Reaction of 2-((.alpha.-R-benzylidene)amino)pyridines [R = CH3, 4-(CH3O)C6H4] with RhCl(L)3 or Rh2Cl2(CO)4: formation and structure of a rhodium(II) dimer

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Reaction of 2-((α-R-Benzylidene)amino)pyridines [R = CH₃, 4-(CH₃O)C₆H₄] with RhCl(L)₃ or Rh₂Cl₂(CO)₄: Formation and Structure of a Rhodium(II) Dimer

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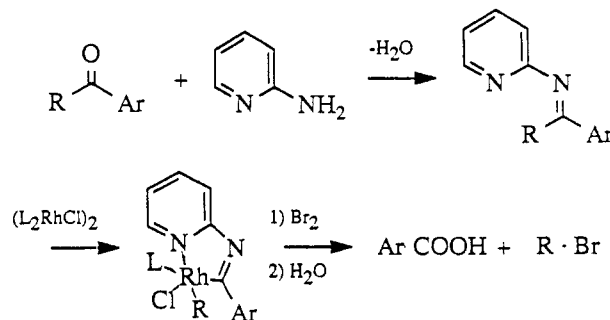*Department of Chemistry, Wayne State University, Detroit, Michigan 48202*

The reaction of 2-((α-methylbenzylidene)amino)pyridine (L_1) with $RhCl(PPh_3)_3$ resulted in the formation of *cis*-$[Cl(PPh_3)_2(L_1)Rh^I]\cdot S$ (**1**, S = solvent). The reaction of 2-[(α-(4-methoxyphenyl)benzylidene)-amino]pyridine (L_2) with $Rh_2Cl_2(CO)_4$ (**4**) under identical conditions resulted in the formation of *cis*-$[Cl(CO)_2(L_2)Rh^I]$ (**2**). The ligand L_1 when treated with the same Rh complex **4** at 90 °C in an autoclave for 18 h resulted in the formation of $[Cl(CO)(L_1-H)Rh^{II}]_2$ (**3**), where the benzene ring of the ligand was ortho-metalated to rhodium. Compound **1** crystallized in the triclinic space group $P\bar{1}$ with $Z = 2$ and lattice parameters $a = 10.9817$ (8), $b = 12.2447$ (12), $c = 17.800$ (3) Å, $\alpha = 94.221$ (10), $\beta = 101.770$ (9), $\gamma = 92.022$ (7)°, $V = 2333.8$ (4) Å³; final $R_w = 3.6\%$. Compound **2** crystallized in the monoclinic space group $P2_1/c$ with $Z = 4$ and lattice parameters $a = 10.845$ (6), $b = 11.161$ (6), $c = 17.161$ (9) Å, $\beta = 86.61$ (1)°, $V = 2073.58$ Å³; final $R_w = 4.9\%$. Compound **3** crystallized in the monoclinic space group $P2_1/c$ with $Z = 4$ and lattice parameters $a = 8.0708$ (16), $b = 20.907$ (6), $c = 16.373$ (2) Å, $\beta = 90.078$ (14)°, $V = 2762.6$ (1.0) Å³; final $R_w = 3.2\%$. The structures of the complexes reported are compared and contrasted with analogous complexes of rhodium.

Introduction

Study of the synthesis and reactions of cyclometalated complexes formed by the cleavage of C–C and C–H bonds of organic molecules in homogeneous media is a rapidly growing research area.[1] Many metals have been found to insert into C–H and/or C–C bonds. Among the platinum-group metal complexes used to study the activation of these bonds, platinum,[2,3] palladium,[3,4] rhodium,[3,5] and iridium[3,5,6] complexes have been found to be effective.[1] A significant amount of this work has been done on two different organic molecular platforms, 8-substituted quinolines[2,7–9] (A, eq 1) and 2-(benzylideneamino)pyridines

Scheme I

(B, eq 2).[5,10] Precomplexation of the metal complex with the pyridine nitrogen in A or B allows interaction with the appropriate bond on the adjacent group which results in insertion[7] (reactions 1 and 2).
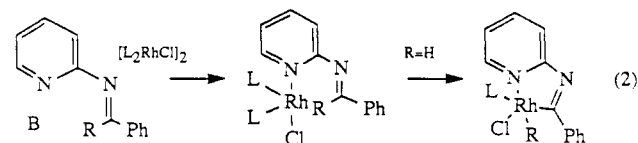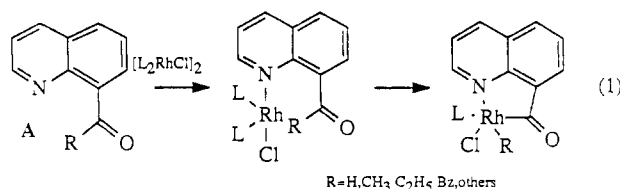
C–H bond insertion has been observed with both the quinoline and Schiff base substrates (A and B, R = H).

(1) (a) DeLaud, J., Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327. (b) Omae, I. *Chem. Rev.* **1979**, *79*, 287. (c) Omae, I. *Coord. Chem. Rev.* **1979**, *28*, 97; **1980**, *32*, 235; **1982**, *42*, 245; **1988**, *83*, 137.

(2) Albinati, A.; Auklin, C. G.; Gunazzoli, F.; Ruegg, H.; Pegosin, P. S. *Inorg. Chem.* **1987**, *26*, 503.

(3) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. *J. Am. Chem. Soc.* **1984**, *106*, 6647.

(4) (a) Janecki, T.; Jeffreys, J. A. D.; Pauson, P. L.; Pietrzykrowski, A.; McCullough, K. J. *Organometallics* **1987**, *6*, 1553. (b) Clark, P. W.; Dyke, S. F.; Smith, G.; Kennard, C. H. L. *J. Organomet. Chem.* **1987**, *330*, 447. (c) Navarro-Ranninger, M. C.; Alvarez-Valdes, A.; Camazon, M. J.; Roman, J.; Lozano, R. *Ibid.* **1987**, *331*, 107. (d) Steel, P. J.; Caygill, G. B. *J. Organomet. Chem.* **1987**, *327*, 101. (e) Pergosin, P. S.; Arz, C. *Magn. Reson. Chem.* **1987**, *25*, 158, and references therein.

(5) (a) Albinati, A.; Arz, C.; Pregosin, P. S. *J. Organomet. Chem.* **1987**, *335*, 379. (b) Craik, A. R. M.; Knox, G. R.; Pauson, P. L.; Hoare, R. J.; Mills, O. S. *J. Chem. Soc. D* **1984**, *106*, 6647.

(6) (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (b) Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 7222. (c) Werner, H.; Hohn, A.; Dziallas, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1090. (d) Lehmkuhl, H.; Bellenbaum, M.; Grundke, J. *J. Organomet. Chem.* **1987**, *330*, C23.

