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Preparation and Characterization of Four- and Five-Coordinate Rhodium(I) Complexes. Crystal Structures of Chloro(2-(phenylazo)pyridine)(norbornadiene)rhodium(I), (2,2'-Bipyridyl)(norbornadiene)rhodium(I) Chloride Hydrate, and Chloro(2,2'-bipyridyl)(norbornadiene)rhodium(I)[1a]

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The ability of 2-(phenylazo)pyridine (Azpy) to stabilize lower oxidation states has been utilized in the preparation of a new rhodium(I) complex. Five-coordinate $[Rh(nbd)(Azpy)Cl]\cdot 0.5CH_2Cl_2$ (I) has been prepared by reaction of $[Rh(nbd)Cl]_2$ with Azpy. Observed lowering of the Azpy azo stretching mode in the infrared region suggests a strong Rh–ligand π-interaction, previously observed in other complexes of this ligand. The complex can be used as a synthetic intermediate. Nitrogen-chelating ligands such as 2,2'-bipyridyl and 1,10-phenanthroline rapidly react with this complex to displace Azpy. With bpy both four-coordinate [Rh(nbd)(bpy)]Cl (II) and five-coordinate [Rh(nbd)(bpy)Cl] (III) can be isolated, depending on the choice of reaction conditions. At 110 K [Rh(nbd)(Azpy)Cl] is found to be triclinic, with a = 8.603 (4) Å, b = 14.792 (6) Å, c = 15.258 (5) Å, α = 112.34 (3)°, β = 91.88 (3)°, γ = 92.69 (4)°, V = 1791 (3) Å^3, Z = 4, and space group $P\bar{1}$. $[Rh(nbd)(bpy)]Cl\cdot H_2O$ is monoclinic, with a = 7.542 (5) Å, b = 19.900 (5) Å, c = 20.613 (5) Å, β = 96.06 (3)°, V = 3976 (2) Å^3, Z = 8, and space group $P2_1/c$. [Rh(nbd)(bpy)Cl] is orthorhombic, with a = 12.507 (4) Å, b = 16.045 (3) Å, c = 14.418 (4) Å, V = 2893 (2) Å^3, Z = 8, and space group *Cmca*. Both I and II contain two crystallographically independent rhodium(I) complexes. In I the two complexes have different conformations of the phenyl groups of the Azpy ligands. The Rh–Cl distances 2.496 Å in I and 2.590 Å in III indicate a weaker Rh–Cl interaction in the bpy complex.

Introduction

Complexes containing the bidentate ligand 2,2'-bipyridyl (bpy), particularly those of ruthenium(II), have recently been the source of much investigation.[2] Since bpy has proven to be quite useful for studying many phenomena such as luminescence and photoreduction/oxidation, it is expected that other ligands might be of interest as well. It is for this reason that studies with 2-(phenylazo)pyridine (Azpy) were undertaken in these laboratories several years ago. Both Azpy and bpy are conjugated nitrogen chelating ligands and as much are expected to show similar coordination chemistry. However, the azo-linkage of Azpy should lead to differences in ligator properties.

A number of studies of complexes containing Azpy have been reported. Those existing include investigation of complexes of iron(II),[3,4] nickel(II),[4] mercury(II),[5] osmium(II),[6] ruthenium(II),[7-13] chromium(0), molybdenum(0), and tungsten(0),[14] chromium(II),[15] and copper(I).[16] The mass spectrum of a rhodium(III) Azpy complex has been reported,[17] but no other details were given. In view of these studies and extensive work in these laboratories, it is known that Azpy is a strong π-accepting ligand; unlike bpy it tends to stabilize lower oxidation states. This has lead us to an investigation of rhodium(I) with Azpy.

Perhaps the most widely studied rhodium(I) complexes contain π-acid ligands such as phosphines and dienes,[18] the lower oxidation state being stabilized by such ligands. While the most common rhodium(I) structure is four-coordinate (square planar), five-coordinate rhodium(I) compounds are also known.

The present study is concerned with the properties of [Rh(nbd)(Azpy)Cl] (nbd = norbornadiene). A crystal structure determination showed this compound to be five-coordinate. For comparison crystal structures were also determined for two similar complexes, [Rh(nbd)(bpy)Cl] and four-coordinated $[Rh(nbd)(bpy)]Cl\cdot H_2O$. Also, we find the complex [Rh(nbd)(Azpy)Cl] is a potentially valuable precursor for the synthesis of other rhodium(I) complexes.

Experimental Section

Materials. All chemicals were reagent grade and were used as received except as noted. Rhodium(III) chloride trihydrate was obtained from J. Bishop & Co. Platinum Works, Malvern, PA, organic solvents were obtained from Fisher Scientific Co., Fairlawn, NJ, bicyclo[2.2.1]hepta-2,5-diene (nbd) (distilled immediately before use), 2,2'-bipyridyl (bpy), and 1,10-phenanthroline (*o*-phen) were obtained from Aldrich Chemical Co., Inc., Milwaukee, WI, spectrophotometric grade acetonitrile and chloroform from J. T. Baker Chemical Co., Phillipsburg, NJ, ammonium hexafluorophosphate, sodium tetrafluoroborate, and tetrafluoroboric acid were obtained from Alfa Products, Danvers, MA, tetrapropylammonium (TPA) and tetrabutylammonium (TBA) bromide were obtained from Eastman Kodak Co., Rochester, NY, and thin-layer chromatography (TLC) aluminum backed sheets, precoated with silica gel of 0.2 mm layer thickness, were obtained from E. M. Reagents. Azpy,[8] tetrapropylammonium tetrafluoroborate $(TPA(BF_4))$[19] and $[Rh(nbd)Cl]_2$[20] were prepared as described in the literature. In the last preparation a final wash with pentane was used to remove residual nbd.

