Organometallics 1985, *4*, 863–866

Coordination of the 2-Anilinopyridine Ligand via Ortho Metalation: Synthesis and Crystal and Molecular Structure of $RhCl_2py_2[(C_6H_4)NHpy]$

Akhil R. Chakravarty, F. Albert Cotton,* and Derek A. Tocher

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843

Received November 1, 1984

The title compound was obtained by reaction of rhodium trichloride with the sodium salt of 2-anilinopyridine $[(C_6H_5)NHpy]$ in ethanol. The orange crystals were formed on addition of pyridine and subsequent evaporation. The complex crystallizes in the monoclinic space group $P2_1/n$, with unit-cell dimensions $a = 9.029$ (4) Å, $b = 13.217$ (3) Å, $c = 13.388$ (3) Å, $\beta = 94.23$ (2)°, and $V = 2069$ (1) Å^3, with $Z = 4$. The structure was refined to $R = 0.043$ ($R_w = 0.066$). The complex is unusual in that the 2-anilinopyridine ligand is not only coordinated through the pyridine nitrogen atom but also through an ortho carbon atom of the phenyl ring, thus forming a *six-membered* metallocyclic ring. The uncoordinated amine nitrogen atom, which retains a hydrogen atom, participates in hydrogen bonding with a chlorine atom of an adjacent molecule, thus leading to the formation of dimeric units linked by hydrogen bonds. The six-membered ring "RhN_2C_3" is fused to two benzenoid rings thus making the "$Rh[(C_6H_4)NHpy]$" moiety a formal metalloheterocyclic analogue of anthracene.

Introduction

In the past year considerable interest has been evidenced in the ligand 2-(*N*-anilino)pyridine.[1-6] Much of this interest has been focused on the numerous modes of coordination that are possible for this ligand. Unidentate coordination may occur through either the pyridine or the amine nitrogen atoms. Bidentate modes of coordination to either a single metal center, to give a chelate ring, or across two metal centers, to form a three-atom bridge, have also been observed. The reports which have appeared so far have dealt solely with these modes of coordination through the nitrogen atoms. However, the geometry of the ligand is such that an ortho-metalation reaction leading to another mode of coordination is also feasible, and it is to the realization of that possibility that this paper addresses itself.

Experimental Section

$RhCl_3{\cdot}3H_2O$ was purchased from Johnson Matthey, Inc. Solvents used were of analytical grade and were distilled under nitrogen prior to use.

Preparation of $RhCl_2py_2[(C_6H_4)NHpy]$. $RhCl_3{\cdot}3H_2O$ (0.20 g, 0.76 mmol) was dissolved in ethanol (20 mL) to which was added Na metal (0.08 g, 3.5 mmol) and 2-anilinopyridine (0.60 g, 3.5 mmol). The solution was refluxed under N_2 for 16 h after which time it had become red. The solvent was removed under vacuum, and the residue was extracted with methanol (15 mL). Addition of pyridine (0.5 mL, 6.8 mmol) gave a yellow solution from which a homogeneous mass of orange crystals were deposited upon slow evaporation; yield 0.24 g (63%).

The complex, which does not melt below 240 °C, is practically insoluble in $C_6H_5CH_3$, CH_2Cl_2, CH_3OH, $(CH_3)_2CO$, CH_3CN, and C_6H_6 but slightly soluble in $(CH_3)_2SO$. Anal. Calcd. for $RhCl_2N_4C_{21}H_{19}$: C, 50.3; H, 3.8; N, 11.2. Found: C, 51.1; H, 3.9; N, 11.5. Infrared spectrum (Nujol mull, CsI plates): 3280 (s), 3136 (w), 1618 (s), 1590 (m), 1570 (m), 1522 (s), 1295 (m), 1255 (w), 1212 (m), 1160 (w), 1152 (w), 1143 (w), 1063 (m), 1022 (w), 1011 (w), 1000 (w), 896 (w), 760 (m), 742 (s), 697 (m), 666 (m), 621 (w), 542 (w), 521 (w), 477 (w), 439 (w), 351 (m) cm^{-1} (s, strong; m, medium; w, weak). Proton NMR ($(CH_3)_2SO$-d_6 solvent, $(CH_3)_4Si$ reference): δ 6.5–8.5 (complex multiplets).

