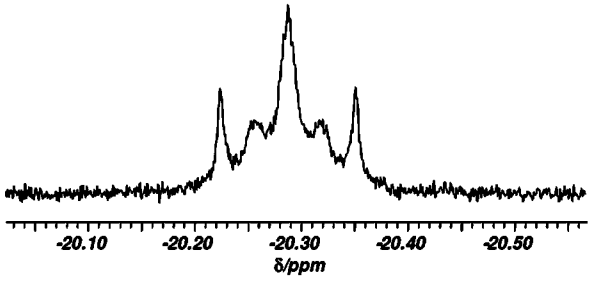

Figure 2. Part of the ^{1}H NMR spectrum (400 MHz) of complex **2**.

The structure of the cluster [{Rh(Cl)(H)(tbbpy)}]$_4$ (**2**) was determined by X-ray diffraction analysis at 100 K (Figure 3). Suitable crystals were obtained from a benzene solution at 293 K. Selected bond lengths and angles are summarized in Table 2. The hydrides in **2** could not be located. The structure exhibits D_{2d} symmetry and shows a distorted tetrahedral arrangement of the four rhodium atoms. The molecule is located on a S_4 axis, which generates the four equivalent rhodium centers. The geometry at the rhodium centers is approximately octahedral. The Rh1–Rh1#3 distance of 2.7910(9) Å is longer in comparison to the Rh1–Rh1#1 and the Rh1#2–Rh1#3 bonds lengths

[2.5820(12) Å]. The four bipyridine ligands are coordinated each to one rhodium center. The Rh1–N1 distance to the bipyridine ligand [2.043(7) Å] is shorter in comparison to the Rh1–N1 bond length found in **1** [2.086(3) Å].

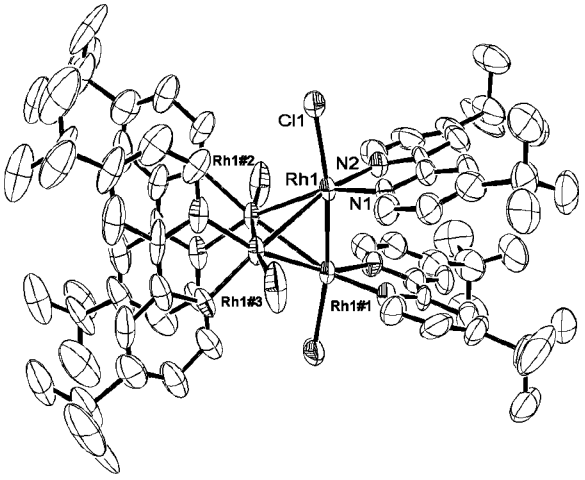

Figure 3. An ORTEP diagram of **2**. Ellipsoids are drawn at the 50% probability level.

Table 2. Selected bond lengths [Å] and angles [°] in **2**.[a]

Rh1–Cl1	2.567(3)	Rh1–Rh1#1	2.5820(12)
Rh1–N1	2.043(7)	Rh1–Rh1#3	2.7910(9)
Rh1–N2	2.014(8)		
Cl1–Rh1–N1	85.4(2)	N1–Rh1–N2	79.6(3)
Cl1–Rh1–N2	90.2(2)	Rh1#1-Rh1–Rh1#2	62.448(11)
Rh1#2-Rh1–Rh1#3	55.10(2)		

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x$, $-y + 1$, z; #2: $-y + 1/2$, $x + 1/2$, $-z + 1/2$; #3: $y - 1/2$, $-x + 1/2$, $-z + 1/2$.

The Rh_4 distorted tetrahedron configuration in **2** is comparable to the arrangement of the rhodium atoms in the cluster $[Rh(H)(cod)]_4$ (cod = cyclooctadiene), which has also D_{2d} symmetry, even though the latter is a Rh^I compound.[21] Although, we could not elucidate the positions of the hydrogen atoms in the solid state, cluster **2** is, to the best of our knowledge, the only Rh_4 cluster that has been described and that includes rhodium centers in the formal oxidation state +II. The iridium(II) cluster $[Ir_4(H)_4(\mu\text{-}H)_4](CO)_4(PPh_3)_4]$ exhibits four terminal hydrides and four hydrogen atoms that are located on four edges of a distorted Ir_4 tetrahedron.[22] A comparable arrangement for **2** is feasible with bridging hydrogen atoms at the four longer Rh–Rh edges, which are not perpendicular to the S_4 axis. A μ_3-arrangement with the hydrogen atoms at the faces of the Rh_4 unit is also conceivable, as it has been found for $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu_3\text{-}H)\}_4]^{2+}$ by a neutron diffraction study.[23]

