

Novel Examples of Simultaneous Reductive Azo Cleavage and Oxidative Aromatic Ring Amination in Rhodium Complexes of 2-(Arylazo)pyridine

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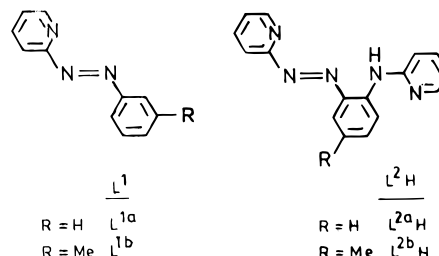
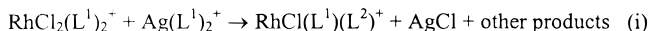
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The reaction of $[\text{AgL}^1_2]\text{ClO}_4$ ($\text{L}^1 = \text{NH}_4\text{C}_5\text{N}=\text{NC}_6\text{H}_4(\text{R})$) with $[\text{RhCl}_2\text{L}^1_2]\text{ClO}_4$ (**1**) in boiling ethanol affords green complexes of the type $[\text{RhClL}^1\text{L}^2](\text{ClO}_4)$ (**2**; $\text{L}^2 = \text{NH}_4\text{C}_5\text{N}=\text{NC}_6\text{H}_3(\text{R})\text{NC}_5\text{H}_4\text{N}$). This reaction is an unprecedented example wherein the anionic tridentate N,N,N-donor L^2 is formed by the fusion of the pyridyl imide fragment $[\text{PyN}]^{2-}$ to a pendant aromatic ring of the coordinated ligand L^1 . The $[\text{PyN}]^{2-}$ originates from the splitting of a diaza function of coordinated L^1 . The complexes have been fully characterized, and structures of the two representative complexes **1a** and **2a** ($\text{R} = \text{H}$) are reported. A reaction pathway based on the reduction potentials of the coordinated ligand L^1 is proposed for the above transformation.

Introduction

The examples of reductive cleavage^{1–4} of a coordinated diaza function resulting in metal organoimido species is an important class of chemical transformation. Metal imido complexes, in turn, have been shown to be potential intermediates for the metal-promoted organic transformations^{5–9} involving the formation of nitrogen–carbon bonds. Reductive azo cleavage and oxidative aromatic ring amination occurring in a concerted way at a single metal site was, however, not known in the literature. This unusual transformation was observed when $\text{RhCl}_2(\text{L}^1)_2^+$ was reacted with $\text{Ag}(\text{L}^1)_2^+$ in ethanol (eq i).



Results and Discussion

A. Starting Material. Synthesis of the starting cationic complex $[\text{RhCl}_2(\text{L}^1)_2](\text{ClO}_4)$ (**1**) was reported by us¹⁰ about a decade ago. Due to the unsymmetric nature of bidentate L^1 , there exists five geometrical isomer possibilities for **1**. The structure solution of the representative complex **1a** indicates a *cis,trans,cis* geometry.^{10,11} A view of the cationic part of **1a** is shown in Figure 1. The coordination sphere around rhodium is approximately octahedral. The metal ion is located at the crystallographic 2-fold axis; only half of it occupies the asymmetric unit. The cation $\text{Rh}(\text{III})$ is a much poorer donor than $\text{Ru}(\text{II})/\text{Os}(\text{II})$, and hence, $d\pi-\pi\pi$ interactions in **1** are unimportant. The N–N distance in **1a** is 1.255(5) Å (Table 1), which is almost identical with that¹² (1.258(5) Å) in $[\text{L}^1\text{H}]\text{ClO}_4$. The average N–N distance in the corresponding $\text{Ru}(\text{II})$ and $\text{Os}(\text{II})$ com-

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(11) With consideration of the coordinated atoms in three pairs, viz. Cl/Cl, N(py)/N(py), and N(azo)/N(azo) the stereochemistry of the isomers can be defined by setting the relative positions (*cis* (c) or *trans* (t)) within the pair of identical atoms.