Table I. Crystallographic Parameters for $RhCl_2py_2[(C_6H_4)NHpy]$

formula	$RhCl_2N_4C_{21}H_{19}$
fw	501.22
space group	$P2_1/n$
systematic absences	$0k0$, $k = 2n$; $h0l$, $h + l = 2n$
a, Å	9.029 (4)
b, Å	13.217 (3)
c, Å	17.388 (3)
α, deg	90.0
β, deg	94.23 (2)
γ, deg	90.0
V, Å^3	2069 (1)
Z	4
d_{calcd}, g/cm^3	1.609
cryst size, mm	0.3 × 0.3 × 0.2
μ(Mo Kα), cm^{-1}	10.86
data collectn instrument	Nicolet P3
radiatn (monochromated in incident beam)	Mo Kα (λ = 0.710 73 Å)
orientatn reflctns, no. range (2θ)	25, $20 \leq 2\theta \leq 28°$
temp, °C	25 ± 1
scan method	ω-2θ
data col range 2θ, deg	$4 \leq 2\theta \leq 45°$
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	2109, 1918
no. of parameters refined	259
trans factors, max, min	99.96%, 88.18%
R^a	0.043
$R_w{}^b$	0.066
quality-of-fit indicator^c	1.504
largest shift/esd, final cycle	0.18
largest peak, e/Å^3	0.66

^{a} $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c} Quality of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

Measurements. Elemental analyses were performed by Galbraith Laboratories, Inc. Infrared spectra were recorded on

---

[1] Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 469.

[2] Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 700.

[3] Chakravarty, A. R.; Cotton, F. A.; Shamshoum, E. S. *Inorg. Chim. Acta* **1984**, *86*, 5.

[4] Chakravarty, A. R.; Cotton, F. A.; Shamshoum, E. S. *Inorg. Chem.* **1984**, *23*, 4216.

[5] Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1985**, *24*, 172.

[6] Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1984**, *23*, 4693.

0276-7333/85/2304-0863$01.50/0 © 1985 American Chemical Society

Table II. Positional Parameters and Their Estimated Standard Deviations for $RhCl_2py_2[(C_6H_4)NHpy]$[a]

atom	x	y	z	B, Å^2
Rh(1)	0.10489 (6)	0.21238 (5)	0.15506 (4)	2.78 (1)
Cl(1)	0.2153 (2)	0.0534 (2)	0.1301 (1)	3.39 (4)
Cl(2)	−0.0140 (2)	0.3668 (2)	0.1724 (2)	4.57 (5)
N(1)	0.3181 (7)	0.2828 (5)	0.1656 (4)	3.1 (1)
N(2)	0.1488 (8)	0.1883 (5)	0.2825 (4)	4.2 (2)
N(3)	−0.0816 (7)	0.0993 (5)	0.0134 (4)	3.5 (1)
N(4)	−0.0962 (7)	0.1405 (5)	0.1467 (4)	3.9 (2)
C(1)	0.0886 (8)	0.2384 (6)	0.0407 (4)	2.6 (2)
C(2)	0.164 (1)	0.3181 (7)	0.0090 (5)	4.1 (2)
C(3)	0.179 (1)	0.3262 (8)	−0.0684 (6)	5.2 (2)
C(4)	0.116 (1)	0.2525 (9)	−0.1192 (6)	5.7 (3)
C(5)	0.030 (1)	0.1768 (7)	−0.0906 (5)	4.7 (2)
C(6)	0.0136 (9)	0.1727 (6)	−0.0097 (5)	3.3 (2)
C(7)	−0.1508 (8)	0.0920 (6)	0.0818 (5)	2.9 (2)
C(8)	−0.2801 (9)	0.0292 (6)	0.0805 (6)	4.4 (2)
C(9)	−0.352 (1)	0.0206 (7)	0.1458 (6)	4.8 (2)
C(10)	−0.304 (1)	0.0730 (7)	0.2140 (6)	4.3 (2)
C(11)	−0.1754 (9)	0.1321 (7)	0.2128 (5)	4.3 (2)
C(12)	0.429 (1)	0.2495 (7)	0.1251 (5)	3.8 (2)
C(13)	0.5696 (9)	0.2954 (7)	0.1304 (5)	4.1 (2)
C(14)	0.595 (1)	0.3809 (7)	0.1779 (5)	4.3 (2)
C(15)	0.4777 (9)	0.4138 (7)	0.2194 (5)	4.1 (2)
C(16)	0.3424 (9)	0.3643 (6)	0.2121 (5)	3.6 (2)
C(17)	0.081 (1)	0.2435 (9)	0.3362 (6)	5.4 (2)
C(18)	0.118 (1)	0.234 (1)	0.4148 (6)	7.4 (3)
C(19)	0.227 (1)	0.162 (1)	0.4410 (7)	7.5 (3)
C(20)	0.293 (1)	0.1035 (8)	0.3858 (6)	5.8 (3)
C(21)	0.253 (1)	0.1200 (7)	0.3080 (5)	4.4 (2)
H3N	−0.121 (9)	0.053 (6)	−0.019 (5)	5*