(7) (a) Suggs, J. W.; Wovkulich, M. J.; Cox, S. D. *Organometallics* **1985**, *4*, 1101. (b) Suggs, J. W.; Cox, S. D. *J. Organomet. Chem.* **1981**, *221*, 199. (c) Suggs, J. W.; Jun, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 4679. (d) Dias, S. A.; Downs, A. W.; Mewhinnie, W. R. *J. Chem. Soc. D* **1975**, 162.

(8) (a) Garber, A. R.; Garron, P. E.; Hartwell, G. E.; Smas, M. J.; Wilkinson, J. R.; Todd, L. J. *J. Organomet. Chem.* **1975**, *86*, 219. (b) Suggs, J. W.; Jun, C. H. *J. Am. Chem. Soc.* **1984**, *106*, 3054.

(9) Suggs, J. W.; Jun, C.-H. *J. Chem. Soc., Chem. Commun.* **1985**, 92.

(10) (a) Suggs, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 489. (b) Albinati, A.; Arz, C.; Pregosin, P. S. *Inorg. Chem.* **1987**, *26*, 508. (c) Arz, C.; Pregosin, P. S.; Anklin, C. *Magn. Reson. Chem.* **1987**, *25*, 158.

Complexes that bring about this reaction include $RhCl(PPh_3)_3$, $[RhX_2Cl]_2$ (X = C_2H_4 or CO), $[MCl(\mu\text{-}Cl)L]_2$ (M = Pd(II) or Pt(II) and L = phosphines and others), and $[M(\mu\text{-}Cl)(cyclooctene)_2]_2$ (M = Ir(I) or Rh(I)).[2,7,10]

C–C bond insertion has been reported only for the quinoline series[7-9] and is apparently a more demanding reaction to bring about both sterically and electronically. Results in this series indicate that while the above complexes bring about insertion in the C–H bond, they are not all effective for C–C bond insertion. By far the most effective complex for C–C bond insertion is the ethylene complex $[Rh(C_2H_4)_2Cl]_2$, which has been shown to undergo C–C bond insertion with a variety of Q-C(O)R ketones (Q = 8-quinolyl, R = $-CH_2Ph$, $-C_2H_5$, $-CH_3$, $-C_6H_5$, and others).[8] Formation of the C–C bond insertion product is rendered irreversible by displacement of the ethylene ligands with pyridine.[7] Suggs et al. have rationalized these results on the basis of the reactivity of the ligands.[7] Indeed if the C–C inserted product is treated with a strong σ-bonding ligand like a phosphine or carbon monoxide, the insertion reaction is reversed and a Rh(I) complex is regenerated. There also is evidence to indicate that the greater rigidity of the 8-substituted quinoline molecule is more favorable to C–C bond insertion than the more flexible 2-(benzylideneamino)pyridines. However, even in the quinoline series if other reactions are possible, they tend to be more favorable than C–C bond insertion.

Our interest in this area stems from the desire to develop a process that will allow clean cleavage of C–C bonds adjacent to carbonyl groups. Thus, preformation of the 2-(benzylideneamino)pyridine from 2-aminopyridine and a ketone would allow activation of the carbonyl group for such cleavage, and afterward decomposition of the complex would regenerate the aminopyridine and allow separation of the fragments. Overall, the proposed reaction series is shown in Scheme I.

To bring successful cleavage about, C–C bond cleavage of the alkyl substituted 2-(benzylideneamino)pyridines would have to succeed, and as pointed out above, this reaction has not been studied. Thus, we initiated an investigation of this cleavage. We have not succeeded in C–C bond cleavage of the desired substrate, but our results do support Suggs and co-workers mechanistic conclusions.[7] The unexpected course of one reaction affording a $Rh_2(II)$ dimer expands the scope of the Rh(I) reaction scheme and provides another example of a divergent pathway for this series.

Materials and Equipment

IR, NMR, MS, and GC-MS spectra were recorded on an MX-S FTIR (Nicolet), an EM 390 or a VXR 300 (Varian), 21-491 mass spectrometer (Du Pont), and 5790 GC with a 5970 MSD (Hewlett-Packard) spectrometers, respectively. Elemental analyses were obtained from M-H-W Laboratories (Phoenix, AZ). HR-MS were determined at the Midwest Center for Mass Spectrometry, University of Nebraska–Lincoln.

All solvents employed were dried, distilled, and degassed following standard procedures before use. All syntheses of metal complexes were carried out in an atmosphere of prepurified nitrogen with standard high-vacuum and Schlenkware techniques. 2-Aminopyridine, 4-methoxybenzophenone, and rhodium(III) chloride trihydrate were purchased from Aldrich Chemical Co. and used as received. Tris(triphenylphosphine)rhodium(I) chloride, $(RhCl(PPh_3)_3)$, was synthesized from rhodium(III) chloride trihydrate following a published procedure;[11] tetracarbonyl bis(μ-dichloro)dirhodium(I) $(Rh_2Cl_2(CO)_4)$ was either purchased from Aldrich or synthesized.[12]

2-((α-Methylbenzylidene)amino)pyridine [NC_5H_4N=C-$(CH_3)C_6H_5$, L_1]. 2-Aminopyridine (4.7 g, 500 mmol) and acetophenone (6.0 g, 500 mmol) were refluxed in toluene (100 mL) over activated molecular sieve (4 Å) with a catalytic amount of concentrated H_2SO_4 for 24 h. The solvent and unreacted starting materials were removed from the reaction mixture by distilling under vacuum. The remaining reddish yellow, oily liquid was doubly distilled at 120 °C/2 mmHg to give 3.0 g of the pure, yellow, oily liquid L_1: HR-MS calcd exact mass for $C_{13}H_{12}N_2$ 196.099, found 196.0974; IR 1637 cm^{-1} (ν(C=N), s); ^{13}C NMR (CDCl$_3$) δ 167.5 (C7), 163.4 (C2), 148.7 (C6), 138.9 (C8), 137.5 (C4), 130.1 (C11), 128.2 (C9), 127.3 (C10), 118.7 (C5), 115 (C3), 18.1 (CH$_3$).[13]

