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Intermolecular Metal-Metal Interaction in Chlorotris(2,6-dimethyl-4-bromophenyl isocyanide)rhodium(I)[1]

Yasuhiro Yamamoto,* Yasuo Wakatsuki, and Hiroshi Yamazaki

The Institute of Physical and Chemical Research (RIKEN), Wako-shi, Saitama 351, Japan

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Reaction of $[Rh(cod)Cl]_2$ with 2,6-dimethyl-4-bromophenyl isocyanide gave two kinds of crystals of composition $Rh(2,6\text{-}Me_2\text{-}4\text{-}BrC_6H_2NC)_3Cl$ (purple **1a** and brownish yellow **2a**). The deep purple complex was characterized by single-crystal X-ray diffraction. Crystal data: space group $P2_1/n$, $a = 11.178$ (3) Å, $b = 25.465$ (12) Å, $c = 9.962$ (3) Å, $\beta = 98.95$ (3)°, $U = 2801.0$ (18) Å^3, and $Z = 4$. The molecule **1a** was shown to be a discrete dimer with a Rh(I)-Rh(I) distance of 3.451 (2) Å. The electronic spectrum of **1a** in the solid state showed a band at 540 nm attributable to a Rh-Rh interaction, absent in solutions of low concentration. Some evidence was found for association in the high concentration range. The association constant of the neutral complex **1a** is lower by 10^{-1}-10^{-2} than those of the cationic $[Rh(RNC)_4]^+$ complexes. Extended Hückel molecular orbital calculation of $Rh(HNC)_3Cl$ and $[Rh(HNC)_4]^+$ complexes showed that a tendency to undergo oligomerization in the former is lower than that in the latter. Complex **2a** is a monomer on the basis of its electronic spectrum.

There has been recent interest in investigations of the electronic properties of the complexes in which metal (d^8)-metal (d^8) interactions are present.[2] It has been established that the cationic $[Rh(RNC)_4]^+$ units oligomerize in solution, yielding species such as $[Rh(RNC)_4]_n^{n+}$ and that the structures of these oligomers feature face to face contact of $[Rh(RNC)_4]^+$ units as revealed by the crystal structure analyses of the $[Rh_2(RNC)_8]^{2+}$ complexes (R = Ph,[2h] $4\text{-}FC_6H_4$,[2i] and $4\text{-}NO_2C_6H_4$[2i]).

No association has been observed in the neutral type of yellow complexes such as $Rh(RNC)_3X$ (R = $2,6\text{-}Me_2C_6H_3$, $2,4,6\text{-}Me_3C_6H_2$, or $2,4,6\text{-}t\text{-}Bu_3C_6H_2$; X = Cl, Br, or I).[3] However, the $Rh(RNC)_3Cl$ complex having 2,6-dimethyl-4-bromophenyl isocyanide as ligands showed deep purple color. This is reminiscent of the presence of a metal-metal interaction.[2h] We report here the crystallographic structural analysis of the purple complex and the electronic properties of its related complexes.

Results and Discussion

Preparation of $Rh(RNC)_3X$. Treatment of $[Rh(cod)Cl]_2$ with 6 equiv of 2,6-dimethyl-4-bromophenyl isocyanide in CH_2Cl_2 gave a yellow solution, from which two kinds of complexes (deep purple **1a** and brownish yellow **2a**) having the same composition were obtained, depending on the method of crystallization. Slow crystallization from CH_2Cl_2-benzene yielded the deep purple complex **1a**. Addition of a large amount of hexane to the yellow solution gave the brownish yellow complex **2a**. Slow crystallization of the redissolved **2a** gave **1a**, showing that these complexes are interconvertible. The corresponding purple, crystalline bromide and iodide complexes **1b** and **1c** were obtained by metathesis of **1a** with KBr or KI in methanol (eq 1).