[a] Atoms with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table III. Bond Distances (Å)[a] in $RhCl_2py_2[(C_6H_4)NHpy]$

Rh(1)-Cl(1)	2.379 (2)	C(2)-C(3)	1.367 (11)
-Cl(2)	2.336 (2)	-C(4)	1.407 (13)
-N(1)	2.134 (5)	C(4)-C(5)	1.378 (12)
-N(2)	2.244 (7)	C(5)-C(6)	1.428 (10)
-N(4)	2.045 (6)	C(7)-C(8)	1.431 (9)
-C(1)	2.012 (6)	C(8)-C(9)	1.351 (11)
N(1)-C(12)	1.338 (9)	C(9)-C(10)	1.412 (11)
-C(16)	1.355 (9)	C(10)-C(11)	1.399 (10)
N(2)-C(17)	1.365 (10)	C(12)-C(13)	1.404 (10)
-C(21)	1.355 (10)	C(13)-C(14)	1.409 (11)
N(3)-C(6)	1.375 (9)	C(14)-C(15)	1.395 (10)
-C(7)	1.387 (9)	C(15)-C(16)	1.383 (10)
-H(3N)	0.89 (7)	C(17)-C(18)	1.389 (13)
N(4)-C(7)	1.359 (9)	C(18)-C(19)	1.42 (2)
-C(11)	1.402 (9)	C(19)-C(20)	1.396 (14)
C(1)-C(2)	1.388 (10)	C(20)-C(21)	1.391 (12)
-C(6)	1.377 (10)		

[a] Estimated standard deviations (esd's) in parentheses.

a Perkin-Elmer 785 spectrophotometer. Proton NMR spectra were recorded on a Varian EM-390 instrument.

X-ray Crystallography Procedures. The structure of $RhCl_2py_2[(C_6H_4)NHpy]$ was determined by applying the general procedures described elsewhere.[7-8] A detailed description is available as part of the supplementary material. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I. Table II lists atomic coordinates and isotropic equivalent thermal parameters, while Tables III and IV contain important bond distances and angles, respectively. The compound crystallizes in the monoclinic space group $P2_1/n$ with the complete molecule constituting the asymmetric unit. The position of the rhodium atom was derived from a three-dimensional Patterson map and the remainder of the structure obtained using least-squares refinement and difference electron density maps.