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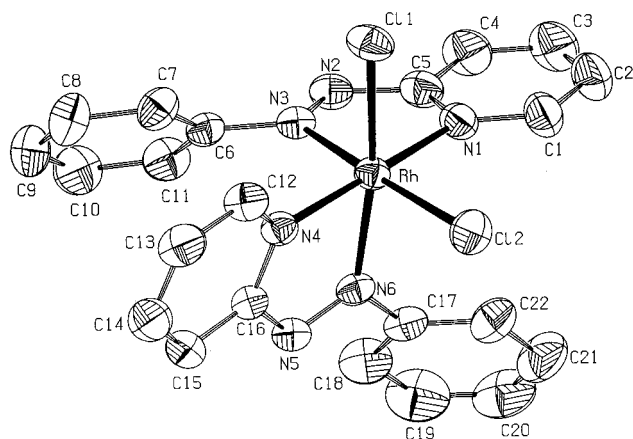


Figure 1. ORTEP plot and atom-numbering scheme for $[\text{RhCl}_2(\text{L}^{1a})_2]^+$ in $[\text{RhCl}_2(\text{L}^{1a})_2]\text{ClO}_4$. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å)

| $[\text{RhCl}_2(\text{L}^{1a})_2]\text{ClO}_4$ (1a) | | | |
|---|-----------|-------------|------------|
| Rh–N(1) | 2.026(4) | Rh–Cl(1) | 2.3321(14) |
| Rh–N(3) | 2.035(3) | Rh–Cl(2) | 2.3104(14) |
| Rh–N(4) | 2.007(3) | N(2)–N(3) | 1.255(5) |
| Rh–N(6) | 2.031(3) | N(5)–N(6) | 1.258(5) |
| $[\text{RhCl}(\text{L}^{1a})(\text{L}^{2a})]\text{ClO}_4$ (2a) | | | |
| Rh(1)–N(8) | 1.955(7) | N(7)–N(8) | 1.307(10) |
| Rh(1)–N(15) | 2.037(7) | N(8)–C(9) | 1.348(11) |
| Rh(1)–N(28) | 2.039(7) | C(9)–C(14) | 1.430(12) |
| Rh(1)–N(35) | 2.045(6) | C(14)–N(15) | 1.343(10) |
| Rh(1)–N(4) | 2.051(7) | N(28)–N(29) | 1.256(9) |
| Rh(1)–Cl(1) | 2.318(2) | N(29)–C(30) | 1.421(11) |
| N(4)–C(5) | 1.347(10) | C(30)–N(35) | 1.340(10) |
| C(5)–N(7) | 1.396(10) | N(15)–C(16) | 1.418(10) |

plexes of L^1 is considerably longer¹³ due to extensive π -interactions. The distances between central rhodium and coordinating atoms are normal.

B. The Reaction. The problems encountered in the synthesis of halide-free rhodium compounds from a rhodium(III) starting material are due to its inertness toward halide substitution reactions. In view of our recent experience,¹⁴ it was anticipated that this problem of chloride substitution from **1** by another L^1 could be overcome by the use of $[\text{Ag}(\text{L}^1)_2]^+\text{ClO}_4$ as a synthon.¹⁵ Unexpectedly, the reaction of **1** with $[\text{Ag}(\text{L}^1)_2]^+$ has led to unusual transformations of coordinated L^1 as shown in eq (i). The formation of the cationic compound **2** (in 65–60% yield) from the above reaction has been authenticated by structural analysis of a representative example, $[\text{RhCl}(\text{L}^{1a})(\text{L}^{2a})]\text{ClO}_4$, (**2a**). We wish to note here that we have recently shown¹⁶ that amination of the pendant aryl ring of L^1 can be achieved via its coordination to transition-metal ions due to C–H activation.

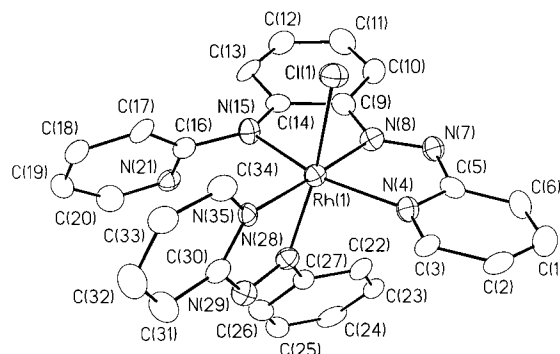


Figure 2. ORTEP plot and atom-numbering scheme for $[\text{RhCl}(\text{L}^{1a})(\text{L}^{2a})]^+$ in $[\text{RhCl}(\text{L}^{1a})(\text{L}^{2a})]\text{ClO}_4$. Hydrogen atoms are omitted for clarity.