Methods. Infrared spectra from 200 to 4000 cm^{-1} were obtained on a Perkin-Elmer 283 spectrophotometer, by using mineral oil and halocarbon mulls smeared on polished CsI plates. For [Rh(nbd)(Azpy)Cl], [Rh(nbd)(bpy)Cl], and [Rh(nbd)(bpy)]Cl, spectra were also obtained on a Perkin-Elmer 1800 double beam FT-IR from 500 to 150 cm^{-1}, by using mineral oil mulls supported on polyethylene windows. Mulls were prepared by grinding in a dental amalgamator ("Wig-L-Bug"). Ultra-

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violet–visible spectra from 200 to 750 nm in acetonitrile and from 250 to 750 nm in chloroform were recorded on a Cary 17-D spectrophotometer with matched, 1 cm path length silica cells. Cyclic voltammetry data were obtained with a Bioanalytical Systems Inc. electrochemical unit, Model CV-27, on acetonitrile solutions ca. 2×10^{-3} M in complex and 0.1 M in TPA(BF_4) supporting electrolyte. The standard three-electrode configuration was employed using platinum working and auxillary electrodes and a micro platinum "quasi-reference" electrode. Data were converted to the hydrogen scale with a ferrocene standard,[21] and the midpoint between anodic and cathodic scan peaks was taken as the formal potential.

For TLC, methylene chloride solutions of [Rh(nbd)(bpy)]Cl, [Rh(nbd)(bpy)]BF_4, [Rh(nbd)(*o*-phen)]Cl, and [Rh(nbd)(*o*-phen)]BF_4 were spotted on plates and developed in 0.25 M tetraethylammonium bromide in ethanol. R_f values (color): 50 (red/orange); 50 (red/orange); 47 (red/orange); 47 (red/orange). A methylene chloride solution of [Rh(nbd)(Azpy)Cl]·$5CH_2Cl_2$ was developed in 0.01 M tetraethylammonium bromide in ethanol. R_f value (color): 83 (blue). An acetonitrile solution of [Rh(nbd)(*o*-phen)]PF_6 was spotted on the plate and developed in 0.25 M tetraethylammonium bromide in ethanol. R_f value (color): 47 (orange).

All preparations were routinely dried in vacuo over P_4O_{10}. Yields reported are based on rhodium.

Analyses. C, H, N, Cl, and P analyses were performed by the microanalytical laboratory at the H. C. Ørsted Institute, Copenhagen, Denmark, and Baron Consulting Co., Orange, CT.

Preparations. Chloro(2-(phenylazo)pyridine)(norbornadiene)rhodium(I) Dichloromethane Hemisolvate, [Rh(nbd)(Azpy)Cl]·$0.5CH_2Cl_2$ (I). $[Rh(nbd)Cl]_2$ (0.560 g) in 12 mL of benzene, outgassed with argon, was added to 0.880 g of Azpy in 8 mL of benzene; an additional 5 mL of solvent was used in the transfer. The solution immediately turned deep blue; after 8 h, the solid that had formed was isolated by filtration and washed with benzene. The yield was 1.02 g (92%). The sample was recrystallized from methylene chloride (0.807 g in 15 mL) by the addition of an equal amount of pentane. After the mixture was allowed to stand, the resulting the dark blue crystalline product was isolated by filtration and washed with an equal volume of methylene chloride/pentane, yielding 0.464 g (57%). Anal. Calcd for $RhC_{18}H_{17}N_3Cl·0.5CH_2Cl_2$: C, 48.70; H, 3.98; N, 9.21; Cl, 15.55. Found: C, 49.04, 48.98; H, 4.10, 4.08, N, 9.07, 9.17; Cl, 14.73, 14.90.

(2,2′-Bipyridyl)(norbornadiene)rhodium(I) Chloride Hydrate, [Rh(nbd)(bpy)]Cl·H_2O (II). [Rh(nbd)(Azpy)Cl]·$0.5CH_2Cl_2$ (0.484 g dissolved in 16 mL of CH_2Cl_2) was added to 1.646 g (10.5 mmol) of bpy in 9 mL of CH_2Cl_2, giving an immediate color change from deep blue to purple. An additional 5 mL of CH_2Cl_2 was used for transfer. Five milliliters of pentane was added, and the stoppered mixture was kept overnight on ice. The red-colored product was collected by filtration and washed with 6 mL of a cold 5:1 CH_2Cl_2/pentane mixture. The yield was 0.259 g (60%). Anal. Calcd for $RhC_{17}H_{18}N_2OCl$: C, 50.45; H, 4.49; N, 6.92; Cl, 8.76. Found: C, 50.48; H, 4.28; N, 7.00; Cl, 8.86.

Chloro(2,2′-bipyridyl)(norbornadiene)rhodium(I), [Rh(nbd)(bpy)Cl] (III). This compound was prepared as the one above except that the product was allowed to crystallize at room temperature for 6 h. It was obtained in 33% yield. Anal. Calcd for $RhC_{17}H_{16}N_2Cl$: C, 52.80; H, 4.18; N, 7.25; Cl, 9.17. Found: C, 52.17; H, 4.12; N, 7.21; Cl, 10.13.

(2,2′-Bipyridyl)(norbornadiene)rhodium(I) Tetrafluoroborate, [Rh(nbd)(bpy)]BF_4. This compound was prepared from [Rh(nbd)(bpy)]Cl by metathesis with $NaBF_4$ in water in 78% yield. Anal. Calcd for $RhC_{17}H_{16}N_2BF_4$: C, 46.61; H, 3.68; N, 6.40. Found: C, 46.84; H, 3.46; N, 6.15.

(1,10-Phenanthroline)(norbornadiene)rhodium(I) Tetrafluoroborate, [Rh(nbd)(*o*-phen)]BF_4. [Rh(nbd)(Azpy)Cl]·$0.5CH_2Cl_2$ (0.800 g dissolved in 20 mL of CH_2Cl_2) was added to 0.313 g (1.74 mmol) of 1,10-phenanthroline in 10 mL of CH_2Cl_2. An immediate orange-colored precipitate of the chloride salt was formed. This was collected by filtration and washed with CH_2Cl_2, yielding 0.429 g (60%).

The chloride salt was impure, but conversion to the fluoroborate in aqueous solution resulted in a melon-colored precipitate (92% yield), which was pure. Anal. Calcd for $RhC_{19}H_{16}N_2BF_4$: C, 49.38; H, 3.49; N, 6.06. Found: C, 49.08; H, 3.20; N, 6.35.

(1,10-Phenanthroline)(norbornadiene)rhodium(I) Hexafluorophosphate, [Rh(nbd)(*o*-phen)]PF_6. The fluorophosphate salt was formed in a similar fashion as a peach-colored precipitate in 98% yield. Anal. Calcd for $RhC_{19}H_{16}N_2PF_6$: C, 43.87; H, 3.10; N, 5.39. Found: C, 43.85; H, 2.76; N, 5.68.