Table IV. Bond Angles (deg)[a] in $RhCl_2py_2[(C_6H_4)NHpy]$

Cl(1)-Rh(1)-Cl(2)	176.28 (7)
-N(1)	90.8 (2)
-N(2)	90.5 (2)
-N(4)	87.6 (2)
-C(1)	88.4 (2)
Cl(2)-Rh(1)-N(1)	91.6 (2)
-N(2)	92.6 (2)
-N(4)	90.1 (2)
-C(1)	88.7 (2)
N(1)-Rh(1)-N(2)	83.4 (2)
-N(4)	178.0 (2)
-C(1)	90.6 (2)
N(2)-Rh(1)-N(4)	95.5 (2)
-C(1)	173.8 (2)
N(4)-Rh(1)-C(1)	90.6 (3)
Rh(1)-C(1)-C(6)	121.2 (5)
C(1)-C(6)-N(3)	123.3 (7)
C(6)-N(3)-C(7)	129.0 (6)
N(3)-C(7)-N(4)	121.4 (6)
C(7)-N(4)-Rh(1)	122.9 (5)

[a] Estimated standard deviations (esd's) in parentheses.

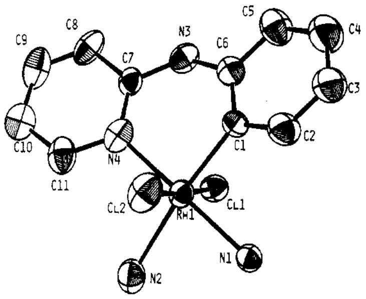

Figure 1. An ORTEP drawing of the central portion of the $RhCl_2py_2[(C_6H_4)NH(py)]$ molecule. Atoms are represented by thermal vibration ellipsoids at the 50% level.

Results

The complex is prepared in a straightforward manner in good yield. It can be obtained as a homogeneous crystalline solid directly from the reaction mixture without further recrystallization. Unfortunately, the complex is essentially insoluble in all common solvents except dimethyl sulfoxide, in which it is sparingly soluble. The proton NMR in this solvent shows broad, weak multiplets between δ 6.5 and 8.5. It was impossible to discern any peak unequivocally assignable to the amine proton.

The infrared spectrum provided several important structural pointers. The position, 3280 cm^{-1}, and strength of the ν(N-H) stretch are consistent with the involvement of this proton in a hydrogen bond between nitrogen and chlorine atoms, as discussed below. The occurrence of only a single ν(Rh–Cl) stretch at 351 cm^{-1} was indicative of the trans geometry of the chloride ligands. A strong band at 1618 cm^{-1} would be assigned to the skeletal vibrations of the pyridine rings while, in retrospect, the bands at 1522 and 1570 cm^{-1} may be assigned to the metalated phenyl ring.[12,29]

---

(7) Calculations were done on the VAX-11/780 computer at the Department of Chemistry, Texas A&M University, College Station, TX, with VAX-SDP software package.

(8) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227. North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 351.

(9) Cole-Hamilton, D. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 797.

(10) Bennett, M. A.; Kilner, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 6983.

(11) The equation for the least-squares plane takes the form $(0.5946)x + (0.4964)y - (0.6325)z = 0.00$.

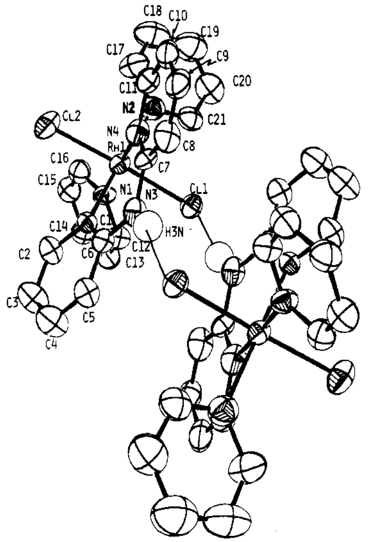

Figure 2. An ORTEP drawing of the $\{RhCl_2py_2[(C_6H_4)NH(py)]\}_2$ dimer. Atoms are represented by thermal vibration ellipsoids at the 50% level, and the atomic labeling scheme in the crystallographically independent unit is defined.

Crystal and Molecular Structure of $RhCl_2py_2[(C_6H_4)NHpy]$. Tables III and IV contain the important bond distances and angles, respectively, for this molecule. Figure 1 shows the coordination sphere about the Rh(III) ion and the ortho-metalated ligand, while Figure 2 shows the nature of the dimerization through the pair of hydrogen bonds.