L_1 L_2
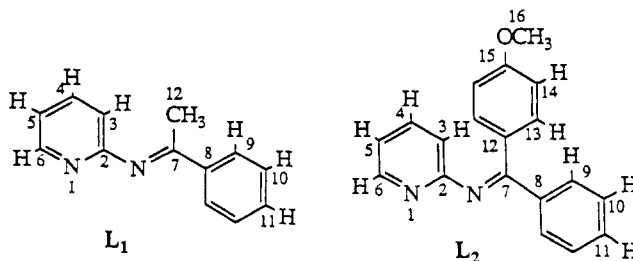
2-[(α'-(4'-Methoxyphenyl)benzylidene)amino]pyridine [NC_5H_4N=C(C_6H_5)(4'-CH$_3$OC$_6H_4$), L_2]. 4-Methoxybenzophenone (2.12 g, 10 mmol) and 2-aminopyridine (0.94 g, 10 mmol) were refluxed in o-xylene (50 mL) over activated molecular sieve (4 Å) with a catalytic amount of p-toluenesulfonic acid for 96 h. The solvent and unreacted starting materials were distilled from the reaction mixture under reduced pressure. Addition of ether (10 mL) to the residual pasty mass precipitated an off-white solid. The solid was filtered quickly and washed with ether (3 × 5 mL) and dried under vacuum; yield 40%; mp 83–84 °C; IR 1620 cm^{-1} (ν(C=N), s); ^{13}C NMR (CDCl$_3$) 169.4 (169.8 C7), 163.7 (163.8, C2), 162.1 (160, C11), 148.5 (148.6, C6), 137.0 (137.2, C4), 136.4 (139.5, C12), 131.5 (131.3, C9), 129.8 (125.6, C8), 129.2 (C13), 128.6 (C15), 127.8 (128.0, C14), 118.2 (sh, C5), 115.6 (115.4, C3), 113.5 (113.2, C10), 55.4 (55.2, OCH$_3$).[13] [Note both stereoisomers were formed in a ratio of 3:1. The chemical shifts for the minor isomer are in parentheses with the assigned carbon. Only the p-methoxyphenyl anti isomer was found in the product complex 2.] Anal. Calcd for $C_{19}H_{16}N_2O$ (MW 288.131): C, 79.13; H, 5.59; N, 9.71. Found (MW 288.13 MS): C, 79.05; H, 5.48; N, 9.78.

cis-[Cl(PPh$_3$)$_2$(L)Rh^I](C_2H_5)$_2$O, L_1 = NC_5H_4N=C(CH$_3$)-C$_6H_5$ (1). A solution of RhCl(PPh$_3$)$_3$ (324 mg, 1.00 mmol) in THF (50 mL) was added dropwise to a stirred solution of L_1 (196 mg, 1.00 mmol) dissolved in THF (5 mL) at 55 °C. After 24 h the solvent was reduced to ca. 15 mL in vacuo, and then hexane (30 mL) added. A yellow solid separated slowly. The solid was filtered, washed with ether (3 × 10 mL), and dried under vacuum overnight. The compound was recrystallized (CH$_2$Cl$_2$/(C$_2$H$_5$)$_2$O) by the vapor diffusion technique to give bright red crystals suitable for elemental analyses and X-ray crystallography; yield 75%; mp 200 °C (dec); IR (KBr) 1631 cm^{-1} (s, C=N). Anal. Calcd for $C_{53}H_{50}N_2ClOP_2Rh$: C, 68.3; H, 5.41; N, 3.00; Cl, 3.81; P, 6.65. Found: C, 67.86; H, 5.17; N, 2.89; Cl, 3.81; P, 6.89.

[Cl(CO)(L$_1$-H)Rh^I]$_2$, L_1-H = NC_5H_4=C(CH$_3$)C$_6H_4$ (3). A solution of L_1 (99 mg, 0.5 mmol) in benzene (3 mL) was added dropwise to a solution of [Cl(CO)$_2$Rh]$_2$ (98 mg, 2.5 mmol) in benzene (7 mL). Addition of the ligand to the complex turned the solution from yellow to red. The mixture was transferred to a 30-mL high-pressure autoclave (Parr Instruments Co. No. A53314) which was heated at 90 °C for 18 h. After cooling the autoclave, the solution was transferred to a flask. Removal of the solvent from the reaction mixture under vacuum yielded a reddish semisolid mass, which on trituration with ether precipitated a yellow solid. The solid was filtered, washed with ether (3 × 10 mL), and dried under vacuum. The compound was

(11) McCleverty, J. A.; Wikinson, G. *Inorg. Synth.* **1966**, *8*, 24. Ryabov, A. D. *Synthesis* **1985**, 223.

(12) Suggs, J. W. *J. Organomet. Chem.* **1986**, *307*, 71.
(13) ^{13}C NMR assignments were made by analogy to the components assignments before imine formation. See: Formacek, V.; Desnoyer, L.; Kellernals, H. P.; Keller, T.; Clerc, J. T. ^{13}C *Data Bank*; Brucker Physik: Karlsruhe, 1976; Vol 1, Spectra 117, 174 and 247.

Table I. Experimental Crystallographic Data

	[Cl(PPh₃)₂(L₁)Rh]·Et₂O (1)	Cl(CO)₂(L₂)Rh (2)	[Cl(CO)(L₁-H)Rh]₂ (3)
formula	$RhClP_2ON_2C_{53}H_{52}$	$RhClO_3N_2C_{21}H_{16}$	$Rh_2Cl_2O_2N_4C_{28}H_{22}$
mol wt	933.32	482.73	733.22
cryst dimens, mm	0.48 × 0.20 × 0.32	0.50 × 0.53 × 0.60	0.20 × 0.12 × 0.12
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
cell dimens[a]			
a, Å	10.9817 (8)	10.845 (6)	8.0708 (16)
b, Å	12.2447 (12)	11.161 (6)	20.907 (6)
c, Å	17.800 (3)	17.161 (9)	16.373 (2)
α, deg	94.221 (10)		
β, deg	101.770 (9)	86.61 (1)	90.078 (14)
γ, deg	92.022 (7)		
V, Å³	2333.8 (4)	2073.58	2762.6 (1)
Z	2	4	4
calcd density, g cm⁻³	1.328	1.55	1.739
2θ range, deg	5–52	$0 \le 2\theta \le 54.86$	6–45
no. indep rflctns	9215	4719	3637
R (averaging equiv data)			.0325
obsd data	7477	3390	1828
octants coll	+h, ±k, ±l	h, k, ±l	+h, +k, ±l
reflecting criterion	$I_o \ge 2.5\sigma(I)$	$I_o \ge 3\sigma(I)$	$I_o \ge 2.5\sigma(I)$
μ, cm⁻¹	5.23	9.42	14.04
trans coeff	0.87–0.80		0.84–0.82
F_{000}	968	968	1432
R, R_w ($w = (\sigma F)^{-2}$), %	4.0, 3.6	3.2, 4.9	5.4, 3.2

recrystallized from $(CHCl_3/(C_2H_5)_2O)$ giving red crystals: yield 45%; mp 150 °C (dec); IR (KBr) 2098 (s) and 2010 (s, νCO), 1610 cm⁻¹ (s, ν(C=N)). Anal. Calcd for $C_{28}H_{22}N_4Cl_2O_2Rh_2$: C, 46.47; H, 3.04; N, 7.74; Cl, 9.82. Found: C, 46.69; H, 3.14; N, 7.79; Cl, 9.92.

cis-[Cl(CO)₂(L₂)Rh¹], L₂ = $NC_5H_4N=C(C_6H_5)(4-CH_3OC_6H_4)$ (2). Compound 2 was synthesized by following the exact procedure of the synthesis of complex 3 above. After workup, the compound was recrystallized $(CHCl_3/(C_2H_5)_2O)$ by the vapor diffusion technique to obtain reddish-yellow crystals: yield 40%; mp 180 °C (dec); IR (KBr) 2085 (s) and 2022 cm⁻¹ (s, ν(CO)). Anal. Calcd for $C_{21}H_{16}N_2ClO_3Rh$: C, 52.23; H, 3.32; N, 4.80; Cl, 7.35. Found: C, 52.52; H, 3.41; N, 5.88; Cl, 7.45.