Table I. Electronic Spectra of $Rh(2,6\text{-}Me_2\text{-}4\text{-}BrC_6H_2NC)_3X$

X	λ_{max},[a] nm (ϵ)	λ_{max},[b,c] nm
Cl	408 (3910), 335 (41 050), 259 (46 970), 251 (66 800)	548
Br	400 (389), 334 (40 220), 256 (44 000)	544
I	370 sh, 334 (81 360), 249 (98 040)	542

[a] CH_2Cl_2. [b] KBr. [c] $1b_u$-$2a_g$.

Table II. Association Constants of $Rh(2,6\text{-}Me_2\text{-}4\text{-}BrC_6H_2NC)_3X$[a]

X	K, M^{-1}
Cl	4.2
Br	5.5
I	5.8

[a] In CH_2Cl_2 at 24 °C.

$$[Rh(cod)Cl]_2 + 6\,2,6\text{-}Me_2\text{-}4\text{-}BrC_6H_2NC \rightarrow 2\,Rh(2,6\text{-}Me_2\text{-}4\text{-}BrC_6H_2NC)_3Cl \quad (1)$$

The electronic and infrared spectra of **1a** and **2a** are the same in solution and resemble those of known yellow species $Rh(RNC)_3X$.[3] The infrared spectra (KBr) showed the characteristic N≡C stretching frequencies: a strong singlet at 2090 cm^{-1} for **1a** and doublet at 2116 and 2088 cm^{-1} for **2a**. The electronic spectrum of **1a** in the solid state displayed a band at ca. 540 nm that is absent in the solution spectrum (Figure 1). This can be compared with that observed at 568 nm for the cationic dimer $[Rh(PhNC)_4]_2^{2+}$.

From the energy diagram of the cationic rhodium complexes described by Gray et al.,[2h] two allowed electronic transitions are predicted for the neutral dimer (C_{2h} symmetry), one at higher energy ($1a_g$-$2b_u$) and one at lower energy ($1b_u$-$2a_g$) than the a_1-b_2 excitation in the monomer (C_{2v} symmetry). Thus the band at ca. 540 nm is assigned to the $1b_u$-$2a_g$ transition. The band at ca. 400 nm is assigned to the a_1-b_2 transition expected for the monomer. No bands assignable to higher oligomers were observed in the lower energy region below 18 520 cm^{-1} (540 nm). This is not surprising because the closest interdimer Rh-Rh distance is 8.51 Å (vide infra).

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[1] Studies on interaction of isocyanide with transition metal complexes. 24. For the preceding paper, see: Yamamoto, Y; Aoki, K.; Yamazaki, H. (Organometallics, **1983**, *2*, 0000).

[2] (a) Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* **1976**, *20*, 1. (b) Isci, H.; Manson, W. G. *Inorg. Chem.* **1974**, *13*, 1175. (c) Miskowski, V. M.; Nobinger, G. L.; Kliger, D. S.; Hammond, G. S.; Lewis, N. S.; Mann, K. R.; Gray, H. B. *J. Am. Chem. Soc.* **1978**, *100*, 485. (d) Mann, K. R.; Thich, J. A.; Bell, R. A.; Coyle, C. L.; Gray, H. B. *Inorg. Chem.* **1980**, *19*, 2462. (e) Balch, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 8049. (f) Mann, K. R.; Gordon, J. G.; Gray, H. B. *Ibid.* **1976**, *98*, 3553. (g) Balch, A. L.; Olmstead, M. M. *Ibid.* **1976**, *98*, 2354. (h) Mann, K. R.; Lewis, N. S.; Williams, R. M.; Gray, H. B.; Gordon, J. G. *Inorg. Chem.* **1978**, *17*, 828. (i) Endres, H.; Gottstein, N.; Keller, H. J.; Martin, R.; Rodemer, W.; Steiger, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 827. (j) Miya, S.; Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1982**, *21*, 1486.

[3] Yamamoto, Y.; Aoki, K.; Yamazaki, H. *Inorg. Chem.* **1979**, *18*, 1681.