A reaction of the rhodium dimer $[Rh(\mu\text{-}Cl)(coe)_2]_2$ with 4,4′-di-*tert*-butyl-2,2′bipyridine in thf followed by the addition of *tert*-butylisocyanide affords the black product [Rh(Cl)(tbbpy)(CN*t*Bu)] (**3**) after 12 h (Scheme 1). Complex **3** is stable in the solid state under an atmosphere of argon for a few weeks. The carbonyl complexes [RhI(bpy)(CO)] and [RhI(dmbpy)(CO)], which are comparable to **3**, were reported by Haynes et al. and Stufkens and coworkers.[18b,18d]

The IR spectrum of **3** shows two strong absorption bands at 2089 and 2056 cm^{-1} in the solid state, which can be assigned to vibrations that correspond to the CN*t*Bu ligand. For comparison, the IR spectrum of complex *trans*-$[Rh(Cl)(P\textit{i}Pr_3)_2(CNR)]$ (R = neopentyl) exhibits a strong band at 2056 cm^{-1} and a weak band at 2032 cm^{-1}, whereas for *trans*-$[Rh(Cl)(P\textit{i}Pr_3)_2(CNR)]$ (R = 2,6-xylyl) both bands at 2047 and at 2016 cm^{-1} are strong.[24] Multiple splitting of absorption bands in the IR spectra of other isocyanide complexes is documented in the literature.[25] The ^1H NMR spectrum of **3** reveals two signals at low field at 10.02 ppm ($^3J_{H,H}$ = 4.0 Hz) and at 9.09 ppm ($^3J_{H,H}$ = 4.0 Hz) for H-6 or H6′, which are located in the *ortho* positions to the aromatic nitrogen in heteroaryl ligand **1**. Two singlets in the ^1H NMR spectrum at 1.03 and 1.02 ppm can be attributed to the *t*Bu groups of the bipyridine ligand and a singlet at 1.25 ppm to the *t*Bu group of the metal-bound isocyanide.

The molecular structure of **3** was also confirmed by X-ray diffraction analysis at 150 K (Figure 4). Suitable crystals of **3** were obtained from a C_6D_6 solution at 293 K. Selected bond lengths and angles are summarized in Table 3. The molecular structure reveals a square-planar configuration. The rhodium–nitrogen bond lengths of the bipyridine ligand in **3** are fairly identical to the rhodium nitrogen bonds lengths in **1**. The rhodium–carbon bond length to the isocyanide group in **3** of 1.865(3) Å is slightly shorter than the comparable distances found in the complex *trans*-$[Rh(4\text{-}C_5NF_4)(CN\textit{t}Bu)(PEt_3)_2]$ [1.905(3) Å] and slightly longer than in *trans*-$[Rh(Cl)(P\textit{i}Pr_3)_2(CNR)]$ [R = 2,6-xylyl, 1.834(4) Å; R = neopentyl, 1.830(5) Å].[24,26] As it has been observed for *trans*-$[Rh(4\text{-}C_5NF_4)(CN\textit{t}Bu)(PEt_3)_2]$ [172.5(3)°], compound **3** displays a bent C–N–CMe_3 linkage with a C19–N3–C20 angle of 172.2(3)°.[26]

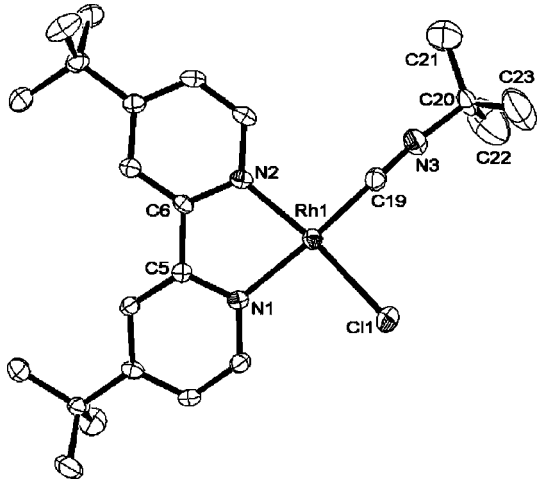

Figure 4. An ORTEP diagram of **3**. Ellipsoids are drawn at the 50% probability level.