X-ray Diffraction Studies. Red–orange crystals of compounds 1 and 3 were grown by methods described above. The diffraction data were measured with a Nicolet R3 automated diffractometer equipped with Mo Kα radiation (λ = 0.7107 Å) and a graphite monochromator at ambient temperature. Details of data collection in common were scan method $\theta/2\theta$, scan range 1.0° below Kα_1 to 1.0° above Kα_2, scan rate variable 2–5°/min, and ratio of background/scan time 0.5. Both structures 1 and 3 were solved by Patterson methods and refined in either a full matrix (3) or a blocked matrix (1) with the programs of SHELX-76.[14] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in a combination of observed and calculated positions. Isotropic temperature factors for the hydrogen atoms were tied to a single variable. The 10 hydrogen atoms in the solvent molecule of 1 were not placed. Neutral atom scattering factors and corrections for anomalous dispersion were from *International Tables for X-ray Crystallography*.[15] Absorption corrections were made by empirical methods.[16] No extinction corrections were made. Other details of the crystallographic experiment are given in Table I. Although the R values for structures 1 and 3 reported herein are similar, the quality of the structural determinations is markedly different. This is due mainly to the fact that a small, poorly diffracting sample was used for the [Cl(CO)(L₁–H)Rh]₂ structural analysis, because that was the best sample that could be prepared. This is reflected in the large number of unobserved reflections (50%) collected for 3 (cf. only 19% unobserved data for 1). The result is large esd's for the structural parameters in 3. Care must be taken to acknowledge

Table II. Selected Bond Lengths (angstroms) and Angles (degrees) for [Cl(PPh₃)₂(L)Rh]•Et₂O (1)

Bond Distances			
Rh(1)–P(1)	2.2069 (9)	P(2)–C(19)	1.837 (4)
Rh(1)–P(2)	2.247 (1)	P(2)–C(25)	1.840 (3)
Rh(1)–Cl(1)	2.4009 (9)	P(2)–C(31)	1.852 (4)l
Rh(1)–N(1)	2.113 (3)	N(1)–C(37)	1.356 (5)
P(1)–C(1)	1.840 (4)	N(1)–C(41)	1.346 (4)
P(1)–C(7)	1.844 (3)	N(2)–C(41)	1.392 (5)
P(1)–C(13)	1.848 (3)	N(2)–C(42)	1.270 (4)

Bond Angles			
Rh(1)–P(1)–C(1)	121.7 (1)	P(1)–Rh(1)–P(2)	99.66 (3)
Rh(1)–P(1)–C(7)	114.3 (1)	P(1)–Rh(1)–Cl(1)	170.49 (4)
Rh(1)–P(1)–C(13)	114.3 (1)	P(1)–Rh(1)–N(1)	91.05 (7)
Rh(1)–P(2)–C(19)	114.4 (1)	P(2)–Rh(1)–Cl(1)	85.65 (3)
Rh(1)–P(2)–C(25)	110.1 (1)	P(2)–Rh(1)–N(1)	169.24 (7)
Rh(1)–P(2)–C(31)	123.8 (1)	Cl(1)–Rh(1)–N(1)	83.61 (7)
Rh(1)–N(1)–C(37)	119.9 (2)	C(41)–N(2)–C(42)	122.2 (3)
Rh(1)–N(1)–C(41)	120.9 (2)		

this disparity in quality when comparing the two structures.

A yellow crystal of compound 2 was mounted on a glass fiber with silicone adhesive and utilized for an X-ray structure determination.[17] The diffraction data were measured with a Picker diffractometer automated with a Crystal Logic control system. All data were measured with Mo Kα radiation (λ = 0.7107 Å). Intensity data were collected at a scan rate of 6.0°/min and the intensities of three standard reflections were monitored after every 97 data. The standards remained statistically constant over the course of data collection. Some 40 reflections exceeded the maximum allowable count rate of 50 000 cps and could not be processed. These data were recollected on a different crystal at

(14) Sheldrick, G. M. SHELX-76, University Chemical Laboratory, Cambridge, England, 1976.

(15) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4 (present distributor D. Reidel, Dordrecht).

(16) Sheldrick, G. M. SHELXTL, University of Gottingen, Federal Republic of Germany, 1978.

(17) The program used in this structure determination were supplied by Crystal Logic. The Crystal Logic package includes modified versions of the following programs: REDUCE (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; MULTAN (main), package of programs, including direct methods, structure factor normalization, Fourier transform, and peak search; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix least-squares refinement; ORFFE (Busing, Martin, and Levy), distance, angle, and error calculations; ABSORB (Coppens, Edwards and Hamilton), absorption correction calculation; ORTEP (Johnson), figure plotting; HYDROGEN (Trueblood), calculation of hydrogen atomic positions. All calculations were performed on a DEC MicroVax II computer. Scattering factors and corrections for anomalous dispersion were taken from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV. $R = (\sum|F_o - F_c|/\sum|F_o|)$; $R_w = (\sum w|F_o - F_c|^2/\sum w|F_o|^2)^{1/2}$, where F_o and F_c are observed and calculated structure factors, respectively, and $w = 1/\sigma^2(F_o)$.

Table III. Selected Bond Lengths (angstroms) and Angles (degrees) in Cl(CO)$_2$(L$_2$)Rh (2)

Bond Distances			
Rh–C(21)	1.845 (5)	C(07)–C(08)	1.394 (6)
Rh–C(20)	1.860 (4)	C(08)–C(09)	1.399 (6)
Rh–N(01)	2.120 (3)	C(09)–C(10)	1.354 (8)
Rh–Cl(1)	2.359 (1)	C(10)–C(11)	1.395 (8)
C(01)–N(01)	1.340 (4)	C(11)–C(12)	1.414 (7)
C(01)–C(02)	1.398 (5)	C(13)–C(14)	1.403 (5)
C(01)–N(02)	1.409 (4)	C(13)–C(18)	1.407 (5)
C(02)–C(03)	1.390 (6)	C(14)–C(15)	1.380 (5)
C(03)–C(04)	1.377 (6)	C(15)–C(16)	1.390 (5)
C(04)–C(05)	1.369 (6)	C(16)–C(17)	1.387 (6)
C(05)–N(01)	1.364 (4)	C(16)–O(1)	1.399 (5)
C(06)–N(02)	1.294 (4)	C(17)–C(18)	1.390 (5)
C(06)–C(13)	1.469 (5)	C(19)–O(1)	1.429 (6)
C(06)–C(07)	1.520 (5)	C(20)–O(2)	1.150 (5)
C(07)–C(12)	1.381 (5)	C(21)–O(3)	1.142 (5)