X-ray Crystallography. Suitable crystals for structure determinations were obtained in the above experiments. Room-temperature Weissenberg photographs were used to establish the crystal symmetry. The low-temperature diffraction data were collected with an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation obtained from a graphite monochromator. An Enraf-Nonius gas-flow low-temperature device was used for cooling the crystals during data collection. The temperature was monitored throughout the experiment with a thermocouple placed in the exhaust pipe a few centimeters above the crystal. The temperature remained constant within 1 K. For each data collection, the selection of scan mode and scan range was based on detailed analyses of reflection profiles.

Table I. Crystallographic Data and Refinement Results for [Rh(nbd)(Azpy)Cl]·$0.5CH_2Cl_2$ (I), [Rh(nbd)bpy)]Cl·H_2O (II), and [Rh(nbd)(bpy)Cl] (III)

	I	II	III
formula	$RhCl_2C_{18.5}H_{18}N_3$	$RhClC_{17}H_{18}N_2O$	$RhClC_{17}H_{16}N_2$
fw	456.18	404.70	386.69
space group	$P\bar{1}$	$P2_1/c$	*Cmca*
T, °C	−163	−163	−163
a, Å	8.603 (4)	7.542 (5)	12.507 (4)
b, Å	14.792 (6)	19.900 (5)	16.045 (3)
c, Å	15.258 (5)	20.613 (5)	14.418 (4)
α, deg	112.34 (3)	90	90
β, deg	91.88 (3)	96.06 (3)	90
γ, deg	92.69 (4)	90	90
V, Å^3	1791 (3)	3076 (2)	2893 (2)
Z	4	8	8
λ, Å	0.71073	0.71073	0.71073
d_{calcd}, g cm^{-3}	1.691	1.670	1.766
μ, cm^{-1}	12.44	12.70	13.42
$R(F_o)$	0.027	0.040	0.036
$R_w(F_o)$	0.041	0.051	0.040

The maximum scan time in all cases was 180 s, and the background was defined by extending the scan range by 25% at each side. Intensities of three standard reflections were measured after every 10000 s. The orientation of each crystal was checked by a determination of the setting angles for 10 reflections after every 300 reflections. These measurements showed that no misalignment or deterioration of the crystals had occurred during the data collection. Data reductions included corrections for Lorentz, polarization, and background effects.

The structures were solved by standard Patterson and difference Fourier methods and were refined by least-squares methods minimizing $\sum w(|F_o| - |F_c|)^2$. After anisotropic thermal parameters had been introduced for non-hydrogen atoms, the subsequent difference Fourier maps clearly showed positions of all hydrogen atoms in the structures except those in I, where hydrogen atoms of the methylene chloride molecule could not be detected. Positional parameters of the hydrogen atoms were included in the refinement, and they were given a common fixed isotropic thermal parameter of 2 Å^2. Crystallographic computations were performed on a MicrovaxII computer using the Enraf-Nonius structure determination package.[22] Atomic scattering factors by Cromer and Mann[23] and the anomalous dispersion corrections for Rh, Cl, N, and C by Cromer and Liberman[24] were used as contained in the program system. Table I contains a summary of crystal data, data collection, and refinement results for the three compounds. Positional parameters for non-hydrogen atoms in the three structures are listed in Tables II–IV. Anisotropic thermal parameters, positions for the hydrogen atoms, and lists of observed and calculated structure amplitudes are provided as part of the supplementary material; additional details are given in the following.

[Rh(nbd)(Azpy)Cl]·$0.5CH_2Cl_2$ (I). The dark, platelike crystals of this compound were found to be triclinic. Twenty reflections ($9.9 < \theta < 23°$) were used to determine the cell parameters and orientation matrix. In the final refinement cycle the maximum shift of the parameters was 0.04σ. The maximum and minimum peaks in the final difference Fourier map were +1.1 and −1.32 e Å^{-3} and were found close to the chloride atoms in the methylene chloride.

[Rb(nbd)(bpy)]Cl·H_2O (II). The red needles, elongated in the direction of the *a* axis, were found to belong to the monoclinic system. Systematically absent reflections are only consistent with the space group $P2_1/c$. Unit cell parameters at 110 K were determined from 20 reflections ($16 < \theta < 23°$). In the final cycle the maximum shift was 0.06σ; in the subsequent difference Fourier map, the maximum and minimum peaks of +0.9 and −0.9 eÅ^{-3} were found close to the rhodium atoms.

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Table II. Positional Parameters and Equivalent Isotropic Temperature Factors for [Rh(nbd)(Azpy)Cl]·0.5CH_2Cl_2