Exposure of **3** to molecular oxygen rapidly leads to the generation of the pale yellow dioxygen complex [Rh(Cl)-(O_2)(tbbpy)(CN*t*Bu)] (**4a**) within a few minutes (Scheme 1).

Table 3. Selected bond lengths [Å] and angles [°] in **3**.

Rh1–Cl1	2.3510(9)	Rh1–N1	2.068(2)
Rh1–C19	1.865(3)	Rh1–N2	2.006(2)
C19–N3	1.174(4)	N3–C20	1.445(4)
Cl1–Rh1–N1	94.13(6)	N1–Rh1–N2	79.19(9)
Cl1–Rh1–C19	90.72(9)	Cl1–Rh1–N2	172.34(7)
N2–Rh1–C19	96.29(11)	N1–Rh1–C19	172.65(11)

Similarly, treatment of **3** with $^{18}O_2$ gives the peroxido complex [Rh(Cl)($^{18}O_2$)(tbbpy)(CN*t*Bu)] (**4b**). The formation of **4a** proceeds in the solid state. Compounds **4a** and **4b** are only soluble in very polar solvents such as acetonitrile or 1,2-difluorobenzene. The reaction in thf solution also gives certain amounts of **4a** according to the IR spectra, but the conversion is less selective and several other products could not be characterized. It should be noted that O_2 is bonded strongly and did not dissociate under vacuum or by bubbling argon through a solution of **4a** in acetonitrile.[9]

Complex **4a** was characterized by its spectroscopic data. The IR spectrum of **4a** exhibits one absorption band at 2195 cm^{-1}, which can be assigned to the isocyanide stretching vibration. For comparison, an absorption band at 2161 cm^{-1} was found for the peroxido complex *trans*-[Rh(O_2)(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$].[4] The latter includes the tetrafluoropyridyl ligand, which is considered to have some stabilizing properties.[4–6,26,27] The conversion of **3** into dioxygen complex **4a** was readily followed by the appearance of a strong band at 880 cm^{-1}. The band shifts to 830 cm^{-1} for ^{18}O-labeled isotopologue **4b** and can be assigned unequivocally to the O–O stretching vibration of the η^2-peroxido ligand (Figure 5).[11,28] The difference $\Delta\nu$ = 50 cm^{-1} is compatible with a simple model for a diatomic harmonic oscillator.[29] The complex *trans*-[Rh(O_2)(4-C_5F_4N)(CN*t*Bu)(PEt_3)$_2$] and its ^{18}O-labeled isotopologue show a difference of $\Delta\nu$ = 47 cm^{-1} for the corresponding O–O stretching vibration.[4] Furthermore, the IR spectrum of **4a** reveals absorption bands at 500 cm^{-1} for [Rh(Cl)($^{16}O_2$)(tbbpy)(CN*t*Bu)] and 482 cm^{-1} for [Rh(Cl)($^{18}O_2$)(tbbpy)(CN*t*Bu)], which we assign to the RhO_2 moiety.[30]

In the ^1H NMR spectrum of **4a**, two singlets at 1.19 and 1.11 ppm can be attributed to the unequivalent *t*Bu groups of the bipyridine ligand. The signal at 1.32 ppm for the *t*Bu group of the isocyanide appears at the expected chemical shift. HRMS (ESI) was used to determine the accurate mass of **4a** and **4b** in the anionic mode in acetonitrile. The exact mass for **4a**/Cl^- was found to be 556.1011 [M + Cl]$^-$ (**4b**/Cl^-: 560.1092 [M + Cl]$^-$). To obtain more information on the geometry and bond lengths in complex **4a**, its structure was determined by X-ray diffraction analysis (Figure 6). Crystals were grown from an acetonitrile solution at 243 K. Selected bond lengths and angles are summarized in Table 4. Although the data are of poor quality, the analysis reveals the configuration at rhodium. Peroxido complex **4a** adopts a distorted octahedral structure with the peroxido ligand in the *trans* position to the chlorido and bipyridyl ligand, if the oxygen is treated as a bidentate ligand. Alternatively, if the dioxygen is treated as occupying a single coordination site, the structure is approximately trigonal-bipyramidal.