Bond Angles			
C(21)–Rh–C(20)	89.34 (18)	C(10)–C(09)–C(08)	119.19 (49)
C(21)–Rh–N(01)	91.41 (14)	C(09)–C(10)–C(11)	120.65 (44)
C(21)–Rh–Cl(1)	77.28 (14)	C(10)–C(11)–C(12)	120.81 (46)
C(20)–Rh–N(01)	179.01 (14)	C(07)–C(12)–C(11)	118.08 (43)
C(20)–Rh–Cl(1)	90.24 (13)	C(14)–C(13)–C(18)	117.30 (31)
N(01)–Rh–Cl(1)	89.04 (8)	C(15)–C(14)–C(13)	122.23 (31)
N(01)–C(01)–C(02)	121.73 (31)	C(14)–C(15)–C(16)	118.99 (36)
N(01)–C(01)–N(02)	116.31 (29)	C(17)–C(16)–C(15)	120.74 (35)
N(01)–C(01)–C(06)	123.70 (24)	C(17)–C(16)–O(1)	115.71 (33)
C(03)–C(02)–C(01)	119.05 (37)	C(15)–C(16)–O(1)	123.56 (37)
C(04)–C(03)–C(02)	119.11 (37)	C(16)–C(17)–C(18)	119.61 (32)
C(05)–C(04)–C(03)	119.08 (35)	C(17)–C(18)–C(13)	121.07 (33)
N(01)–C(05)–C(04)	122.86 (36)	O(2)–C(20)–Rh	178.49 (35)
N(02)–C(06)–C(13)	119.90 (29)	O(3)–C(21)–Rh	178.41 (40)
C(12)–C(07)–C(08)	120.17 (35)	C(01)–N(01)–C(05)	118.14 (30)
C(12)–C(07)–N(02)	109.91 (28)	C(01)–N(01)–Rh	122.15 (22)
C(08)–C(07)–N(02)	122.19 (30)	C(05)–N(01)–Rh	119.70 (25)
C(07)–C(08)–C(09)	121.05 (43)	C(16)–O(1)–C(19)	118.21 (34)

Figure 1. Metal complex Cl(PPh$_3$)$_2$(L$_1$)Rh^I (1). Ellipsoids represent 50% probability. Phenyl groups are labeled consecutively around the ring.

Table IV. Selected Bond Lengths (angstroms) and Angles (degrees) for [Cl(CO)(L$_1$-H)Rh]$_2$ (3)

Bond Distances			
Rh(1)–Rh(2)	2.639 (2)	N(1)–C(1)	1.35 (2)
Rh(1)–Cl(2)	2.466 (4)	N(1)–C(5)	1.35 (2)
Rh(1)–N(1)	2.26 (1)	C(5)–N(2)	1.40 (2)
Rh(1)–N(4)	2.09 (1)	N(2)–C(6)	1.32 (2)
Rh(1)–C(26)	1.99 (1)	N(3)–C(14)	1.32 (2)
Rh(1)–C(27)	1.82 (2)	N(3)–C(18)	1.37 (2)
Rh(2)–Cl(1)	2.462 (4)	C(18)–N(4)	1.40 (2)
Rh(2)–N(2)	2.05 (1)	N(4)–C(19)	1.28 (2)
Rh(2)–C(13)	2.00 (2)	C(27)–O(1)	1.16 (2)
Rh(2)–N(3)	2.25 (1)	C(28)–O(2)	1.16 (2)
Rh(2)–C(28)	1.83 (1)		

Bond Angles			
Rh(1)–Rh(2)–Cl(1)	163.6 (1)	Rh(2)–Rh(1)–C(27)	94.4 (5)
Rh(1)–Rh(2)–N(2)	77.7 (3)	Rh(2)–N(2)–C(5)	118 (1)
Rh(1)–Rh(2)–C(13)	100.4 (4)	Rh(2)–N(2)–C(6)	119 (1)
Rh(1)–Rh(2)–N(3)	79.9 (3)	Rh(2)–N(3)–C(14)	123.3 (9)
Rh(1)–Rh(2)–C(28)	97.1 (4)	Rh(2)–N(3)–C(18)	117.5 (9)
Rh(1)–N(1)–C(1)	121 (1)	Rh(2)–C(28)–O(2)	178 (1)
Rh(1)–N(1)–C(5)	118 (1)	Cl(1)–Rh(2)–N(2)	90.3 (4)
Rh(1)–N(4)–C(18)	116.5 (9)	Cl(1)–Rh(2)–C(13)	88.0 (5)
Rh(1)–N(4)–C(19)	116.4 (9)	Cl(1)–Rh(2)–N(3)	90.3 (3)
Rh(1)–C(27)–O(1)	176 (1)	C(13)–Rh(2)–N(3)	173.9 (5)
Rh(2)–Rh(1)–Cl(2)	165.5 (1)	C(13)–Rh(2)–C(28)	95.0 (6)
Rh(2)–Rh(1)–N(1)	78.5 (4)	N(3)–Rh(2)–C(28)	91.0 (5)
Cl(1)–Rh(2)–C(28)	96.1 (4)	C(14)–N(3)–C(18)	119 (1)
Cl(2)–Rh(1)–N(1)	89.2 (4)	N(2)–Rh(2)–C(13)	78.8 (6)
Cl(2)–Rh(1)–N(4)	94.8 (3)	N(2)–Rh(2)–N(3)	95.3 (4)
Cl(2)–Rh(1)–C(26)	89.1 (4)	N(2)–Rh(2)–C(28)	171.0 (5)
Cl(2)–Rh(1)–C(27)	94.1 (5)	C(18)–N(4)–C(19)	126 (1)
N(1)–Rh(1)–N(4)	94.5 (5)	N(4)–Rh(1)–C(26)	79.3 (6)
N(1)–Rh(1)–C(26)	173.4 (6)	N(4)–Rh(1)–C(27)	167.9 (6)
N(1)–Rh(1)–C(27)	93.9 (6)	C(26)–Rh(1)–C(27)	92.6 (7)
Rh(2)–Rh(1)–N(4)	78.8 (3)		
Rh(2)–Rh(1)–C(26)	102.2 (4)		

Figure 2. Metal complex Cl(CO)$_2$(L$_2$)Rh^I (2). Ellipsoids represent 50% probability.

techniques[17] were utilized to find all non-hydrogen atoms, which were refined isotropically to produce an R value of 8.2%. Refinement continued, treating each non-hydrogen atom anisotropically and with the inclusion of the 13 ring hydrogen atoms as fixed contributions at their theoretical positions. This final refinement converged with an R value of 3.2% and R_w of 4.9%.[17] Selected bond lengths and angles for 1–3 are in Tables II–IV, respectively.