The coordination about the rhodium atom is that of a distorted octahedron (Figure 1). The angles between adjacent atoms in the coordination sphere lie in the range 83.4 (2)–95.5 (2)°. The smallest of these angles is that between nitrogen atoms of the pyridine rings, N(1) and N(2), and probably arises from the fact that the flat $(C_6H_4)NH(C_5NH_4)$ ligand exerts a compressive force on this angle through the hydrogen atoms attached to the C(2) and C(11) atoms of the anilinopyridine ligand. The bonds to N(1) and N(2), 2.134 (5) and 2.244 (7) Å, respectively, differ considerably in length but in a manner consistent with the expected order of trans influences for Rh–N and Rh–C bonds. The chlorine ligands are trans to each other, and the bond lengths 2.379 (2) and 2.336 (2) Å to Cl(1) and Cl(2), respectively, are significantly different in a way that is consistent with the involvement of Cl(1) in a hydrogen bond, as discussed below. This interaction may also contribute to the slight deviation from linearity for the Cl(1)–Rh(1)–Cl(2) angle, 176.28 (7)°.

The anilinopyridine ligand is coordinated to the metal center through N(4) and C(1), with bond lengths of 2.045 (6) and 2.012 (6) Å, respectively, while the amine nitrogen atom, N(3), is left uncoordinated. It is to be noted that our identification of the N(4) and C(1) atoms cannot reasonably be reversed for several reasons. First, the Rh–N and Rh–C distances make better sense as we have them than if reversed. Second, the different Rh–N(1) and Rh–N(2) distances are consistent, on the basis of expected trans influences, with the assignments given, as already noted. Finally, an attempt to refine the structure with the assignments reversed led to higher residuals and somewhat less plausible thermal parameters.

It is interesting that in the solid state, pairs of these complexes are associated into dimers about the inversion center at (0,0,0) via two hydrogen bond bridges, viz., N(3)–H(3N)–Cl(1)* and Cl(1)–H(3N)*–N(3)* (where the starred atoms are those generated by the inversion center). The hydrogen atom was located from a difference Fourier map and refined. The bridging unit is almost linear (∠N(3)–H(3N)–Cl(1)* = 168.5°) and no atom deviates by more than 0.08 Å from the least-squares plane[30] of the two N–H···Cl units. The N(3)–Cl(1)* separation is 3.36 Å, making this a fairly weak hydrogen bonding interaction.

Discussion

Published reports prior to this concerning the behavior of 2-anilinopyridine as a ligand fall into three groups. There are two papers[1,2] dealing with the lithiated species $[Ph(2\text{-}py)NLi]\cdot(HMPA)\cdot[Ph(2\text{-}py)NH]$[1] and $\{[Ph(2\text{-}py)NLi]\cdot[OP(NMe_2)_3]\}_2$ (two isomers).[2] The former exhibits both chelating and unidentate (through the pyridyl nitrogen) coordination of the ligand to the lithium ion, while in the latter there is one isomer containing only chelating $[PhN(2\text{-}py)]^-$ ligands and another in which the amine nitrogen bridges two lithium atoms each of which is also coordinated to a pyridyl nitrogen. There is then a report[3] describing chelate coordination to a transition-metal ion. The reaction of $Li[PhN(2\text{-}py)]$ with $RuCl_2(PPh_3)_3$ gives a complex of stoichiometry $Ru[PhN(2\text{-}py)]_2(PPh_3)_2$ which exists as two isomers.[3] The final group of earlier reports,[4–6] which are of intrinsically greater interest to us, deals with reactions that give rise to metal–metal bonded complexes in which the 2-(*N*-anilino)pyridine anion serves as a three-atom bridging ligand. The molybdenum and tungsten complexes are typical of a great number of species having asymmetric bridging ligands, i.e., a centrosymmetric arrangement in the "$M_2(XYZ)_4$" core.[4] The ruthenium complex $Ru_2(PhNpy)_4Cl$[5] is unusual in that the molecule has a totally polar arrangement of the bridging ligands; i.e., there are four pendant phenyl groups at one end of the molecule. Another complex in this last group is a triply bonded osmium(III) species, $Os_2Cl_3(PhNpy)_3$, in which only three ligands bridge the Os≡Os bond, the other two equatorial positions being occupied by chloride ions.[6]

The different modes of coordination found in the metal–metal bonded complexes can, we believe, be attributed to the varying strength of axial ligation in these three complexes and it was in the course of our further investigations into this phenomenon that we serendipitously encountered the novel ortho-metallated rhodium complex $RhCl_2py_2[(C_6H_4)NHpy]$, that is described here.