C. Characterization. A view of the cationic part of the molecule $[\text{RhCl}(\text{L}^{1a})(\text{L}^{2a})]\text{ClO}_4$ is shown in Figure 2. In this complex, the rhodium center is surrounded by a distorted-octahedral coordination environment by one chloride ligand, the bidentate chelating ligand L^{1a} and the tridentate monoanionic bis-chelating ligand L^{2a} . The complex as a whole is monocationic, and the crystallographic asymmetric unit also contains one unit of perchlorate. The chelate bite angle of L^{1a} , $\text{N}(28)\text{--Rh}(1)\text{--N}(35)$, is $77.2(3)^\circ$, while the corresponding $\text{N}(\text{pyridyl})\text{--Rh--N}(\text{aza})$ angle in the tridentate ligand, viz. $\text{N}(4)\text{--Rh}(1)\text{--N}(8)$, has a value of $79.1(3)^\circ$. The second chelate of L^{2a} , formed by the aza nitrogen $\text{N}(8)$ and the deprotonated amino nitrogen $\text{N}(15)$, has a bite angle of $81.2(3)^\circ$.

The bond distances (Table 1) along the ligand backbones indicate different levels of conjugation in the two coordinated ligands. For the neutral L^{1a} ligand, the N–N distance $\text{N}(28)\text{--N}(29)$ is $1.256(9)$ Å, while the corresponding distance in the anionic tridentate ligand, $\text{N}(7)\text{--N}(8)$, is $1.307(10)$ Å. The two bonds on either side of the aza moiety are shorter in the L^{2a} ligand than they are in L^{1a} ; for L^{1a} , $\text{C}(27)\text{--N}(28) = 1.430(10)$ Å and $\text{N}(29)\text{--C}(30) = 1.421(11)$ Å, while the corresponding distances in the tridentate ligand are $\text{N}(8)\text{--C}(9) = 1.348(11)$ Å and $\text{C}(5)\text{--N}(7) = 1.396(10)$ Å. Taken together, the lengthening of the aza N=N distance in L^{2a} and the foreshortening of the N–C distances alongside the aza moiety, with respect to the corresponding distances in L^{1a} itself, indicate greater delocalization of π -electron density in L^{2a} . The central Rh–N bond of the anionic L^{2a} ligand, $\text{Rh}(1)\text{--N}(8) = 1.955(7)$ Å, is significantly shorter than the other four Rh–N distances, which are all near their average value of 2.04 Å.

The rhodium(III) compounds (**2**) are diamagnetic ($\text{Rh}(\text{III})$, $4d^6$). These are 1:1 electrolytes in acetonitrile and showed intense transitions in the visible region (Figure 3). The multiple low-energy transitions are believed to be due to charge transfer transitions involving both metal and ligand orbitals, while the transitions occurring in the UV region are assigned to transitions involving predominantly ligand orbitals. We wish to note here that such low-energy transitions in rhodium(III) complexes are uncommon¹⁷ and may have usefulness with regard to the development of photocatalysts active in the long-wavelength region of the visible

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Table 2. Solution Spectral and Voltammetric Data

| compd | abs ^a λ_{max} , nm (ϵ , M ⁻¹ cm ⁻¹) | cyclic voltammetric data ^c | |
|--|--|---------------------------------------|---|
| | | oxidn | redn |
| [RhCl(L ^{1a})(L ^{2a})]ClO ₄ | 795 (6300), 730 (5700), 660, ^b 365 (17 400), 280, ^b 215 (46 100) | 1.21 ^d | -0.04, -0.59 ^e , -1.40, ^f -1.78 ^f |
| [RhCl(L ^{1a})(L ^{2b})]ClO ₄ | 795 (5300), 735 (4900), 665, ^b 365 (14 800), 290, ^b 215 (40 000) | 1.17 ^d | -0.06, -0.67 ^e , -1.47, ^f -1.83 ^f |
| [RhCl(L ^{1b})(L ^{2a})]ClO ₄ | 795 (5300), 735 (5000), 665, ^b 365 (14 800), 290, ^b 215 (40 000) | 1.17 ^d | -0.06, -0.67 ^e , -1.47, ^f -1.83 ^f |
| [RhCl(L ^{1b})(L ^{2b})]ClO ₄ | 795 (5600), 740 (5450), 665, ^b 365 (14 000), 280, ^b 215 (41 600) | 1.13 ^d | -0.10, -0.67 ^e , -1.51, ^f -1.85 ^f |