Results and Discussion

To study the C–C or C–H bond activation of Schiff base type of ligands, we have synthesized and characterized ligands, L, where the benzylidene proton is replaced by R, i.e., L = 2-pyridyl-N=C(C$_6$H$_5$)R, where R = CH$_3$ (L$_1$) and, p-(CH$_3$OC$_6$H$_4$) (L$_2$). The ligand L$_1$ (where R = CH$_3$) was found to react differently with different rhodium(I) complexes, i.e., RhCl(PPh$_3$)$_2$ or [Rh(CO)$_2$Cl]$_2$, under different reaction conditions. Whereas ligand L$_1$ reacted with RhCl(PPh$_3$)$_3$ to give RhCl(L$_1$)(PPh$_3$)$_2$ (1), it gave the dimeric rhodium(II) complex 3 when treated with [Rh(CO)$_2$Cl]$_2$ at 90 °C in benzene in an autoclave. In the complex (OC)$_2$Rh$_2$(L$_1$-H)$_2$Cl$_2$ (3) the phenyl ring of the ligand was ortho-metalated to the rhodium showing an arene C–H bond cleavage. Reactions of L$_2$, where R = p-(CH$_3$O)C$_6$H$_4$ with [Rh(CO)$_2$Cl]$_2$ under idential conditions resulted in the formation of cis-[Cl(CO)$_2$(L$_2$)Rh^I] (2). In this paper we report the syntheses, characterization, and X-ray structures of the complexes mentioned above.

Description of Structures. A. Rh(I) Complexes cis-[Cl(PPh$_3$)$_2$(L$_1$)Rh(I)][O(CH$_2$CH$_3$)$_2$] (1) and cis-[Cl(CO)$_2$L$_2$Rh(I)] (2). Figures 1 and 2 illustrate the molecular geometry and labeling of 1 and 2. Selected bond

reduced power settings and included in the data set. They were given a separate scale factor in refinement. Patterson and Fourier

lengths and angles are presented in Tables II and III.

The ligands are approximately square planar around Rh in both 1 and 2 with the triphenylphosphines in 1 cis as are the two CO's in 2. In-plane distortions of the ideal geometry for 1 are significant, and the adjacent coordination angles follow our expectations on the basis of size disparities; the coordination angles range from 83.61 (7)° for Cl(1)–Rh–N(1) to 99.66 (3)° for P(1)–Rh–P(2). In 2 the smaller CO ligands result in much less distortion with the Cl(1)–Rh–N(1) angle of 89.04 (8)° and 89.34 (18)° for C(20)–Rh–C(21). Concurrent out-of-plane distortions for 1 are also steric in origin with P(1) and Cl(1) somewhat below the best coordination plane (−0.073 (1) and −0.80 (1) Å, respectively) and N(1), P(2), and Rh above it (+0.082 (3), +0.071 (1), and +0.0814 (3) Å, respectively). The axial positions are unoccupied. Out of plane distortions for the coordination sphere in 2 are also much smaller than for 1. The average deviation for the plane defined by C(20), C(21), N(01), and Cl(1) is 0.03 Å.

Mutually trans Rh(I)–P(Ph)$_3$ lengths are normally $\sim$ 2.33 Å in square-planar complexes,[18] and it is known that this distance decreases significantly when the trans ligand is Cl[18a,b,19] due to the decreased π-acidity of Cl. The Rh–P(1) and RhCl(1) lengths reported here for 1 [Rh–P(1) = 2.2069 (9) Å, Rh–Cl(1) = 2.4099 (9) Å] are typical for those trans ligands. The Rh–P(2) length (2.247 (1) Å) is significantly longer than the Rh–P(1) distance, indicating that the ligand L$_1$ is competing more effectively than Cl as a ligand trans to a phosphine. A quite similar situration pertains for 2: the Rh–CO trans to L$_2$ is longer at 1.860 Å than that trans to Cl(1) or 1.845 Å. The Rh–Cl(1) length is 2.359 (2) Å. The Rh–N(01) distance is 2.120 (3) Å in 2 and is quite similar to that in 1 (Rh–N(1) = 2.113 (3) Å). These Rh–ligand bond lengths all follow the trans influence series derived from coupling constants established for Rh(I) phosphine complexes, which has been determined[20] to be, in part, PR$_3$ $\sim$ CO $\sim$ CH$_3^-$ > py > Cl$^-$.

The ligand L$_1$ is bound to the Rh atom through the N atom of the pyridine functional, and the py ring is at right angles to the best coordination plane (dihedral angle of 91.9 (1)°). In 2 this angle is not as large (60.9°), possibly reflecting less steric interaction due to the lack of the large Ph$_3$P ligands or crystal packing, which may tend to flatten the whole structure somewhat relative to 1. The substituent atom N(2) lies significantly out of the py plane (0.169 (3) Å) and is 3.121 Å from the Rh atom in 1. N(2) in 2 deviates by 0.07 Å from the plane of the py ring and is nearly the same distance from Rh (3.14 Å). The pendent phenyl ring of L$_1$ in 1 is planar, and the backbone atoms N(2), C(42), and C(43) are within 0.1 Å of this phenyl plane (displacements of 0.095 (1), 0.051 (4), −0.009 (4) Å, respectively). The dihedral angle between the two L$_1$ ring planes is 105.9 (2)°. This ligand is very similar to the uncoordinated molecule N-(2-pyridyl)benzimidoyl cyanide[21] (code word CAZRIE in the Cambridge Structural Database[22]), the only chemical difference being that a
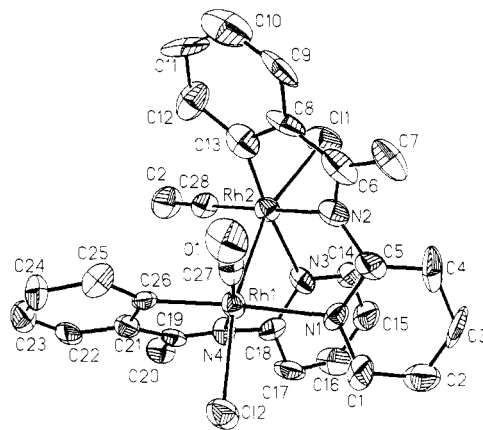
(18) (a) Hitchcock, P. B.; McPartlin, M.; Mason, R. *J. Chem. Soc. D* **1969**, 1367. (b) Bennett, M. J.; Donaldson, P. B. *Inorg. Chem.* **1977**, *16*, 655. (c) DeBoer, J. L.; Rogers, D.; Skapski, A. C.; Troughton, P. G. *Chem. Commun.* **1966**, 756. (d) Pimbett, G.; Garner, C. D.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1985**, 1977.

(19) (a) Jones, R. A.; Real, F. M.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 511. (b) Nappier, Jr., T. E.; Meek, D. W.; Kirchner, R. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 4194. (c) Jones, R. A.; Real, F. M.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 126.

(20) Christoph, G. G.; Blum, P.; Liu, W. C.; Elia, A.; Meek, D. W. *Inorg. Chem.* **1979**, *18*, 894.

(21) Teulade, J. C.; Escale, R.; Viols, H.; Chapat, J. P.; Grassy, G.; Carpy, A.; Legar, J. M. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2663.