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Table III. Selected Bond Lengths, Angles, and Nonbonded Contacts

(a) Bond Lengths (Å)

Rh-Rh	3.451 (2)	C(11)-N(11)	1.179 (17)
Rh-Cl	2.383 (4)	C(21)-N(21)	1.149 (17)
Rh-C(11)	1.876 (13)	C(31)-N(31)	1.176 (17)
Rh-C(21)	1.970 (13)	N(11)-C(12)	1.361 (18)
Rh-C(31)	1.917 (14)	N(21)-C(22)	1.397 (17)
		N(31)-C(32)	1.422 (17)

(b) Bond Angles (deg)

Cl-Rh-C(11)	173.1 (4)	Rh-C(11)-N(11)	173.6 (12)
Cl-Rh-C(21)	87.4 (4)	Rh-C(21)-N(21)	175.4 (11)
Cl-Rh-C(31)	87.7 (4)	Rh-C(31)-N(31)	176.0 (11)
C(11)-Rh-C(21)	92.7 (6)	C(11)-N(11)-C(12)	173.5 (15)
C(11)-Rh-C(31)	91.9 (6)	C(21)-N(21)-C(22)	168.7 (13)
C(21)-Rh-C(31)	174.7 (5)	C(31)-N(31)-C(32)	166.6 (12)

(c) Nonbonded Contacts (Å)

Rh-C(21)	3.537 (13)^2	C(24)-C(39)	3.474 (16)^3
Rh-C(36)	3.563 (14)^2	C(31)-C(37)	3.530 (19)^4
N(31)-C(39)	3.567 (14)^3	C(31)-C(39)	3.569 (18)^4
C(14)-C(23)	3.500 (19)^1	Rh-Rh	8.513 (2)^3
C(21)-C(31)	3.519 (17)^2	Rh-Cl	4.324 (4)^5
C(22)-N(31)	3.474 (16)^3	Cl-Cl	6.070 (5)^5

[a] Superscript number refer to the symmetry: 1, x, y, z; 2, $-x, -y, -z$; 3, $1 - x, -y, -z$; 4, $1 - x, 1 - y, 1 - z$; 5, $-x, 1 - y, -z$.

Table IV. Rh(I)-Rh(I) Distances in Binuclear Rh(I) Complexes

complex	Rh-Rh, Å		ref
[Rh$_2$(PhNC)$_8$](BPh$_4$)	3.193 (0)	staggered	*a*
[Rh$_2$(4-FC$_6$H$_4$NC)$_8$]Cl$_2$	3.207 (2)	eclipsed	*b*
[Rh$_2$(4-NO$_2$C$_6$H$_4$NC)$_8$]Cl$_2$	3.25 (1)	eclipsed	*b*
[Rh$_2$(bridge)$_4$](BPh$_4$)$_2$(MeCN)	3.242 (1)	eclipsed	*c*
[Rh$_2$(TM-4-bridge)$_4$](PF$_6$)$_2$(MeCN)$_2$	3.262 (1)	partially staggered	*c*
[Rh$_2$(2,6-Me$_2$-4-BrC$_6$H$_2$NC)$_6$Cl$_2$	3.451 (2)	eclipsed	this paper

[a] Mann, K. R.; Lewis, N. S.; Williams, R. M.; Gray, H. B.; Gordon, J. G., II *Inorg. Chem.* **1978**, *17*, 828-834. [b] Endres, H.; Gottstein, N.; Keller, H. J.; Martin, R.; Rodemer, W.; Steiger, W. *Z. Naturforsh., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 827-833. [c] Mann, K. R.; Thich, J. A.; Bell, R. A.; Coyle, C. L.; Gray, H. B. *Inorg. Chem.* **1980**, *19*, 2462-2468.