atom	x	y	z	B,[a] Å^2
Molecule 1				
Rh1	0.11118 (2)	0.05460 (1)	0.28403 (1)	0.704 (3)
Cl1	0.26909 (6)	−0.05817 (4)	0.16004 (4)	1.232 (9)
N1	−0.1472 (2)	0.0162 (1)	0.1439 (1)	1.03 (3)
N110	0.0648 (2)	0.1338 (1)	0.2023 (1)	0.96 (3)
C111	0.1509 (3)	0.2107 (2)	0.1981 (2)	1.21 (4)
C112	0.1208 (3)	0.2472 (2)	0.1285 (2)	1.46 (4)
C113	0.0001 (3)	0.2039 (2)	0.0602 (2)	1.54 (4)
C114	−0.0913 (3)	0.1268 (2)	0.0653 (2)	1.35 (4)
C115	−0.0574 (3)	0.0939 (2)	0.1376 (1)	0.98 (4)
N120	−0.0920 (2)	−0.0097 (1)	0.2101 (1)	0.89 (3)
C121	−0.1814 (3)	−0.0896 (2)	0.2184 (1)	0.90 (4)
C122	−0.1041 (3)	−0.1709 (2)	0.2173 (2)	1.22 (4)
C123	−0.1894 (3)	−0.2492 (2)	0.2254 (2)	1.51 (4)
C124	−0.3491 (3)	−0.2450 (2)	0.2370 (2)	1.34 (4)
C125	−0.4241 (3)	−0.1636 (2)	0.2385 (2)	1.20 (4)
C126	−0.3416 (3)	−0.0853 (2)	0.2287 (2)	1.04 (4)
C130	0.2903 (3)	0.1081 (2)	0.5170 (2)	1.23 (4)
C131	0.3373 (3)	0.0492 (2)	0.4153 (2)	1.11 (4)
C132	0.3160 (3)	0.1243 (2)	0.3688 (2)	1.17 (4)
C133	0.1875 (3)	0.1774 (2)	0.4109 (2)	1.16 (4)
C134	0.1330 (3)	0.1361 (2)	0.4841 (2)	1.12 (4)
C135	0.0639 (3)	0.0358 (2)	0.4144 (1)	1.00 (4)
C136	0.1897 (3)	−0.0189 (2)	0.3723 (2)	1.04 (4)
Molecule 2				
Rh2	0.68901 (2)	0.39730 (1)	0.29747 (1)	0.750 (3)
Cl2	0.40494 (7)	0.42616 (4)	0.31389 (5)	1.74 (1)
N2	0.5988 (2)	0.1933 (1)	0.2585 (1)	0.97 (3)
N210	0.6205 (2)	0.2906 (1)	0.1676 (1)	0.93 (3)
C211	0.5907 (3)	0.3020 (2)	0.0855 (2)	1.33 (4)
C212	0.5147 (3)	0.2298 (2)	0.0077 (2)	1.52 (4)
C213	0.4625 (3)	0.1417 (2)	0.0139 (2)	1.41 (4)
C214	0.4938 (3)	0.1276 (2)	0.0974 (2)	1.12 (4)
C215	0.5731 (3)	0.2039 (2)	0.1727 (2)	0.96 (4)
N220	0.6545 (2)	0.2729 (1)	0.3251 (1)	0.86 (3)
C221	0.6708 (3)	0.2626 (2)	0.4148 (1)	0.88 (3)
C222	0.6281 (3)	0.3388 (2)	0.4959 (2)	1.07 (4)
C223	0.6336 (3)	0.3272 (2)	0.5823 (2)	1.23 (4)
C224	0.6844 (3)	0.2412 (2)	0.5876 (2)	1.20 (4)
C225	0.7308 (3)	0.1670 (2)	0.5066 (2)	1.25 (4)
C226	0.7243 (3)	0.1769 (2)	0.4194 (2)	1.13 (4)
C230	0.9651 (3)	0.6064 (2)	0.3773 (2)	1.40 (4)
C231	0.7843 (3)	0.5949 (2)	0.3709 (2)	1.26 (4)
C232	0.7519 (3)	0.5214 (2)	0.2671 (2)	1.14 (4)
C233	0.8769 (3)	0.4588 (2)	0.2481 (2)	1.29 (4)
C234	0.9861 (3)	0.4956 (2)	0.3386 (2)	1.38 (4)
C235	0.8795 (3)	0.4632 (2)	0.4014 (2)	1.19 (4)
C236	0.7563 (3)	0.5250 (2)	0.4225 (2)	1.14 (4)
Solvent Molecule				
C3	0.2065 (8)	0.5243 (3)	0.1281 (3)	5.4 (1)
Cl31	0.2395 (1)	0.64623 (8)	0.13480 (8)	4.53 (2)
Cl32	0.2199 (3)	0.4378 (1)	0.0134 (1)	7.78 (5)

[a] The equivalent isotropic temperature factors are calculated from the anisotropic thermal parameters $B(i,j)$ as $^4/_3[a^{*2}B(1,1) + b^{*2}B(2,2) + c^{*2}B(3,3) + a^*b^*(\cos\gamma)B(1,2) + a^*c^*(\cos\beta)B(1,3) + b^*c^*(\cos\alpha)B(2,3)]$.

[Rh(nbd)(bpy)Cl] (III). These crystals are red-brown plates obviously different from those of II. The compound crystallizes in the orthorhombic system; the systematically absent reflections hkl ($h + k = 2n + 1$), $h0l$ ($l = 2n + 1$), and $hk0$ ($h = 2n + 1$) are consistent with the space groups *Cmca* (No. 64) and *C2cb*, a nonstandard setting of *Aba*2 (No. 41). Unit cell parameters were determined from 18 reflections ($17 < \theta < 23°$). The structure solution showed the correct space group to be *Cmca* with the molecule on a crystallographic mirror plane. In the final cycle the maximum shift was 0.25σ; in the subsequent difference Fourier the maximum and minimum peaks of +0.7 and −0.7 e Å^{-3} were found close to the Rh atom.

Results and Discussion

Synthesis. In our initial attempts to prepare a rhodium complex with Azpy, $RhCl_3·3H_2O$ was used as a source material. This yielded a complicated reaction mixture from which no pure materials could be obtained. Furthermore, there was evidence for

Table III. Positional Parameters and Equivalent Isotropic Temperature Factors for [Rh(nbd)(bpy)]Cl·H_2O