The ortho-metalation reaction[12] is an important one for ligands containing phenyl groups bonded to donor atoms such as phosphorus or nitrogen. The vast majority of complexes of this type contain either four or five-membered rings.[13–21] The occurrence of three-membered cyclometalated rings is also known, for example, in $\mathrm{Cp_2\overline{Ti{:}NCRC_3H_3C}}$ (R = Me, Ph, or vinyl).[22]

In contrast, less than a dozen reports have appeared concerning six-membered rings in ortho-metalated tran-

---

[12] Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73.

[13] Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139.

[14] Carty, A. J. *Organomet. Chem. Rev., Sect. A* **1972**, *7*, 191.

[15] Bruce, M. I.; Goodall, B. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 687.

[16] Churchill, M. R.; Wasserman, J. H.; Young, G. J. *Inorg. Chem.* **1980**, *19*, 762.

[17] Tolman, C. A.; English, A. D.; Ittel, S. D.; Jesson, J. P. *Inorg. Chem.* **1978**, *17*, 2374.

[18] Bruce, M. I.; Goodall, B. L.; Matsuda, J. *Aust. J. Chem.* **1975**, *28*, 1259.

[19] Foot, R. G.; Heaton, B. T. *J. Chem. Soc., Chem. Commun.* **1973**, 838.

[20] Ronoyama, M. *J. Organomet. Chem.* **1974**, *74*, 115.

[21] Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *J. Chem. Soc., Chem. Commun.* **1984**, 501.

[22] Klei, B.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1978**, 659.

sition-metal complexes,[23-30] and the majority of these reports deal with complexes of platinum and palladium. However, there is one report in the literature, concerning the rhodium-catalyzed reaction between aniline and ethylene, in which the six-membered cyclometalated rhodium complex $HX\overline{Rh(H_2N\cdot C_6H_4\cdot CH_2C}H_2)$ is postulated as an intermediate.[31] We do, however, believe that the complex reported here is the first example to be isolated and characterized by X-ray crystallography of a rhodium compound, containing a six-membered chelate ring that includes an ortho-metalated ring.

A point of some interest in this structure is whether the "$Rh[(C_6H_4)NHpy]$" moiety is aromatic. Clearly both the pyridyl and phenyl rings are individually aromatic systems and the bond distances and angles (see Tables III and IV) do not deviate significantly from the ideal values. In addition, neither ring shows any significant deviation from planarity.[32] However, the dihedral angle between the planes of these two rings is 22.7°.

The chelate ring, consisting of the atoms Rh(1)–C(1)–C(6)–N(3)–C(7)–N(4), although not truly planar,[33] does not show large deviations from planarity, and thus it is not unreasonable to look further into the possibility that it might have a delocalized π system and hence be aromatic (or antiaromatic). The deviations from planarity that do exist may be attributed to the size of the rhodium atom. Both Rh and N(3) lie below the least-squares plane, in what would be described as a boat type configuration for a saturated ring system. However, these displacements[33] are only about 0.22 Å. The angle at the metal, i.e., C(1)–Rh(1)–N(4), is 90.6 (3)°, is obviously much less than the ideal value for a flat aromatic ring. However the greater bond lengths to the metal partly compensate for this, and the angles at N(4) and C(1), 122.9 (5)° and 121.2 (5)°, respectively, are close to the ideal value of 120°. At N(3), however, the angle C(6)–N(3)–C(7), 129.0 (6)°, is significantly larger than the ideal value. It is possible, of course, that the involvement of N(3) in hydrogen bonding, as discussed above, also plays some part in this observation. The virtual equality of the bonds C(6)–N(3) and N(3)–C(7), 1.375 (9) and 1.387 (9) Å, respectively, also argues for the delocalized nature of the ring system. It has been our previous experience with this ligand that N(amine)–pyridyl bonds lie in the range 1.33–1.36 Å, while N(amine)–phenyl bonds are typically 1.42 –1.43 Å.[5,6] The average length observed here, 1.381 ± 0.006 Å, is consistent with a significant amount of delocalized π bonding.