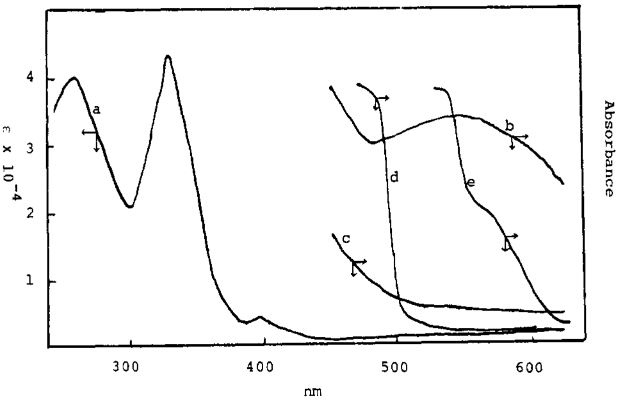

Figure 1. Electronic spectra of [Rh(2,6-Me$_2$-4-BrC$_6$H$_2$NC)$_3$Cl] in solution and in the solid state: a, CH$_2$Cl$_2$ (3.786 × 10^{-5} M); b, **1a** in the solid state (KBr); c, **2a** in the solid state (KBr); d, CH$_2$Cl$_2$ (1.06 × 10^{-4} M); e, CH$_2$Cl$_2$ (5.49 × 10^{-2} M).

Complex **2a** is proposed to exist as a monomeric unit because of the absence of the band near 540 nm in the electronic spectrum in the solid state.

In an attempt to examine the solution behavior of the dimeric complexes **1a–c**, the electronic spectra were measured in a range of concentrations from 3 × 10^{-5} to 1 × 10^{-1} M. Because of the low solubility of the complexes the concentration range was limited but some evidence was found for association. The association constant K_1 is calculated to be ca. 5 M^{-1} in the concentration range from 3 × 10^{-2} to 1 × 10^{-1} M^{-1} (Table II).[4] It is clearly compatible with the weakness of the metal–metal interaction in the crystal structure of the complex (vide infra) that the association occurs only at high concentrations and the association constants are lower than those found in the cationic Rh(RNC)$_4$$^+$ complexes: K_1 = 35 M^{-1} (MeCN) for Rh(PhNC)$_4$$^+$,[2h] 250 M^{-1} (H$_2$O) for Rh(*t*-BuNC)$_4$$^+$,[2h] 8500 M^{-1} (MeOH–H$_2$O) for Rh(PhMeCHNC)$_4$$^+$,[2i] and 500 M^{-1} (MeOH) for Rh$_2$[CN(CH$_2$)$_3$NC]$_4$$^{2+}$.

The ^{1}H NMR spectra of **1a** and **2a** in CDCl$_3$ gave the same spectral pattern [two singlets at δ 2.34 and 2.46 (1:2 ratio) for *o*-methyl groups] and were in agreement with the structure of the monomeric compound. The ^{13}C NMR spectrum of **1a** showed one singlet at δ 18.76 assignable to the *o*-methyl groups, resulting from accidental degeneracy of two kinds of *o*-methyl groups. The ^{13}C NMR spectra in the solid state are not significantly different from those in solution, except that the half-widths of signals in the former are greater than those in the latter. The ^{13}C NMR solid-state spectrum of **1a** also is not significantly different from that of **2a**. However, in the measurement of the spectra the tuning adjustment for the sample **1a** was more difficult than that for **2a**. This fact is probably due to the increase of electronic conductivity and/or dielectric polarization brought about by dimer formation.

Description of Structure. Purple Rh(2,6-Me$_2$-4-BrC$_6$H$_2$NC)$_3$Cl (**1a**) exists as a dimer in the crystal [Rh(2,6-Me$_2$-4-BrC$_6$H$_2$NC)$_3$Cl]$_2$. The molecular structure is illustrated in Figure 2. Selected bond lengths and angles are given in Table III. The molecule has an idealized C_{2h} symmetry and consists of two square-planar Rh(2,6-Me$_2$-4-BrC$_6$H$_2$NC)$_3$Cl units connected to each other via a metal–metal bond, each unit adopting an eclipsed con-

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(4) See ref 2h and 2j for the determination of equilibrium constants.