^a Data obtained from absorption spectra: solvent CH₃CN. ^b Shoulder. ^c Experiments were carried out in CH₃CN at 298 K using 0.1 M NEt₄ClO₄ as supporting electrolyte: reported data correspond to a scan rate of 50 mV s⁻¹; working electrode, platinum for oxidation processes and glassy carbon for reduction processes; reference electrode, Ag-AgCl; solute concentration, 10⁻³ M. ^d Irreversible response: the potential corresponds to $E_{\text{p,a}}$. ^e Reversible response with current height ca. 2 times larger than a single-electron-transfer process. ^f Irreversible response: the potential corresponds to $E_{\text{p,c}}$.

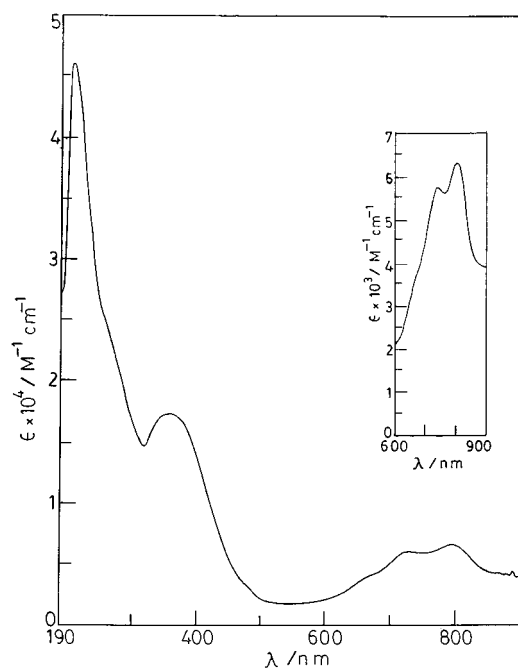


Figure 3. UV-vis spectrum of [RhCl(L^{1a})(L^{2a})]ClO₄ in acetonitrile solution. Inset: enlarged spectrum in the range 600–900 nm.

spectrum. The compounds show all characteristic vibrations for the coordinated ligands. The $\nu(\text{Rh}-\text{Cl})$ band occurs at 350 cm⁻¹. The spectral characterization data are collected in Table 2.

Use of substituted L¹ species as reactants also afforded similar compounds. The ¹H NMR spectra of the cationic complex **2** contain several overlapping resonances in the aromatic region, owing to the large numbers of unique protons in these complexes. However, the methyl resonances for the reactions using complexes of L^{1b} ligands have been particularly useful for the confirmation of the pyridyl amide fusion reaction (eq i). Thus, the reaction product **2bb** obtained from the reaction of [RhCl₂(L^{1b})₂]⁺ with [Ag(L^{1b})₂]⁺ shows only two methyl resonances at δ 2.17 and 2.15. The fact that the reaction product **2ba** obtained from the reaction of [RhCl₂(L^{1b})₂]⁺ and [Ag(L^{1a})₂]⁺ shows only one methyl resonance at δ 2.15 confirms the cleavage of one of the two coordinated ligands L^{1b} present in the starting rhodium compound. Interestingly, the products obtained from the reactions of (a) [RhCl₂(L^{1b})₂]⁺ with [Ag(L^{1a})₂]⁺ and of (b) [RhCl₂(L^{1a})₂]⁺ with [Ag(L^{1b})₂]⁺ are identical. The chemical shift of the lone methyl resonance for

these two compounds **2ab** and **2ba** matches with one of the methyl resonances for **2bb** occurring at a higher field.

D. Rationale for the Transformation L¹ → L². The reaction (i) exemplifies an unprecedented chemical reaction wherein an anionic tridentate N,N,N donor (L²) is formed by the oxidative fusion^{16,18} of the pyridyl imide fragment [PyN]²⁻ to a pendant aromatic ring of a coordinated diaza ligand. The pyridyl imide fragment [PyN]²⁻ is presumably formed by the reductive fission of one of the coordinated diaza ligands. The conversion L¹ → L² occurs within the coordination sphere.