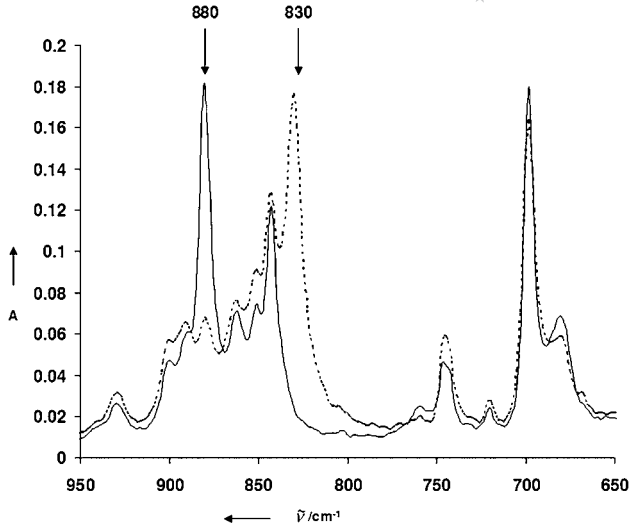

Figure 5. Part of the IR spectra of **4a** (——) and **4b** (-----) (ATR, diamond).

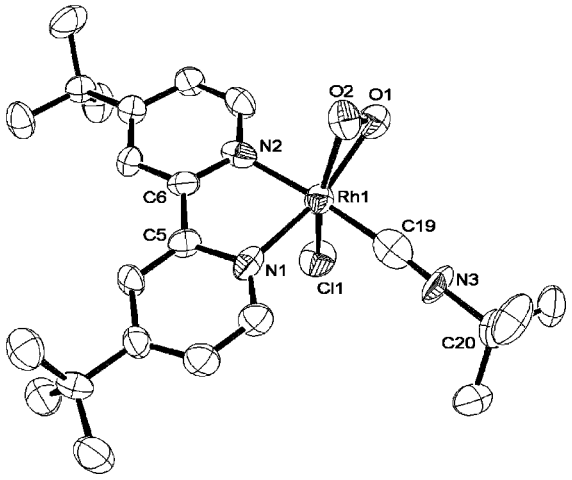

Figure 6. An ORTEP diagram of **4a**. Ellipsoids are drawn at the 50% probability level.

Table 4. Selected bond lengths [Å] and angles [°] in **4a**.

Rh1–O1	1.985(8)	Rh1–N1	2.072(8)
Rh1–O2	1.996(7)	Rh1–N2	2.051(9)
O1–O2	1.406(9)	C19–N3	1.201(14)
Rh1–Cl1	2.398(3)	N3–C20	1.466(12)
Rh1–C19	1.931(12)		
O2–Rh1–N2	90.4(3)	N2–Rh1–C19	175.4(4)
O2–Rh1–N1	120.6(3)	N1–Rh1–N2	79.6(3)
O2–Rh1–C19	92.3(4)	Cl1–Rh1–N2	88.8(2)
Cl1–Rh1–N1	85.9 (2)	C19–N3–C20	177.8(10)
Cl1–Rh1–C19	90.6(3)	O2–Rh1–O1	41.4(3)

Conclusions

In conclusion, we described the synthesis of new highly reactive bipyridine Rh^I compounds. Reactivity studies led

to the isolation of an unusual Rh^{II} cluster as well as to the formation of Rh^{III} peroxido compound **4a**. Complex **4a** might be suitable for oxygenation reactions, because it does not contain any ligands that are themselves prone to oxygenation reactions.[31]

Experimental Section

General Methods and Instrumentation: The synthetic work was carried out with a Schlenk line or an argon-filled glove box with oxygen levels below 10 ppm. All solvents were purified and dried by conventional methods and distilled under an atmosphere of argon before use. 1,2-Difluorobenzene was obtained from ABCR and was distilled before use. 4,4′-Di-*tert*-butyl-2,2′bipyridine, *tert*-butylisocyanide, and $^{16}O_2$ were obtained from Aldrich. $^{18}O_2$ was purchased from CAMPRO Scientific. The complex $[Rh(\mu\text{-}Cl)(coe)_2]_2$ was prepared according to the literature.[32] NMR spectra were recorded with a Bruker AV 400 NMR or a Bruker DPX 300 spectrometer at 25 °C. The ^1H NMR chemical shifts were referenced to residual C_6D_5H at 7.15 ppm. Microanalyses were performed with a Leco CHNS–932 elemental analyzer. Infrared spectra were recorded with a Bruker Vector 22 spectrometer that was equipped with an ATR unit (ZnSe or diamond). The ESI mass spectra were recorded with an Esquire 3000 ion-trap mass spectrometer (Bruker).