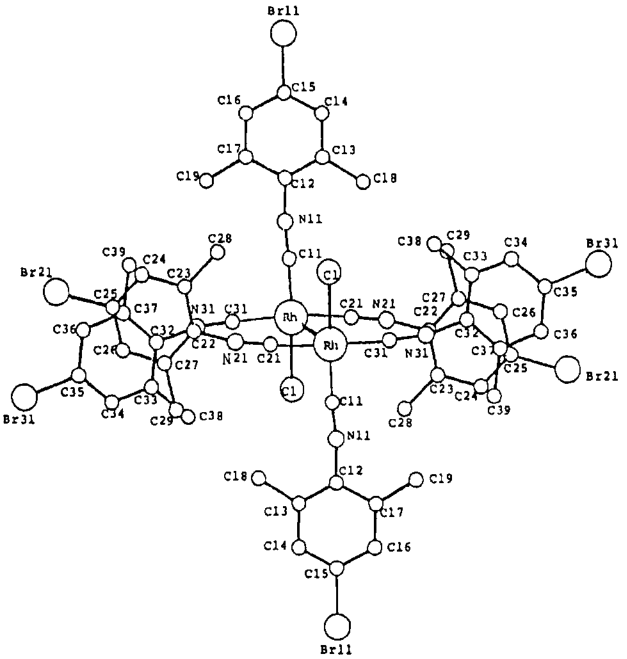

Figure 2. Molecular structure of **1a**.

figuration (torsion angle Cl–Rh–Rh–Cl = 3.3°). The Rh(I)–Rh(I) distance of 3.451 (2)Å is considerably longer than that in Rh metal (2.69 Å)[5] or in Rh(I) compounds where there is a conventional single bond. This distance also is longer by ca. 0.21 Å than those found in the cationic isocyanide complexes $[Rh_2(PhNC)_8]^{2+}$ (3.193 Å), $[Rh_2(4\text{-}NO_2C_6NC)_8]^{2+}$ (3.25 Å), and $[Rh_2(4\text{-}FC_6H_4NC)_8]^{2+}$ (3.242 Å). This suggests that the metal–metal interaction in $Rh_2(2,6\text{-}Me_2\text{-}4\text{-}BrC_6H_2NC)_6Cl_2$ is weaker than that in the cationic isocyanide complexes. The Rh(I)–Rh(I) distance of **1a** is comparable to that between dimers observed in the dicarbonyl(2,4-pentanediimine)rhodium(I) dimer (3.418 Å).[6] Despite the relatively long Rh(I)–Rh(I) distance between monomers, the metal–metal interaction accounts for the purple color of the crystals and the pronounced difference between the solution spectrum at low concentration and the solid-state spectrum. It is unlikely that a simple monomer alone would be responsible for the red shift of the band in the solid-state spectrum.

The Rh–C(11) distance in the position trans to the chlorine atom is 1.870 (15) Å and is slightly shorter than the other Rh–C distances. No unusually short intra- and intermolecular contacts were found for the Cl atom and the 2,6-dimethyl-4-bromophenyl isocyanide ligand trans to the Cl atom (the short distances C(14)–C(23) = 3.50 Å and Cl–C(11) ($-x, 1-y, -z$) = 3.74 Å). Thus the relatively short Rh–C(11) distance may arise from an electronic origin, manifesting an electron withdrawal from the Cl atom. The angles C(11)–Rh–C(21) = 92.7 (6)° and C(11)–Rh–C(31) = 91.9 (6)° are larger than the angles C(21)–Rh–Cl = 87.4 (4)° and Cn(31)–Rh–Cl = 87.7 (4)°. The dihedral angles between RhC_3Cl plane and the planes of the phenyl groups of each ligand are ca. 17.5° (Table V).