atom	x	y	z	B,[a] Å^2
Molecule 1				
Rh1	0.06527 (5)	0.23792 (2)	0.90815 (2)	0.821 (6)
N110	0.1715 (5)	0.3328 (2)	0.9224 (2)	1.83 (8)
C111	0.2534 (6)	0.3561 (3)	0.9791 (3)	1.86 (9)
C112	0.3270 (7)	0.4202 (3)	0.9850 (3)	2.00 (9)
C113	0.3137 (7)	0.4608 (3)	0.9308 (3)	1.94 (9)
C114	0.2304 (6)	0.4380 (3)	0.8716 (2)	1.78 (9)
C115	0.1596 (6)	0.3730 (2)	0.8690 (2)	1.66 (9)
N120	0.0137 (6)	0.2780 (2)	0.8152 (2)	1.88 (8)
C121	−0.0698 (7)	0.2465 (3)	0.7626 (3)	1.92 (9)
C122	−0.1089 (7)	0.2794 (3)	0.7028 (3)	2.1 (1)
C123	−0.0600 (7)	0.3464 (3)	0.6977 (3)	2.1 (1)
C124	0.0302 (7)	0.3788 (3)	0.7510 (3)	2.0 (1)
C125	0.0654 (6)	0.3433 (2)	0.8091 (2)	1.68 (9)
C130	−0.0118 (7)	0.0903 (3)	1.0000 (3)	2.13 (9)
C131	0.1455 (7)	0.1138 (2)	0.9361 (3)	1.85 (9)
C132	0.1811 (7)	0.1845 (3)	0.9917 (2)	1.82 (9)
C133	0.0165 (7)	0.2092 (2)	1.0044 (3)	1.88 (9)
C134	−0.1224 (7)	0.1548 (3)	0.9832 (3)	2.1 (1)
C135	−0.1184 (7)	0.1568 (3)	0.9084 (3)	1.97 (9)
C136	0.0470 (6)	0.1313 (2)	0.8957 (2)	1.71 (9)
Molecule 2				
Rh2	−0.45555 (5)	0.40827 (2)	0.72341 (2)	0.877 (6)
N210	−0.3491 (5)	0.4179 (2)	0.8196 (2)	1.85 (7)
C211	−0.2599 (7)	0.4727 (3)	0.8442 (3)	2.01 (9)
C212	−0.1821 (7)	0.4743 (3)	0.9087 (3)	2.3 (1)
C213	−0.1987 (7)	0.4188 (3)	0.9478 (3)	2.6 (1)
C214	−0.2904 (7)	0.3626 (3)	0.9223 (3)	2.3 (1)
C215	−0.3657 (6)	0.3637 (3)	0.8572 (2)	1.79 (9)
N220	−0.5056 (6)	0.3137 (2)	0.7594 (2)	2.09 (8)
C221	−0.5835 (7)	0.2622 (3)	0.4247 (3)	2.5 (1)
C222	−0.6219 (8)	0.2009 (3)	0.7539 (3)	2.8 (1)
C223	−0.5817 (8)	0.1940 (3)	0.8205 (3)	3.0 (1)
C224	−0.4996 (7)	0.2467 (3)	0.8571 (3)	2.5 (1)
C225	−0.4594 (7)	0.3058 (3)	0.8249 (3)	1.97 (9)
C230	−0.5633 (7)	0.5109 (3)	0.5822 (2)	1.96 (9)
C231	−0.3962 (7)	0.4677 (3)	0.6062 (2)	1.83 (9)
C232	−0.3559 (7)	0.4943 (3)	0.6772 (3)	1.88 (9)
C233	−0.5210 (7)	0.5092 (3)	0.6984 (3)	2.0 (1)
C234	−0.6640 (7)	0.4924 (3)	0.6412 (3)	2.1 (1)
C235	−0.6485 (7)	0.4147 (3)	0.6408 (2)	1.91 (9)
C236	−0.4851 (7)	0.3989 (3)	0.6194 (3)	1.90 (9)
Anions and Solvent				
Cl1	0.9397 (2)	0.43040 (6)	0.23414 (6)	1.39 (2)
Cl2	0.6011 (2)	0.27227 (6)	0.06335 (6)	1.22 (2)
O101	0.5527 (5)	0.4058 (2)	0.1496 (2)	1.98 (8)
O102	0.0335 (3)	0.6367 (2)	0.9069 (2)	1.97 (8)

[a] The equivalent isotropic temperature factors are calculated from the anisotropic thermal parameters $B(i,j)$ as $^4/_3[a^{*2}B(1,1) + b^{*2}B(2,2) + c^{*2}b(3,3) + a^*b^*(\cos\gamma)B(1,2) + a^*c^*(\cos\beta)B(1,3) + b^*c^*(\cos\alpha)B(2,3)]$.

Table IV. Positional Parameters and Equivalent Isotropic Temperature Factors for [Rh(nbd)(bpy)Cl]

atom	x	y	z	B,[a] Å^2
Rh	0.000	0.11533 (2)	0.14883 (2)	0.860 (4)
Cl	0.000	0.27674 (6)	0.14662 (8)	1.12 (2)
N10	0.1046 (2)	0.1226 (2)	0.0357 (2)	1.02 (4)
C11	0.2122 (3)	0.1200 (2)	0.0407 (2)	1.26 (5)
C12	0.2778 (3)	0.1405 (2)	−0.0324 (2)	1.39 (5)
C13	0.2313 (3)	0.1653 (2)	−0.1153 (2)	1.45 (6)
C14	0.1209 (3)	0.1672 (2)	−0.1226 (2)	1.15 (5)
C15	0.0590 (3)	0.1452 (2)	−0.0460 (2)	1.01 (5)
C30	0.000	0.0285 (3)	0.3760 (3)	1.40 (8)
C31	0.000	0.1181 (3)	0.3387 (3)	1.27 (7)
C32	0.0938 (3)	0.1153 (2)	0.2694 (2)	1.26 (5)
C33	0.0924 (3)	0.0332 (2)	0.2318 (2)	1.31 (6)
C34	0.000	−0.0111 (3)	0.2801 (4)	1.48 (8)

[a] The equivalent isotropic temperature factors are calculated from the anisotroic thermal parameters $B(i,j)$ as $^4/_3[a^{*2}B(1,1) + b^{*2}B(2,2) + c^{*2}B(3,3) + a^*b^*(\cos\gamma)B(1,2) + a^*b^*(\cos\beta)B(1,3) + b^*c^*(\cos\alpha)B(2,3)]$.

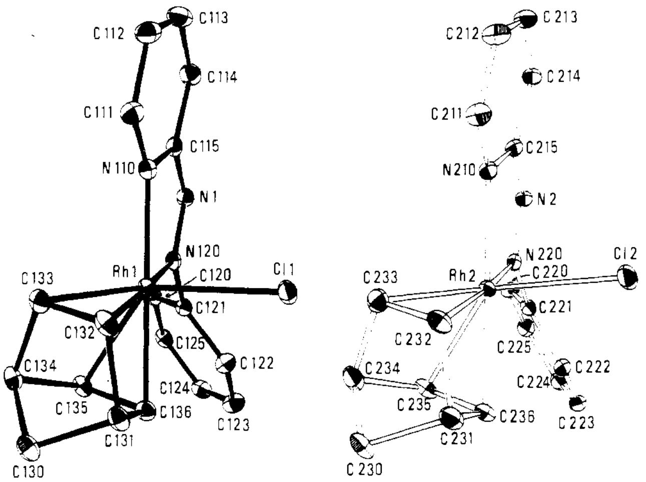

Figure 1. ORTEP drawings (a, left; b, right) of the two crystallographically independent molecules of [Rh(nbd)(Azpy)Cl] illustrating the atomic labeling. The thermal ellipsoids are scaled to include 50% probabilities. The molecule depicted with open bonds ($J = 2$) is related by an inversion center to the molecule generated by the coordinates in Table II.

ligand decomposition. When we then employed $[Rh(nbd)Cl]_2$ as a source, the reaction proceeded smoothly to give [Rh(nbd)(Azpy)Cl] in high yield.