The reductive N=N cleavage of L¹ requires four electrons, whereas the oxidative fusion C-N bond formation involves two electrons. In the present context it may be noted here that the reducible solvent ethanol is essential¹⁹ for this reaction. Important insights into this N=N cleavage process may be obtained by the examination of redox properties of the starting compound, **1**. It undergoes¹⁰ multiple aza reductions: the first reduction occurs at an anodic potential (+0.02 V), implying that upon coordination the ligand L¹ at a Rh^{III} center becomes susceptible to reduction. It is also reasonable¹⁴ that the process of [Ag(L¹)₂]⁺-assisted chloride substitution in **1** occurs via an intermediate where one end of L¹ occupies the position of the leaving Cl⁻. In this intermediate, the reduction potential of coordinated L¹ is expected to move anodic, which further facilitates the reduction of the diaza function leading to N=N cleavage.^{14,20–22} We wish to note here that even in the presence of excess [Ag(L¹)₂]⁺ reagent (>2 times) the reaction (i) does not proceed any further and yielded **2** as the only product. Furthermore, this compound is

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(19) This reaction does not occur in a redox-inert solvent such as acetonitrile.

(20) Our proposal of reductive N=N bond cleavage is based on consideration of (i) the high reduction potential of coordinated L¹, (ii) the inability of the reaction of **1** with free ligand L¹ to bring about the transformation **1** → **2**, and (iii) the partial (one out of two coordinated L¹) transformation of L¹ → L². Admittedly, the proposal is not a unique rationalization of the experimental results. It, however, appears to be the most plausible one.

(21) Similar reactions¹⁴ of MX₂(L¹)₂ (M = Ru(II), Os(II), X = Cl, Br) with 2 mol of [Ag(L¹)₂]⁺ led to formation of [M(L¹)₃]²⁺. A diaza cleavage process was not observed in the cases of Ru(II) and Os(II). For comparison, the first reduction potential²² for coordinated L¹ in MCl₂(L¹)₂ is cathodic by ca. -1.0 V as compared to that in **1**.

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unreactive to AgNO₃. The above observations taken together confirm that chloride dissociation and subsequent L¹ coordination are the two important steps for L¹ → L² transformation. It has been already shown¹⁶ that to promote *ortho* amination of the activated aromatic ring, *cis* coordination of the amine residue is essential. The compound **2** is exceptionally inert to substitution, and further amination of the second L¹ was not observed under the above reaction conditions.

E. Concluding Remarks. The present work further demonstrates that (aryl)pyridine ligands L¹ are susceptible to fascinating metal-mediated chemical transformations. Earlier it has been demonstrated that the aromatic –C₆H₄R moiety of L¹ can be hydroxylated,²³ thiolated,²⁴ and aminated¹⁶ by the C–H activation due to coordination of L¹. Rhenium-mediated aza cleavage of L¹ leading^{2e} to the semibent organoimide function Re^VNC₆H₄R has also been reported. We now have an unprecedented example of simultaneous aza cleavage and *ortho* amination of the –C₆H₄R moiety of coordinated L¹ mediated by rhodium. The resulting rhodium complexes show interesting redox as well as optical properties.

Experimental Section

Materials. The starting rhodium(III) complexes¹⁰ [RhCl₂(L¹)₂](ClO₄) and the silver(I) complexes¹⁵ [Ag(L¹)₂](ClO₄) were synthesized by the reported methods. Chemicals used for syntheses were of analytical grade. Solvents were dried before use. **Caution!** Perchlorate salts of metal complexes are generally explosive. Although no detonation tendencies have been observed, care is advised and handling of only small quantities recommended.

Physical Measurements. A Shimadzu UV 2100 UV/vis spectrophotometer was used to record electronic spectra in solutions. ¹H NMR spectra were measured in CDCl₃ with a Bruker Avance DPX 300 spectrophotometer and SiMe₄ as the internal standard. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (C,H,N). Electrochemical measurements were done under a dry nitrogen atmosphere on a PAR Model 370-4 electrochemistry system as reported earlier.¹² All potentials reported in this work are referenced to an Ag–AgCl electrode and are uncorrected for junction contribution. Electrical conductivities were measured by using a Systronics 304 direct reading conductivity meter. IR spectra were recorded with a Perkin-Elmer 783 spectrophotometer.