Comparison of Association Ability between the $Rh(RNC)_4^+$ and $Rh(RNC)_3Cl$. The monomer orbitals that will interact most strongly in the dimers are those that extend perpendicular to the monomer plane. Figure 3 shows the HOMO–LUMO interaction of two $Rh(HNC)_4^+$ fragments as well as the two $Rh(HNC)_3Cl$ fragments (a C_{2h} symmetry) derived from the extended Hückel MO calculation in which the Rh–Rh distances in the dimeric forms are set equal in both complexes. The orbital overlap populations between the HOMO (a_{1g} or a_1) and the LUMO (a_{2u} or b_2) of the fragments are calculated to be 0.029 for the cationic $Rh(HNC)_4^+$ complex (a_{1g}–a_{2u}) and 0.018 for the neutral $Rh(HNC)_3Cl$ one (a_1–b_2).

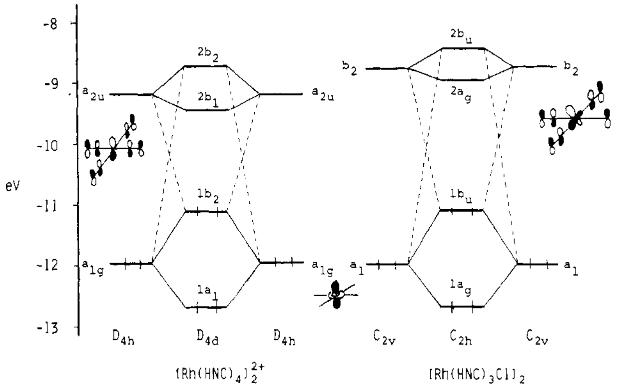

Figure 3. Energy levels of the molecular orbitals in $Rh(HNC)_4^+$ (D_{4h}) and $Rh(HNC)_3Cl$ (C_{2v}).

This suggests that the association ability of the cationic complex is greater than that of the neutral one, in agreement with the experimental observations. The HOMO's are similar in both monomeric units; they are located on the metal and consist of the d_{z^2} function with a small degree of s character. The larger HOMO–LUMO overlap population in the cationic complex can be traced back to the shape of the LUMO's. In contrast to the HOMO, the LUMO is delocalized on the central metal and ligands. In the LUMO of the cationic complex, the metal p_z atomic orbital and the four p_z AO's of isocyanide carbons are in a same phase, leading to good overlap with the HOMO of the other cationic monomer unit. In the LUMO of the neutral complex, however, the p_z AO's of the metal and the Cl atom are in a different phase. As illustrated in Figure 3, the d_{xz} AO of the Rh atom is mixed in to minimize the repulsion and the resulting LUMO is now not well shaped as that of the cationic complex. The neutral species thus cannot have good HOMO–LUMO interaction, and its association ability should be poorer than that of the cationic complex.

Experimental Section

Electronic spectra were recorded on a Hitachi 330 spectrophotometer. A JASCO infrared spectrometer was used to record infrared spectra. Nuclear magnetic resonance spectra were taken on a JEOL FX100. 2,6-Dimethyl-4-bromophenyl isocyanide was prepared by standard procedures from *N*-(2,6-dimethyl-4-bromophenyl)formamide.[7] $Rh(2,6\text{-}Me_2\text{-}4\text{-}BrC_6H_2NC)_3X$ was synthesized by literature procedures.[3]

$Rh(2,6\text{-}Me_2C_6H_2NC)_3Cl$. Purple Complex 1a. $2,6\text{-}Me_2\text{-}4\text{-}BrC_6H_2NC$ (0.26 g, 1.24 mmol) was added to a solution of $[Rh(cod)Cl]_2$ (0.1 g, 0.203 mmol) in CH_2Cl_2 (15 mL) at room temperature. After 20 min, the solution was concentrated to ca. 5 mL under reduced pressure and benzene was added. Purple crystals (0.19 g, 61%) were obtained: IR (KBr) 2090 cm^{-1} (N≡C); ^1H NMR ($CDCl_3$) δ 2.31 (s, 1 Me), 2.46 (s, 2 Me), 7.22 (b s, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 18.76 (CH_3), 121.11, 123.01, 130.91, 135.98, 137.29 (aromatic carbons).[8] Anal. Calcd for $C_{27}H_{24}N_3Br_3ClRh$: C, 42.19; H, 3.15; N, 5.47. Found: C, 42.09; H, 3.11; N, 5.47.