Cyclic voltammetry showed two oxidation waves for [Rh(nbd)(Azpy)Cl]. Formal potentials in acetonitrile are −0.66 and −0.21 V (on the hydrogen scale). The first of these potentials we assign as the Rh(II/I) couple; a 60-mv peak separation suggests reversibility and no change in coordination sphere during this process. The second potential we assign to the Rh(III)/II couple. It is quasireversible (110-mV peak separation). From these data, it is clear that [Rh(nbd)(Azpy)Cl] should be oxidatively unstable. However, we have little difficulty working with the compound in the atmosphere.

Reaction of this compound with bpy or *o*-phen produces the known $[Rh(nbd)(N\text{-}N)]^+$ complex ions[25] in rapid reactions, easily detected by the immediate color change. A displacement of one nitrogen heterocycle by another has been previously noted by Cocevar et al.[26] for $[Rh(COD)(bpy)]^+$ (COD = 1,5-cyclooctadiene). We find that even in the presence of an excess of *o*-phen or a large excess of bpy only Azpy is displaced by the entering ligand. Both the nitrogen heterocycle and the olefin are displaced by an excess of the phosphine diphos. Our new compound is potentially synthetically useful.

Rh(nbd)(bpy)Cl has been obtained both as a hydrate (II) and as an anhydrous compound (III). The only difference between these preparations was the temperature at which the compounds crystallized. Water of hydration in II apparently came from the atmosphere or the solvents; no special efforts were taken to maintain anhydrous conditions.

While these complexes are synthetically labile, they can be chromatographed under TLC conditions with our quaternary salt developers.[7] We find this TLC behavior to be very useful in both the following reactions and characterization of products.

Crystal Structures. $[Rh(nbd)(Azpy)Cl]\cdot 0.5CH_2Cl_2$ crystallizes with two crystallographically independent five-coordinate rhodium(I) complexes and one molecule of solvent per asymmetric unit. As illustrated in the ORTEP drawings in parts a and b of Figure 1, the two independent complexes are virtually identical, with coordination around Rh(I) described as a distorted square pyramid with chloride as the axial ligand. The other four ligators consist of two nitrogens from Azpy and the two olefin bonds in nbd. The irregularity of the coordination geometry leads to an almost planar arrangement of NJ10, NJ20, CJ32, and CJ36 (J = 1, 2). Principal differences between the two complexes are in the orientation of the phenyl group of Azpy as observed earlier in a ruthenium(II) complex.[27] This is illustrated by the torsion angles NJ–NJ20–CJ21–NJ22, which are 127.9 (2) (J = 1) and 138.0 (2)° (J = 2), or by the angles between the planes defined by the pyridine and phenyl rings of 57.6 and 47.9°, respectively, in the two molecules. Rhodium is displaced 0.35 Å toward chloride relative to the plane defined by NJ10, NJ20, and the midpoints of the double bonds CJ32–CJ33 and CJ35–CJ36 in both independent complexes.

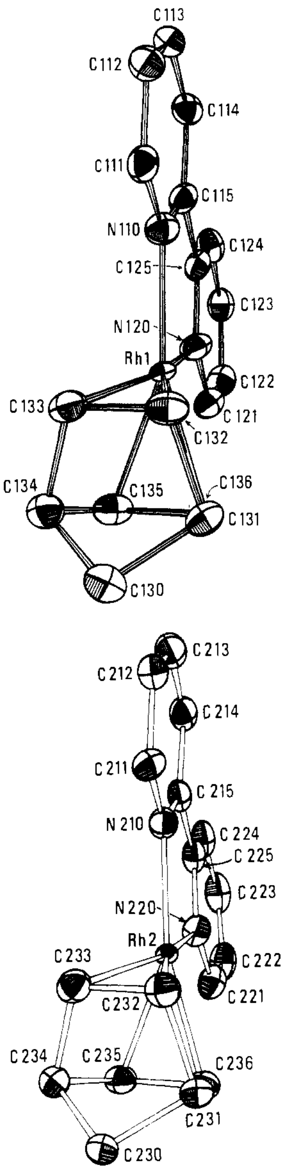

Figure 2. ORTEP illustrations (a, left, b, right) of the two crystallographically independent molecules of $[Rh(nbd)(bpy)]^+$. The labeling and the drawings are made in the same way as described for Figure 1.

It is remarkable that $[Rh(nbd)(bpy)]Cl\cdot H_2O$ also contains two crystallographically independent but in this case four-coordinate rhodium(I) complexes in the asymmetric unit as shown in Figure 2a,b. The two chloride ions and water molecules are linked by hydrogen bonds equal in strength and length (Cl–O distances 3.22–3.30 Å), forming a slightly puckered four-membered ring with alternating O and Cl atoms. In the crystal, the molecules are arranged so that the planes of the bpy ligands in the two independent molecules are almost parallel. The two pyridine planes of bpy are twisted slightly relative to each other, 4° in the first complex (Figure 2a) and 8° in the second complex (Figure

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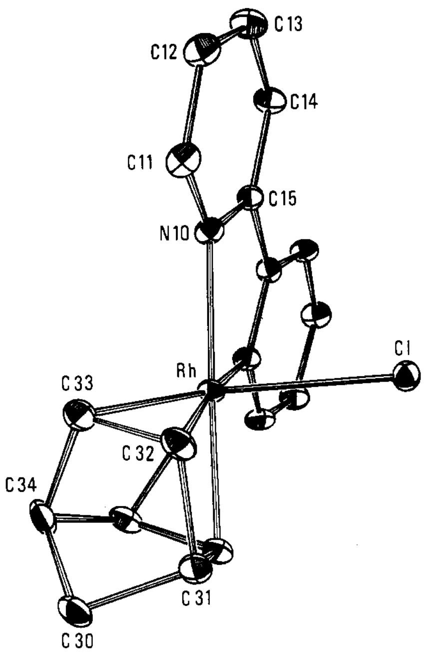

Figure 3. ORTEP drawing showing the molecular geometry and labeling of [Rh(nbd)(bpy)Cl]. The molecule is oriented and illustrated as described for Figure 1.