If it is accepted that there is significant delocalization of π electrons in the central, chelate ring, the question of whether this leads to aromaticity or antiaromaticity presents itself. The rhodium atom itself can be regarded as having a closed-shell 18-electron configuration; it is Rh^{III} (d^6) surrounded by six two-electron donors. If N(3) is assumed to provide a doubly occupied $p\pi$ orbital and the metal atom to contribute no electrons, a 14-electron aromatic system, comparable to anthracene, could be postulated. On the other hand, if the rhodium atom introduces electrons into the overall π system, then it would be best considered nonaromatic or even antiaromatic. We are inclined to think that some significant degree of aromatic character is reasonable in order to account for the stability of the molecule.

We recognize that a further study to determine why the preparative reaction proceeds as it does and, with such efficiency, would be worthwhile. However, we do not plan such a study since this type of reaction was not desired and does not form a part of the program we were pursuing. It had been our intention that reaction of sodium with the 2-anilinopyridine would generate a $[(2\text{-}C_5H_5N)NC_6H_5]^-$ ligand that could react as a bidentate three-atom-bridging ligand, as has been found previously with other metals.[4-6] The role of the sodium may have been quite different and the solvent may also play a role.

Acknowledgment. We are grateful to the Robert A. Welch Foundation for financial support under Grant No. A-494.

Registry No. $RhCl_2py_2[(C_6H_4)NHpy]$, 95552-57-1; $RhCl_3$, 10049-07-7; 2-anilinopyridine, 6631-37-4.

Supplementary Material Available: Full description of structure determination, tables of structure factors and anisotropic thermal parameters, and a complete list of bond distances and angles (22 pages). Ordering information is given on any current masthead page.

---

(23) Bennett, M. A.; Clark, P. W.; Robertson, G. B.; Whimp, P. O. *J. Organomet. Chem.* **1973**, *63*, C15.

(24) Bennett, M. A.; Clark, P. W. *J. Organomet. Chem.* **1976**, *110*, 367.

(25) Jones, C. E.; Shaw, B. L.; Turtle, B. L. *J. Chem. Soc., Dalton Trans.* **1974**, 992.

(26) Cameron, N. D.; Kilner, M. *J. Chem. Soc., Chem. Commun.* **1975**, 687.

(27) Horino, H.; Inoue, N. *Tetrahedron Lett.* **1979**, 2403.

(28) Hiraki, K.; Fuchita, Y.; Takechi, K. *Inorg. Chem.* **1981**, *20*, 4316.

(29) Fuchita, Y.; Hiraki, K.; Kage, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 955.

(30) Fuchita, Y.; Hiraki, K.; Uchiyama, T. *J. Chem. Soc., Dalton Trans.* **1983**, 897.

(31) Diamond, S. E.; Szalkiewicz, A.; Mores, F. *J. Am. Chem. Soc.* **1979**, *101*, 490.

(32) For the ring C(1)–C(6), the equation for the least-squares plane is $-(0.8148)x + (0.5712)y - (0.0995)z = -1.711$, with a maximum deviation –0.051 Å for C(1). For the ring N(4)–C(11), the equation for the least-squares plane is $-(0.5436)x + (0.7903)y - (0.2827)z = -1.3410$, and the maximum deviation is –0.018 Å for N(4).

(33) Least-squares plane given by $-(0.6297)x + (0.7712)y - (0.0939) = -1.6794$. Deviations: Rh(1), –0.238 Å; C(1), 0.214 Å; C(6), 0.011 Å; N(3), –0.215 Å; C(7), 0.049 Å; N(4), 0.179 Å.