[Rh(Cl)(tbbpy)(coe)] (1): A solution of 4,4′-di-*tert*-butyl-2,2′-bipyridine (175 mg, 0.244 mmol) in thf (14 mL) was added within 10 min to a solution of $[Rh(\mu\text{-}Cl)(coe)_2]_2$ (131 mg, 0.488 mmol) in thf (5 mL). A color change from orange to dark blue was observed. The reaction mixture was stirred for 2 h at room temperature and the volatiles were removed in vacuo. The remaining dark blue residue was washed once with a solution of *n*-hexane/thf (10:1, 11 mL) and with *n*-hexane (4 × 7 mL) and then dried under vacuum. An extremely air-sensitive and intense blue solid remained. Yield: 245 mg (86%). IR (ATR): $\tilde{\nu}$ = 2961 (s), 2911 (s), 2869 (m), 1614 (s), 1545 (w), 1482 (m), 1466 (m), 1415 (s), 1367 (m), 1251 (m), 1024 (w), 1124 (w), 1026 (w), 901 (m), 866 (m), 842 (s), 741 (w), 606 (s), 555 (m), 523 (m) cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ = 9.93 (d, $^3J_{H,H}$ = 5.8 Hz, 1 H, H-6 or H-6′), 7.58 (s, 1 H, H-3 or H-3′), 7.39 (s, 1 H, H-3 or H-3′), 7.05 (dd, $^3J_{H,H}$ = 6.3 Hz, 1 H, H-6 or H-6′), 6.81 (dd, $^3J_{H,H}$ = 6.0 Hz, 1 H, H-5 or H-5′), 6.32 (dd, $^3J_{H,H}$ = 6.3 Hz, 1 H, H-5 or H-5′), 4.84 (br. s, 2 H, coe), 2.54 (br. s, 4 H, coe), 1.61 (br. s, 8 H, coe), 1.02 (s, 9 H, *t*Bu-4 or *t*Bu–4′), 1.00 (s, 9 H, *t*Bu-4 or *t*Bu-4′) ppm.

[{Rh(Cl)(H)(tbbpy)}]$_4$ (2): Hydrogen gas was bubbled through a thf (15 mL) solution of [Rh(Cl)(tbbpy)(coe)] (209 mg, 0.404 mmol) for 30 min. After 12 h stirring at room temperature under a hydrogen atmosphere, the volatiles were removed in vacuo. The remaining brown solid was washed with *n*-hexane (2 × 5 mL) and dried under vacuum. Yield: 611 mg (93%). $C_{72}H_{100}Cl_4N_8Rh_4$ (1631.05): calcd. C 53.01, H 6.18, N 6.87; found C 53.27, H 6.21, N 6.30. IR (ATR): $\tilde{\nu}$ = 2959 (s), 2906 (m), 2870 (m), 1612 (s), 1542 (w), 1480 (m), 1465 (m), 1412 (s), 1365 (m), 1251 (s), 1202 (w), 1076 (m), 1021 (m), 900 (m), 844 (s), 801 (s), 742 (w) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ = 10.63 (d, $^3J_{H,H}$ = 6.1 Hz, 8 H, H-6 and H-6′), 7.40 (s, 8 H, H-3 and H-3′), 6.69 (d, $^3J_{H,H}$ = 5.6 Hz, 8 H, H-5 and H-5′), 0.86 (s, 72 H, *t*Bu-4 and *t*Bu-4′), –20.38 (m, 4 H, RhH) ppm.