2b). In the two complexes, coordination around rhodium can be characterized as square planar with two bidentate ligands. The ligators are the two nitrogen atoms in bpy and the two olefin bonds of nbd. A calculation of the least-squares planes defined by the nitrogen atoms in bpy and the midpoints of the double bonds in nbd showed that although rhodium is 0.1 Å out of the plane, they differ slightly in their degree of tetrahedral distortion; in one the four ligators are displaced 0.14 Å relative to the least-squares plane compared to 0.03 Å in the other. It is likely that this difference in tetrahedral distortion is caused by the intermolecular interactions in the crystal, as several interatomic distances are slightly shorter than the sum of the atoms' van der Waals radii. Except for these small conformational differences, the two complex cations have virtually identical geometry and dimensions.

In contrast to these two structure, [Rh(nbd)(bpy)Cl] crystallizes with the complex on a crystallographic mirror plane. The coordination around rhodium is illustrated in Figure 3, and it is apparent that this complex is very similar to the two rhodium complexes in I. The relative displacement of rhodium toward chloride from the base of the pyramid is again 0.35 Å. Intermolecular distances in this structure are all slightly longer than the sum of the relevant van der Waals radii.

The present structure determinations make possible some interesting comparisons between closely related rhodium(I) complexes; Table V contains some selected and averaged bond lengths in the three compounds. Compounds II and III are four- and five-coordinate complexes containing the same two bidentate ligands, bpy and nbd, in an approximately square-planar arrangement. The displacement of rhodium from the plane defined by the four ligators in significantly larger in the five-coordinate [Rh(nbd)(bpy)Cl] than in the four-coordinate [Rh(nbd)(bpy)]$^+$, 0.35 Å compared to 0.10 Å. The five-coordinate compound has slightly longer Rh–N distances than does the four-coordinate compound, 2.094 vs 2.069 Å.

Conversely, the average Rh–C(olefin) distances are longer in the four-coordinate compound, 2.131 vs 2.110 Å, respectively. This observation suggests that the rhodium–olefin bond is stronger in five-coordinate square-pyramidal complexes than in similar rhodium(I) four-coordinate square-planar complexes.

Since the only two rhodium–olefin compounds of different coordination number but with the same equatorial ligands are those reported in this study, it is impossible to say if this is a general trend. Also, there have only been two other structure reports of five-coordinate Rh–nbd compounds.[28,29]

Table V. Selected Bond Lengths (Å) and Angles (deg) in the Three Rh(I) Complexes, with Averaged[a] Values Given for I and II

	I	II	III
Rh–Cl	2.4958 (6)		2.590 (1)
Rh–N10	2.055 (2)	2.064 (3)	2.094 (3)
Rh–N20	2.042 (2)	2.074 (3)	
Rh–C32	2.118 (3)	2.133 (4)	2.098 (3)
Rh–C33	2.130 (3)	2.127 (4)	2.123 (3)
Rh–C35	2.159 (2)	2.125 (4)	
Rh–C36	2.146 (3)	2.139 (4)	
C32–C33	1.415 (3)	1.390 (6)	1.424 (5)
C35–C36	1.401 (3)	1.393 (6)	
Cl–Rh–N10	88.59 (5)		86.24 (8)
Cl–Rh–N20	91.11 (5)		
Cl–Rh–C32	93.75 (7)		90.6 (1)
Cl–Rh–C33	131.89 (7)		128.9 (1)
Cl–Rh–C35	125.57 (6)		
Cl–Rh–C36	89.47 (6)		
N10–Rh–N20	75.74 (8)	79.0 (1)	77.3 (1)
N10–Rh–C32	105.09 (9)	103.2 (1)	107.2 (1)
N10–Rh–C33	96.08 (8)	102.0 (1)	97.7 (1)
N10–Rh–C35	145.60 (8)	158.9 (1)	
N10–Rh–C36	171.71 (10)	162.2 (1)	
N20–Rh–C32	174.98 (8)	165.4 (1)	
N20–Rh–C33	136.39 (9)	156.3 (2)	
N20–Rh–C35	97.36 (9)	102.8 (2)	
N20–Rh–C36	112.35 (9)	105.8 (2)	
C32–Rh–C33	38.89 (9)	38.1 (2)	39.5 (1)
C35–Rh–C36	37.97 (9)	38.1 (2)	
C32–Rh–C35	79.20 (9)	80.5 (2)	80.6 (1)
C32–Rh–C36	67.04 (9)	67.8 (2)	68.0 (2)
C33–Rh–C35	65.48 (9)	67.8 (2)	
C33–Rh–C36	79.33 (9)	80.6 (2)	

[a] The estimated standard deviation given is the larger of the two individual standard deviations.

Table VI. Selected Rhodium–Olefin Bond Distances

compd[a]	av Rh—nbd, Å	av C═C, Å	CN	ref
[Rh(nbd)(bpy)Cl]	2.110 (3)	1.424 (5)	5	*b*
[Rh(nbd)(bpy)]Cl	2.131 (4)	1.391 (6)	4	*b*
[Rh(nbd)(Azpy)Cl]	2.139 (2)	1.408 (3)	5	*b*
[(Cp)Rh(COT)Rh(nbd)]$^+$	2.162 (4)	1.401 (5)	4	*c*
[Rh(nbd)(PNP)]$^+$	2.163 (5)	1.40 (1)	5	*d*
[(CO)$_3$Fe(COT)Rh(nbd)]$^+$	2.174 (5)	1.398 (8)	4	*c*
[Rh(nbd)(PP)]$^+$	2.203 (6)	1.377 (9)	4	*e*

[a] Abbreviations: Cp, cyclopentadienide ion; COT, cyclooctatetraene; PNP, 2-(bis(diphenylphosphino)methyl)pyridine; PP, 2,3-bis(diphenylphosphino)bicyclo[2.2.1]heptane. [b] This work. [c] Bieri, J. H.; Egolf, T.; von Philipsborn, W.; Piantini, U.; Prewo, R.; Ruppli, U.; Salzer, A. *Organometallics* **1986**, *5*, 2413. [d] Anderson, M. P.; Mattson, B. M.; Pignolet, L. H. *Inorg. Chem.* **1983**, *22*, 2644. [e] Davis, R. E.; Meyer, B. B.; Hassett, K. L.; Juri, P. N.; Kyba, E. P. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 21.

Perusal of the literature on Rh–nbd compounds reveals another interesting aspect. In Table VI are summarized data on rhodium–olefin and C═C distances. Only data are included here where the estimated standard deviations of the Rh–C and C═C distances were less than 0.006 and 0.01 Å respectively. We find in general that as the rhodium–carbon distances decreases, the carbon–carbon olefin distance increases. This is reasonable; strengthening of the rhodium–olefin interaction should lead to a diminishing of the olefin bond order.