Preparation of [RhCl(L^{1a})(L^{2a})](ClO₄). A 100 mg (0.156 mmol) portion of the starting complex [RhCl₂(L^{1a})₂](ClO₄) and 180 mg (0.312 mmol) of [Ag(L^{1a})₂](ClO₄) were dissolved in 30 mL of dry ethanol, and the mixture was refluxed over a steam bath for 4 h. A yellowish green solution resulted, which was then cooled and filtered through a quantitative filter paper to remove the insoluble AgCl. The filtrate was then concentrated to 10 mL, and a solid mass was precipitated out by the addition of diethyl ether. The precipitate was redissolved in a minimum volume of dichloromethane and the solution subjected to column chromatography on a silica gel column (1 × 50 cm). A green band was eluted with dichloromethane–acetonitrile (20:1). The solvent was evaporated to dryness under vacuum and recrystallized from a dichloromethane–hexane mixture. Yield: 65% Anal. Found: C, 46.41; H, 2.98; N, 16.07. Calcd for C₂₇H₂₁Cl₂N₈O₄Rh: C, 46.59; H, 3.02; N, 16.10. Λ_M = 140

Table 3. Crystallographic Data Collection Parameters

| | [Rh(L ^{1a}) ₂ Cl ₂](ClO ₄) (1a) | [RhCl(L ^{1a})(L ^{2a})](ClO ₄) (2a) |
|--|--|--|
| formula | C ₂₂ H ₁₈ Cl ₃ N ₆ O ₄ Rh | C ₂₇ H ₂₁ Cl ₂ N ₈ O ₄ Rh |
| mol wt | 639.68 | 695.33 |
| cryst syst | triclinic | triclinic |
| space group | <i>P</i> 1 | <i>P</i> 1 |
| <i>a</i> , Å | 10.471(2) | 8.626(2) |
| <i>b</i> , Å | 11.611(4) | 11.434(4) |
| <i>c</i> , Å | 12.666(5) | 14.425(5) |
| α, deg | 64.28(4) | 104.05(3) |
| β, deg | 69.31(7) | 91.99(3) |
| γ, deg | 73.56(3) | 101.23(2) |
| <i>V</i> , Å ³ | 1282.4(10) | 1348.6(8) |
| <i>Z</i> | 2 | 2 |
| <i>d</i> _{calcd} , g/cm ³ | 1.657 | 1.712 |
| cryst dims, mm | 0.35 × 0.30 × 0.30 | 0.41 × 0.24 × 0.09 |
| temp, °C | 20 | –123 ± 1 |
| radiation (λ, Å) | Mo Kα (0.709 30) | Mo Kα (0.710 73) |
| 2θ range, deg | 1.9–24.9 | 4.0–50.0 |
| total no. of unique rflns | 4490 | 4747 |
| R1, wR2 | 0.0321, 0.0862 | 0.0703, 0.1800 |
| GOF | 1.008 | 0.986 |
| largest diff between peak and trough, e/Å ³ | 0.731, –0.703 | 0.98, –1.17 |

Ω^{–1} M^{–1} cm² (1 × 10^{–3} M in CH₃CN). IR ν/cm^{–1} (KBr): ν(C–N) 1600; ν(ClO₄[–]) 630, 1100; ν(N=N) 1540; ν(Rh–Cl) 350.

Preparation of [RhCl(L^{1a})(L^{2b})](ClO₄). A 100 mg (0.156 mmol) portion of the starting complex [RhCl₂(L^{1a})₂](ClO₄) and 188 mg (0.312 mmol) of [Ag(L^{1b})₂](ClO₄) were used and procedures similar to those given above followed to obtain [RhCl(L^{1a})(L^{2b})](ClO₄) in 65% yield. Anal. Found: C, 47.33; H, 3.28; N, 15.73. Calcd for C₂₈H₂₃Cl₂N₈O₄Rh: C, 47.39; H, 3.24; N, 15.79. Λ_M = 155 Ω^{–1} M^{–1} cm² (1 × 10^{–3} M in CH₃CN). IR ν/cm^{–1} (KBr): ν(C–N) 1585; ν(ClO₄[–]) 625, 1100; ν(N=N) 1560; ν(Rh–Cl) 340.