[Rh(Cl)(tbbpy)(CN*t*Bu)] (3): A solution of 4,4′-di-*tert*-butylbipyridine (166 mg, 0.619 mmol) in thf (4 mL) was added to a solution of $[Rh(\mu\text{-}Cl)(coe)_2]_2$ (222 mg, 0.309 mmol) in thf (10 mL). A color change from orange to dark blue was observed. The reaction mixture was stirred for 5 min at room temperature and then a solution of *tert*-butylisocyanide (70 µL, 0.619 mmol) in thf (2 mL) was added. A color change from blue to black was observed. After stirring for 12 h at room temperature the volatiles were removed in vacuo and the residue was washed with *n*-hexane (3 × 8 mL) and dried under vacuum. A black substance remained. Yield: 296 mg (98%). $C_{23}H_{33}ClN_3Rh$ (489.89): calcd. C 56.39, H 6.79, N 8.58; found C 56.42, H 6.86, N 8.26. IR (ATR): $\tilde{\nu}$ = 2960 (m), 2906 (w), 2871 (w), 2089 (s, C≡N), 2056 (s, C≡N), 1613 (m), 1542 (w), 1506 (s), 1478 (m), 1466 (m), 1411 (m), 1364 (m), 1268 (s), 1024 (s), 1102 (w), 1021 (w), 862 (m), 843 (m), 834 (m), 767 (s), 598 (m), 547 (m), 463 (m) cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ = 10.02 (d, $^3J_{H,H}$ = 4.0 Hz, 1 H, H-6 or H-6′), 9.09 (d, $^3J_{H,H}$ = 4.0 Hz, 1 H, H-6 or H-6′), 7.55 (s, 1 H, H-3 or H-3′), 7.42 (s, 1 H, H-3 or H-3′), 6.83 (d, $^3J_{H,H}$ = 4.8 Hz, 1 H, H-5 or H-5′), 6.51 (d, $^3J_{H,H}$ = 4.5 Hz, 1 H, H-5 or H-5′), 1.25 (s, 9 H, CN*t*Bu), 1.03 (s, 9 H, *t*Bu-4 or *t*Bu-4′), 1.02 (s, 9 H, *t*Bu-4 or *t*Bu-4′) ppm.

[Rh(Cl)(O_2)(tbbpy)(CN*t*Bu)] (4a): A black solid of [Rh(Cl)(tbbpy)(CN*t*Bu)] (**3**; 275 mg, 0.561 mmol) was treated with oxygen for 5 min. The sample turned immediately yellow. After 12 h at room temperature and under an O_2 atmosphere it was treated with *n*-hexane (4 × 10 mL). The pale-yellow residue was dried in vacuo. Yield: 257 mg (88%). $C_{23}H_{33}ClN_3O_2Rh$ (521.89): calcd. C 52.93, H 6.37, N 8.05; found C 53.35, H 6.55, N 7.48. IR (ATR): $\tilde{\nu}$ = 2962 (m), 2907 (w), 2871 (w), 2195 (s, C≡N), 1616 (m), 1545 (w), 1478 (m), 1412 (m), 1370 (m), 1252 (m), 1200 (m), 1041 (w), 880 (s, ^{16}O-^{16}O), 862 (m), 843 (m), 698 (s), 606 (s), 566 (w), 521 (w, $Rh^{16}O_2$), 500 (m, $Rh^{16}O_2$), 458 (w), 427 (m) cm^{-1}. ^1H NMR (400 MHz, C_6D_6, $C_6H_4F_2$): δ = 8.95 (d, $^3J_{H,H}$ = 6.0 Hz, 2 H, H-6 and H-6′), 8.01 (d, $^3J_{H,H}$ = 1.8 Hz, 1 H, H-3 or H-3′), 7.90 (d, $^3J_{H,H}$ = 2.00 Hz, 1 H, H-3 or H-3′), 7.25 (dd, $^3J_{H,H}$ = 5.8 Hz, $^3J_{H,H}$ = 2.0 Hz, 1 H, H-5 or H-5′), 7.19 (dd, $^3J_{H,H}$ = 5.8 Hz, $^3J_{H,H}$ = 2.0 Hz, 1 H, H-5 or H-5′), 1.32 (s, 9 H, CN*t*Bu), 1.19 (s, 9 H, *t*Bu-4 or *t*Bu-4′), 1.11 (s, 9 H, *t*Bu-4 or *t*Bu-4′) ppm. MS (ESI, CH_3CN, $C_{23}H_{33}ClN_3{}^{16}O_2Rh$): *m*/*z* (%) = 556.1011 (100) $[M + Cl]^-$.