Both [Rh(nbd)(bpy)Cl] and [Rh(nbd)(Azpy)Cl] are similar, with rhodium located 0.35 Å above the plane defined by the equatorial ligators. However, the rhodium distance to the axial chloride is much greater in the bpy complex, 2.590 vs 2.490 Å. These distances are also greater than that found in the square-planar [Rh(bdpps)Cl] (2.334 Å) (where bdpps is 2,2′-bis(di-

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Table VII. Ultraviolet and Visible Spectra

complex	λ_{max}, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1}) acetonitrile	chloroform
[Rh(nbd)(Azpy)Cl]	645 (2.34)	
	490 (2.15)	
	345 sh (10.2)	
	301 (12.7)	
[Rh(nbd)(bpy)]Cl	478 (0.852)	500 (0.856)
	323 (12.5)	325 (7.23)
	312 (11.4)	310 sh (8.89)
	269 (11.6)	293 (14.3)
	246 (12.2)	244 (14.4)
[Rh(nbd)(bpy)]BF_4	477 (0.854)	
	322 (13.4)	
	311 (12.2)	
	267 (11.8)	
	247 (12.6)	
[Rh(nbd)(*o*-phen)]BF_4	477 (0.920)	
	273 (26.9)	
	224 (30.2)	

[a] sh = shoulder.

phenylphosphino)-*trans*-stilbene).[30] This indication of a weaker Rh–Cl interaction in [Rh(nbd)(bpy)Cl] than in [Rh(nbd)(Azpy)Cl] could explain why it is possible to obtain both the four- and five-coordinate complexes. Apparently it is energetically more favorable for chloride to hydrogen bond to water than bond to rhodium(I) in a five-coordinate structure so that if sufficient water in present, a four-coordinate structure results. An implication here is that it may be possible to obtain a number of related four- and five-coordinate rhodium(I) complexes by choice of conditions.

Explanations for the existence of five-coordinate rhodium have been advanced. π-Accepting ligands have been observed to stabilize this structure,[31-33] and five-coordination is favored in the presence of ligands with poor σ-donor and good π-acceptor properties.[32,34]

Infrared Spectra. All complexes show the expected peaks in their infrared spectra for the ligands they contain. In free Azpy, the azo stretching mode is found at 1420 cm^{-1}, and on coordination, it frequently decreases, indicative of the π-interaction between the metal ion and the ligand.[7] The lessening of the azo double-bond character brought about by π-back-bonding from the metal results in shifting this mode to a frequency closer to that expected for a N–N single bond.[7,8] The nearly 100-cm^{-1} lowering of this mode in the spectrum of [Rh(nbd)(Azpy)Cl] indicates the presence of a pronounced metal–ligand π-interaction.

The rhodium–halogen stretching frequency has been observed in four-coordinate [Rh(CO)(PPh_3)$_2$Cl] at 309 cm^{-1}[35] and in five-coordinate [Rh(nbd)(2,9-dimethyl(o-phen))Cl] at 252 cm^{-1}.[25] The ν(Rh(I)–Cl) band in [Rh(nbd)(Azpy)Cl]·0.5CH_2Cl_2 we assign to a band observed at 220 cm^{-1}. This low energy is consistent with the observed long bond distance.

The longer Rh–Cl bond in [Rh(nbd)(bpy)Cl] than found in [Rh(nbd)(Azpy)Cl] would suggest an even lower stretching frequency. We have been unable to find a band assignable to this mode. Unfortunately there appears to be no readily observed feature allowing the detection of a weakly bound chloride in the five-coordinate structure.

Electronic Spectra. The absorption spectrum of [Rh(nbd)(Azpy)Cl]·0.5CH_2Cl_2 shows four bands (Table VII). Those transitions at wavelengths below 400 nm are most likely of Azpy origin.[6] Maxima at 645 and 490 nm are assigned as metal–ligand charge-transfer transitions on the basis of intensity.

Fordyce and Crosby[36] have investigated spectra of [Rh(diolefin)(N-N)]$^+$ complexes. While the low-energy bands in these compounds are attributable to $^1A_1$-^1CT(bpy) transitions, maxima at energies higher than 28 000 cm^{-1} appear to be characteristic of π–π^* transitions localized on the heterocyclic ligand.[36]

The spectra of [Rh(nbd)(bpy)]Cl and [Rh(nbd)(bpy)]BF_4 in acetonitrile are identical, indicating no chloride coordination for the former compound in this solvent. Our spectra in acetonitrile are slightly shifted from those obtained on methylene chloride solutions of perchlorate salts by Fordyce and Crosby.[36] We find a somewhat greater shift when [Rh(nbd)(bpy)]Cl is dissolved in chloroform. These differences could be solvent shifts or be due to chloride coordination; unfortunately, solubility limitations prevent further investigation in a range of solvents.

Acknowledgment. We wish to thank Silvio Patticini of Perkin-Elmer Corp. for obtaining a number of infrared spectra and Flemming Hansen, who greatly assisted in the experimental crystallographic work. This research was supported by The Humphrey Chemical Co. (through grants to R.A.K.); the diffractometers and low-temperature equipment were provided by the Danish Natural Science Research Council (through Grants 11-1837 and 511-15964 to S.L.).

Supplementary Material Available: Tables SI (anisotropic thermal parameters), SII (positional parameters for hydrogen atoms), SIV (bond lengths), and SV (bond angles) for [Rh(nbd)(Azpy)Cl]·0.5CH_2Cl_2, Tables SVI (anisotropic thermal parameters), SVII (positional parameters for hydrogen atoms), SIX (bond lengths), and SX (bond angles) for [Rh(nbd)(bpy)]Cl·H_2O, Tables SXI (anisotropic thermal parameters), SXII (positional parameters for hydrogen atoms), SXIV (bond lengths), and SXV (bond angles) for [Rh(nbd)(bpy)Cl], Tables SXVI (crystallographic data and refinement results for the three compounds) and SXVII (infrared bands below 500 cm^{-1} for these compounds), and Figures S1–S3 (crystal packing for these compounds) (18 pages); Tables SIII, SVIII, and SXIII (observed and calculated structure amplitudes) (106 pp). Ordering information is given on any current masthead page.

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