Preparation of [RhCl(L^{1b})(L^{2a})](ClO₄). This compound was prepared similarly by using [RhCl₂(L^{1b})₂](ClO₄) and [Ag(L^{1a})₂](ClO₄) in the proper stoichiometric ratio, and the yield is 60%. Anal. Found: C, 47.38; H, 3.26; N, 15.76. Calcd for C₂₈H₂₃Cl₂N₈O₄Rh: C, 47.39; H, 3.24; N, 15.79. Λ_M = 155 Ω^{–1} M^{–1} cm² (1 × 10^{–3} M in CH₃CN). IR ν/cm^{–1} (KBr): ν(C–N) 1580; ν(ClO₄[–]) 625, 1100; ν(N=N) 1565; ν(Rh–Cl) 340.

Preparation of [RhCl(L^{1b})(L^{2b})](ClO₄). A similar procedure was followed by using [RhCl₂(L^{1b})₂](ClO₄) and [Ag(L^{1b})₂](ClO₄) in the required stoichiometric ratio, which gave a yield of 65%. Anal. Found: C, 48.20; H, 3.42; N, 15.46. Calcd for C₂₉H₂₅Cl₂N₈O₄Rh: C, 48.13; H, 3.45; N, 15.49. Λ_M = 140 Ω^{–1} M^{–1} cm² (1 × 10^{–3} M in CH₃CN). IR ν/cm^{–1} (KBr): ν(C–N) 1595; ν(ClO₄[–]) 630, 1100; ν(N=N) 1550; ν(Rh–Cl) 350.

X-ray Crystallographic Experiment. Crystallographic data for RhCl₂(L^{1a})₂](ClO₄) and [RhCl(L^{1a})(L^{2a})](ClO₄) together with their refinement details are collected in Table 3.

[RhCl₂(L^{1a})₂](ClO₄).²⁵ A suitable dark-colored single crystal of the title compound was mounted on a CAD4 Enraf-Nonius diffractometer. The unit cell parameters and crystal orientation matrix were determined by least-squares refinement of 25 accurately centered reflections. Intensity data were collected in the ω–2θ scan mode using graphite-monochromated Mo Kα radiation. The intensity data were corrected for Lorentz and polarization effects, and spherical absorption corrections

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were carried out using the NRCVAX suite of programs. The structure was solved by the Patterson method followed by successive Fourier and difference Fourier syntheses, using SHELX86 (Sheldrick, 1986). Full-matrix least-squares refinements on F^2 were carried out using SHELXL-93, with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were constrained to ride on the respective carbon atoms with an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of their parent atom.

[RhCl(L^{1a})(L^{2a})]ClO₄.²⁶ Geometric and intensity data were taken from a green platelike crystal of the title compound, mounted at the end of a glass fiber, using a CAD-4 diffractometer. Data were collected with normal procedures, and the unit cell was determined from the coordinates of 24 scattering vectors, each measured at 4 equivalent positions. During intensity data collection 3 reflections were measured after every 1/2 h of accumulated X-ray exposure. Data were corrected for absorption using a posteriori method incorporated in the program SHELXA. The corrections were applied at the point of isotropic convergence. The positions of several atoms were

found by direct methods, and the structure was developed and refined in a series of least-squares cycles and difference Fourier maps. All hydrogen atoms were placed at calculated positions and refined as riding atoms, each with an isotropic displacement parameter set to 1.2 times the value of the equivalent isotropic displacement parameter of its parent carbon atom. All non-hydrogen atoms were refined anisotropically. In the final refinement, 379 parameters were fitted to all 4747 F_o^2 data, for a data-to-parameter ratio of 12.5. The refinement converged with the residuals given in Table 3. The 41 parameters used in the calculation of absorption corrections were accounted for in the calculation of the esd's of the variables refined by least squares.

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Supporting Information Available: Text giving complete details of the X-ray analyses of **1a** and **2a** and tables of bond distances and angles, atomic coordinated, anisotropic displacement parameters, and hydrogen atom coordinates for the two compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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