Figure 3. Binuclear complex [Cl(CO)(L$_1$-H)Rh^{II}]$_2$ (3). Ellipsoids represent 50% probability.

cyano group is present in place of the methyl group at C(43). The significant structural differences between these two molecules concerns the degree of twist (the dihedral angles between the two molecular rings are 38.2° for CAZRIE and 105.9 (2)° for L$_1$) and the N–C lengths in the pyridine ring (N–C averages 1.351 (7) Å for L$_1$ and 1.317 Å in CAZRIE; this difference is consistent with the pyridine nitrogen being the coordination site). In 2 the trans 4-MeOPh ring is nearly coplanar with the reference mean plane containing C(1), N(2), C(6), C(7), and C(13) with an angle of 9.5°, but the other unsubstituted cis phenyl ring shows an angle of 102.9° relative to the same reference plane. The pyridine ring makes an angle of 106.4° with this reference plane in 2 (compare 105.9° in 1). Thus 1 and 2 are very similar in terms of the orientation relative to the plane of Rh coordination except for the py twist angle. In both cases the imine bond is nearly orthogonal relative to the py ring and the imine N(2) is outside the coordination distance to the Rh but sterically occupies one apical site in both complexes. Significantly (as will by shown below) the latter fact results in the imine and thus the attached groups being rotated about C(41)–N(2) in 1 and C(1)–N(2) in 2 away from the metal and the π C=N orbital being roughly oriented toward the metal.

The orientation of the imine C=N bond away from the metal holds the C–C bond, where metal insertion was desired, away from the metal. While this orientation would not prevent insertion in solution, it would tend to increase the activation energy for such a process. Structures of 8-quinolinecarboxaldehyde complexes which do undergo metal C–H insertion show an orientation with the C–H bond of the aldehyde directed toward the metal.[2] Indeed in such Pt complexes where the precursor to insertion can be examined, the R—C(=N)—hydrogen was shown to be 2.43 Å from the metal.[2] In the quinoline-8-carbonyl derivatives examined, the fixed 8-substituents cannot be rotated away from the metal (as they can in 1 and 2) and many Rh derivatives have been shown to insert into such C–H bonds, but the requirements for C–C bond insertion are more demanding in this series (vide supra).

For C–C bond insertion to succeed, a greater interaction between the C–C bond and the potentially reactive metal center will have to be encouraged. We are currently examining several possibilities to do this.

B. The Rh$^{II}_2$ Complex [Cl(CO)(L$_1$-H)Rh^{II}]$_2$ (3). Figure 3 illustrates the molecular geometry and labeling of 3. The structure consists of independent binuclear

(22) *Cambridge Structural Database*; University Chemistry Laboratory: Cambridge, England, 1987; released through Medical Foundation of Buffalo, Buffalo, New York.

molecules with no substantial intermolecular interactions. All atoms occupy general positions in the unit cell. Selected bond lengths and angles for **3** are given in Table IV.

This binuclear Rh(II) complex contains two six-coordinate Rh atoms linked by chelating ligands and exhibiting a short metal–metal distance indicative of a Rh–Rh single bond. The Rh coordination environment is approximately octahedral, and each Rh site is chemically equivalent, having the same ligands and relative arrangement. The two mononuclear Cl(CO)(L)Rh fragments are nearly related by a noncrystallographic 2-fold axis passing through the midpoint of the Rh–Rh bond but not aligned with a unit-cell vector. Angles between adjacent donor atoms within the coordination spheres are in the ranges 78.5–102.2° for Rh(1) and 78.8–100.4° for Rh(2). The two terminal chlorine atoms are mutually bent out of line with the Rh–Rh vector: the Cl–Rh–Rh angles are 165.5 (1) and 163.6 (1)°, and the Cl–Rh–Rh–Cl torsion angle is –27.1 (6)°.

The Rh–Rh distance in this molecule of 2.639 (2) Å is shorter than that observed for the dimer (μ-2-chloro)(8-quinolinylcarbonyl)tricarbonyldirhodium(II),[23] which contains a 2.671 (1) Å Rh(II–Rh(II) bond unsupported by bridging ligands and with Cl ligands trans to Rh. Other examples of Cl–Rh(II)–Rh(II)–Cl trans fragments contain multiple (>3) bridging ligands between the metal ions[24-26] five-membered chelate rings and shorter Rh–Rh distances (2.398–2.588 Å). Even though there is some variation in Rh–Rh distances in these bridged binuclear species[24-26] the Cl···Rh nonbonding distance (the distance *Cl*–Rh–*Rh*) is remarkably constant at 5.06 (3) Å; i.e., the longer Rh–Rh lengths are, not surprisingly, associated with the shorter Rh–Cl lengths.

When viewed down the Rh–Rh vector, the equatorial ligands are in a staggered orientation with the following torsion angles about the Rh–Rh bond: N(1), N(2) –38.6 (5)°; N(4), N(3) –37.9 (4)°; C(27), C(13) –21.5 (7)°; C(25), C(28) –24.4 (6)°. The Rh atom is slightly displaced from the four-donor-ligand equatorial best plane by 0.059 (1) and 0.042 (1) Å for Rh(1) and Rh(2), respectively, toward the closer terminal Cl atom in both cases. These best equatorial planes are mutually canted with respect to the Rh–Rh vector at 75.4 (7) and 75.2 (7)°. The dihedral angle between the two best equatorial donor planes is 28.8 (5)°. This mutual canting of donor planes shortens the chelate span. Figure 4 is convenient for observing this. The Rh–Cl vectors make angles of 89.3 (3) and 87.2 (3)° with respect to their best equatorial donor planes.

The ligand L₁–H functions as a tridentate chelate in this ortho-metalated product and bridges the two metal centers. The ligand chelates to one of the Rh atoms through an ortho-carbon atom of the phenyl group and the imine nitrogen atom. The third ligating atom of L₁–H is the pyridino nitrogen atom, which donates to a different Rh atom. Both phenyl and pyridine rings are individually planar, and the dihedral angle between the rings can be considered the twist angle of L₁–H and is 48.4 (6) and 43.3 (7)° for the two independent ligands. The backbone atoms that link the phenyl and pyridine rings are roughly planar with the phenyl ring. Each phenyl ring is within 10° of the best equatorial plane of its coordinated Rh atom (dihedral angles are 9.3 (5) and 8.7 (5)° while the pyridine
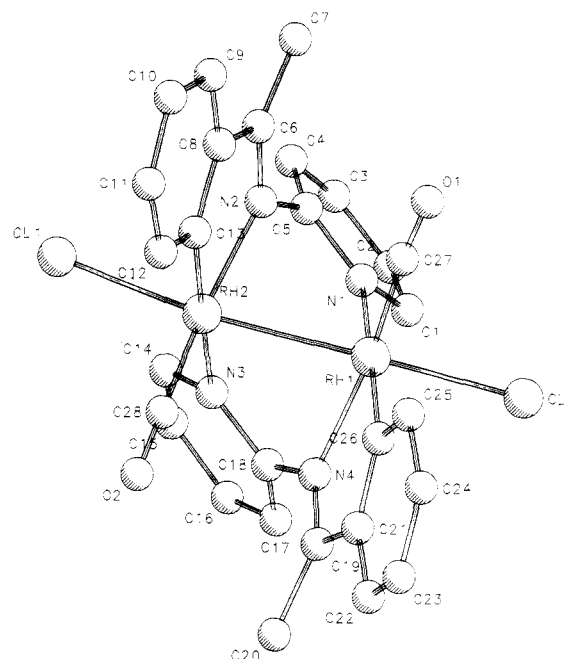
ring forms angles of –60° with the best equatorial plane (dihedral angles are 64.4 (4) and 59.5 (5)°). The bond distances and angles between the two independent L₁–H ligands are essentially equivalent.