Brownish Yellow Complex 2a. (a) The purple complex **1a** was dissolved in CH_2Cl_2. Excess *n*-hexane was added to the yellow

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[5] Donohue, J. "The Structures of the Elements"; Wiley: New York, 1974; p 216.

[6] Dehaven, P. W.; Goedken, V. L. *Inorg. Chem.* **1979**, *18*, 827.

[7] Walborsky, H. M.; Niznik, G. E. *J. Org. Chem.* **1972**, *37*, 187.

[8] The terminal carbon was not observed.

Table VIII. Fractional Coordinates (× 10^4) and Equivalent Isotropic Thermal Parameters (Å^2)^a

atom	*x*	*y*	*z*	*B*(eqv)
Rh	1350 (1)	331 (0)	446 (1)	3.6 (0.0)
Cl	1724 (4)	−36 (2)	2673 (4)	5.8 (0.1)
Br(11)	1178 (2)	2251 (1)	−7196 (2)	7.7 (0.1)
Br(21)	−4522 (2)	1881 (1)	4401 (2)	6.9 (0.1)
Br(31)	2394 (2)	−2994 (1)	5229 (2)	7.1 (0.1)
N(11)	1232 (11)	902 (5)	−2264 (11)	5.1 (0.4)
N(21)	−546 (9)	1039 (5)	1563 (10)	4.2 (0.3)
N(31)	3375 (9)	−405 (4)	−223 (10)	4.1 (0.3)
C(11)	1205 (12)	678 (6)	−1233 (12)	4.2 (0.4)
C(12)	1220 (12)	1209 (6)	−3384 (13)	4.4 (0.4)
C(13)	338 (12)	1602 (6)	−3677 (13)	4.8 (0.4)
C(14)	318 (13)	1915 (6)	−4815 (13)	4.8 (0.4)
C(15)	1211 (14)	1829 (6)	−5623 (13)	5.2 (0.5)
C(16)	2082 (13)	1439 (6)	−5366 (14)	4.9 (0.4)
C(17)	2120 (13)	1120 (6)	−4247 (14)	4.9 (0.4)
C(18)	−619 (14)	1673 (7)	−2707 (16)	6.2 (0.5)
C(19)	3054 (14)	692 (7)	−3921 (17)	6.3 (0.6)
C(21)	143 (11)	790 (5)	1101 (12)	3.6 (0.4)
C(22)	−1430 (11)	1250 (5)	2254 (13)	3.8 (0.4)
C(23)	−1649 (11)	991 (5)	3420 (12)	4.0 (0.4)
C(24)	−2575 (12)	1185 (5)	4115 (14)	4.4 (0.4)
C(25)	−3236 (11)	1614 (6)	3544 (14)	4.6 (0.4)
C(26)	−2986 (12)	1882 (6)	2418 (13)	4.6 (0.4)
C(27)	−2036 (12)	1701 (6)	1734 (13)	4.4 (0.4)
C(28)	−917 (13)	511 (5)	3978 (14)	4.7 (0.4)
C(29)	−1745 (14)	1991 (6)	485 (15)	5.6 (0.5)
C(31)	2592 (11)	−122 (5)	−19 (13)	4.0 (0.4)
C(32)	4339 (12)	−774 (6)	−142 (14)	4.4 (0.4)
C(33)	4439 (13)	−1127 (6)	935 (16)	5.1 (0.5)
C(34)	5361 (13)	−1497 (6)	1030 (16)	5.4 (0.5)
C(35)	6110 (12)	−1494 (5)	33 (15)	4.8 (0.4)
C(36)	6029 (13)	−1146 (6)	−1027 (15)	4.8 (0.4)
C(37)	5078 (12)	−779 (6)	−1152 (15)	5.0 (0.5)
C(38)	3626 (16)	−1111 (7)	2015 (17)	7.2 (0.6)
C(39)	4925 (13)	−384 (7)	−2311 (14)	5.3 (0.5)

^{a} $B_{\mathrm{eqv}} = 4/3\pi^2\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j a_i a_j$.

solution to precipitate brown-yellow crystals of **2a**: IR (KBr) 2116, 2088 cm^{-1} (N≡C). Anal. Found: C, 42.19; H, 3.09; N, 5.48.