[Rh(Cl)($^{18}O_2$)(tbbpy)(CN*t*Bu)] (4b): A black solid of **3** (40 mg, 0.062 mmol) was stirred at –196 °C for 5 min in vacuo. $^{18}O_2$ (0.1 bar) was then added, and the color of the solid turned from black to yellow. After 30 min the resulting yellow solid was washed with *n*-hexane (2 × 3 mL) and benzene (3 × 3 mL). The pale-yellow residue was dried in vacuo. Yield: 34 mg (80%). IR (ATR): $\tilde{\nu}$ = 2962 (m), 2907 (w), 2870 (w), 2194 (s, C≡N), 1616 (m), 1546 (w), 1478 (m), 1412 (m), 1370 (m), 1252 (m), 1200 (m), 1041 (w), 843 (m), 830 (s, ^{18}O-^{18}O), 698 (s), 606 (s), 563 (w), 516 m, 482 m ($Rh^{18}O_2$), 458 (w), 427 (m) cm^{-1}. MS (ESI, CH_3CN, $C_{23}H_{33}ClN_3{}^{18}O_2Rh$): *m*/*z* (%) = 560.1092 (100) $[M + Cl]^-$.

Structure Determination: Diffraction data of **1**·1.5C_6D_6, **3**·2C_6D_6, and **4a**·2CH_3CN were collected with a Stoe IPDS diffractometer. Diffraction data of **2** were collected with a Nonius Kappa CCD diffractometer. Crystallographic data are depicted in Table 5. The structures were solved by direct methods (SHELXTL PLUS or SIR97) and refined with the full-matrix least-squares method on F^2 (SHELX-97).[33–35] Hydrogen atoms were placed at calculated positions and refined using a riding model. The metal bound hydrogen atoms in **2** were not located. CCDC-735970 (for **1**·1.5C_6D_6), -735971 (for **2**), -735972 (for **3**·2C_6D_6), and -735973 (for **4a**·2CH_3CN) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 5. Crystallographic data.

Compound	**1**·1.5C_6D_6	**2**	**3**·2C_6D_6	**4a**·2CH_3CN
Empirical formula	$C_{35}H_{47}ClN_2Rh$	$C_{72}H_{100}Cl_4N_8Rh_4$	$C_{35}H_{45}ClN_3Rh$	$C_{27}H_{39}ClN_5O_2Rh$
Crystal dimensions [mm^3]	0.56 × 0.48 × 0.44	0.24 × 0.10 × 0.06	0.30 × 0.08 × 0.06	0.16 × 0.16 × 0.06
Formula weight	634.11	1631.04	646.10	603.99
Crystal system	triclinic	tetragonal	triclinic	monoclinic
Space group	$P\bar{1}$	$I\bar{4}2d$	$P\bar{1}$	$P2_1/n$
a [Å]	12.147(2)	17.5510(15)	9.8747(18)	13.821(3)
b [Å]	14.964(3)	17.5510(15)	12.500(2)	12.607(2)
c [Å]	20.172(4)	31.5920(16)	15.038(3)	18.008(3)
α [°]	89.12(3)		103.83(2)	
β [°]	73.15(2)		107.03(2)	110.10(2)
γ [°]	69.87(2)		98.00(2)	
V [$Å^3$]	3280.3(11)	9731.5(13)	1679.0(5)	2946.6(10)
Z	4	4	2	4
$D_{calcd.}$ [$g\,cm^{-3}$]	1.284	1.113	1.278	1.361
μ(Mo-K_α) [mm^{-1}]	0.627	0.811	0.614	0.701
θ range [°]	2.39 to 25.93	3.24 to 25.01	2.21 to 25.50	2.25 to 25.0
Reflections collected	16902	28868	17327	27608
Independent reflections	6559	4266	5855	4920
R_{int}	0.0403	0.102	0.0586	0.1843
Goodness-of-fit on F^2	1.007	1.041	0.783	0.907
R_1, wR_2 on all data	0.0489, 0.0887	0.0775, 0.1624	0.0552, 0.0497	0.1699, 0.2640
R_1, wR_2 [$I_o > 2\sigma(I_o)$]	0.0339, 0.0826	0.0564, 0.1519	0.0305, 0.0465	0.0960, 0.2298
Reflect. with $I_o > 2\sigma(I_o)$]	5151	3258	4231	2249
Max diff peak, hole [$e\,Å^{-3}$]	0.786 and –0.448	0.604 and –0.492	0.327 and –0.389	2.345 and –0.760

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