(b) 2,6-Me$_2$-4-BrC$_6$H$_2$NC (0.36 g, 1.71 mmol) was added to a solution of [Rh(cod)Cl]$_2$ (0.14 g, 0.28 mmol) in benzene (15 mL) at room temperature. After 20 min, the brownish yellow precipitate (0.32 g, 74%) was filtered.

Rh(2,6-Me$_2$-4-BrC$_6$H$_2$NC)$_3$X (X = Br and I). A mixture of **1a** and KX in CH$_2$Cl$_2$ and H$_2$O was stirred for 0.5 h at room temperature. The yellow organic layer was dried over Na$_2$SO$_4$. Crystallization from CH$_2$Cl$_2$–hexane gave the title complex.

X = Br: IR (KBr) 2091, 2099 cm^{-1} (N≡C); ^{1}H NMR (CDCl$_3$) δ 2.37 (s, 1 Me), 2.48 (s, 2 Me), 7.23 (b s, aromatic protons). Anal. Calcd for C$_{27}$H$_{24}$N$_3$Br$_4$Rh: C, 39.89; H, 2.98; N, 5.17. Found: C, 38.81; H, 2.94; N, 5.16.

X = I: IR (Nujol) 2088 and 2099 cm^{-1} (N≡C). Anal. Calcd for C$_{27}$H$_{24}$N$_3$Br$_4$IRh: C, 37.71; H, 2.81; N, 4.89. Found: C, 37.68; H, 2.79; N, 4.86.

X-ray Data and Structure Determination. Purple crystals of **1a** were obtained by crystallization from CH$_2$Cl$_2$–benzene. Systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) indicated the space group $P2_1/n$. Crystal data and data collection are given in Table VII. Intensity data were corrected for Lorentz and polarization effects. No absorption correction was made. Atomic scattering factors of the appropriate neutral atoms were taken from ref 9. Both the $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included for all non-hydrogen atoms.[10] The function $\sum\omega(|F_o| - |F_c|)^2$ was minimized during the least-squares refinement process. The calculations were carried out by using the UNICS III system.[11] A three-dimensional Patterson synthesis revealed the position of the rhodium atom. Successive Fourier maps led to the location of the atomic positions of all non-hydrogen atoms. The non-hydrogen atoms were refined anisotropically. The final factors R and R_ω are 0.068 and 0.070, respectively. The final positional and thermal parameters are given in Table VIII.

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Appendix

The parameters used in the EHMO calculations were taken from the literature.[12] The Rh–Rh distance was set to 3.193 Å and to the experimental values of the related complexes in [Rh$_2$(PhNC)$_8$](BPh$_4$)$_2$ (3.193 Å)[2h] and [Rh$_2$(4-FC$_6$H$_4$NC)$_8$]Cl$_2$·H$_2$O (3.207 Å).[2i] All Rh–C and C–N distances were idealized at 1.92 and 1.17 Å, respectively. The Rh–Cl and N–H distances were set to 2.35 and 1.05 Å, respectively. The C–Rh–C and C–Rh–Cl angles were set to 90°, and the Rh–C–N–H bond was idealized to be linear.

Registry No. 1a, 87070-68-6; 1b, 87070-69-7; 1c, 87070-70-0; 2a, 87070-71-1; [Rh(COd)Cl]$_2$, 12092-47-6.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes, Table V, least-squares planes, Table VI, dihedral angles, Table VII, crystal data and data collection, and a table of mean square displacement tensor of atoms (20 pages). Ordering information is given on any current masthead page.

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