The interatomic distances in the ligand L₁ when it functions as a monodentate ligand in Cl(PPh₃)₂(L₁)Rh are equivalent within a few esd's to the bond lengths in [Cl-(CO)(L₁–H)Rh]₂ where L₁–H functions as a tridentate ligand. In an angle comparison, the most notable feature is that the endo ring angles in the rings created by L₁–H chelating to Rh are smaller in [Cl(CO)(L₁–H)Rh]₂ than analogous open angles with L₁ in Cl(PPh₃)₂(L)Rh. Concomitantly, the exo chelate ring angles in L₁–H are larger in [Cl(CO)(L₁–H)Rh]₂ than analogous open angles with L₁ in Cl(PPh₃)₂(L₁)Rh, indicating some strain in the multicoordinated ligand. The low accuracy of the light-atom positions in the structure of [Cl(CO)(L₁)Rh]₂ prevents more careful comparison (vide supra).

In [Cl(CO)(L₁–H)Rh]₂, the Rh–N(pyridino) lengths are 2.25 (1) and 2.26 (1) Å and lie trans to a C(sp²) atom. These Rh–N(pyridino) lengths are long (compare 2.120 and 2.113 Å in **1** (and **2**) and **3**, respectively). In fact, a survey of the Cambridge Structural Database[22] of all compounds containing an aromatic nitrogen atom bound to Rh shows that the only longer Rh–N lengths are those trans to a Rh–Rh bond.[27,28] A compound similar to that reported here, (2-anilinopyridine-*C*,*N*)dichlorobis(pyridine)rhodium(III),[29] contains a Rh–N(pyridine) trans to an sp²-hybridized carbon atom and likewise shows a long Rh–N length (2.244 (7) Å). As a basis for comparison, we have

Figure 4. Perspective view of [Cl(CO)(L₁–H)Rh^{II}]₂ (**3**) sighted down the approximate noncrystallographic 2-fold axis. Atomic spheres are arbitrarily sized.

(23) Suggs, J. W.; Wovkulich, M. J.; Williard, P. G.; Lee, K. S. *J. Organomet. Chem.* **1986**, *307*, 71.

(24) Miskowski, V. M.; Schaefer, W. P.; Sadeghi, B.; Santarsiero, B. D.; Gray, H. B. *Inorg. Chem.* **1984**, *23*, 1154.

(25) Tortorelli, L. J.; Tucker, C. A.; Woods, C.; Bordner, J. *Inorg. Chem.* **1986**, *25*, 3534.

(26) Kochetkova, A. P.; Sveshinkova, L. B.; Stepanovich, V. M.; Sokol, V. I. *Koord. Khim.* **1982**, *8*, 529.

(27) With the exception of the compound bis(μ-2-(bis(diphenylphosphino)methyl)pyridine-*N*,*P*,*P*′)rhodiumgold tetrafluoroborate nitrate-acetone (McNair, R. J.; Nilsson, P. B.; Pignolet, L. J. *Inorg. Chem.* **1985**, *24*, 1935), where a pyridino nitrogen is trans to a phosphino group and a Rh–N length of 2.26 (2) Å is reported, this length seems anomalously long since three other chemically equivalent distances in this structure were 2.18 (2), 2.14 (2) and 2.10 (2) Å. Therefore, the reported Rh–N distance of 2.26 (2) Å must be regarded with some skepticism.

(28) There were 224 literature examples of Rh–N(aromatic) length determinations with values ranging from 1.924 to 2.413 Å. The mean value was 2.09 (8) Å.

(29) Chakravarty, A. R.; Cotton, F. A.; Topucher, D. A. *Organometallics* **1985**, *4*, 863.

Scheme II
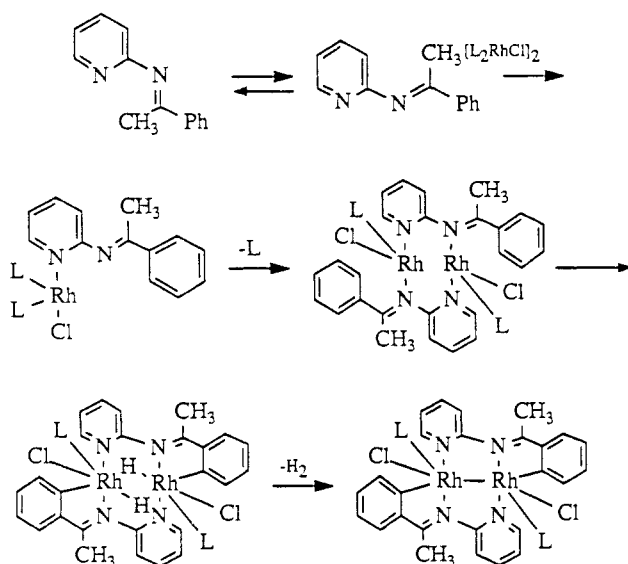
also made a survey[22] of Rh–N(aromatic) lengths where the trans group is also N(aromatic) and found the following averages: Rh(I)–N = 2.03 (1) Å, Rh(II)–N = 2.05 (2) Å, and Rh(III)–N = 2.05 (2) Å. Obviously, the structure of 3 has Rh–N(pyridino) lengths much longer than expected if the trans ligand were another N(aromatic) ligand and the phenyl carbon atom is exerting a significant trans-lengthening.

At 2.05 (1) and 2.09 (1) Å the Rh–N (imino) bonds in $[Cl(CO)(L_1-H)Rh]_2$ (3) are not much longer than what would be expected for a mutually trans Rh–N(aromatic) even though it is trans to a coordinated CO group. There are other examples of Rh–N(sp²) trans to CO in good agreement with the structural parameters presented here: $Rh(Cl)(CO)((\beta\text{-hydroxyquinolinyl})styryl)^{23}$ contains Rh-(I)–N(aromatic) = 2.087 Å trans to Rh–CO =1.887 Å and C–O = 1.133 Å. The same reference[23] also reports $[(CO)_2Rh^I(\mu\text{-}Cl)_2Rh^{II}(CO)quinolinylcarbonyl)]_2$, which

contains Rh(II)–N(pyridino) = 2.079 Å trans to Rh–CO = 1.837 Å and C–O = 1.110 Å. This cumulated evidence implies that although CO is an effective kinetic trans-labilizing group, this ability is not expressed in the ground state. The structural CO trans effect is not nearly as large in Rh–py complexes as that of a σ-phenyl group or a phosphine; that of CO is only marginally more effective than a pyridino group.

The Rh^{II}_2 dimeric complex 3 could arise by a number of detailed pathways, one of which is shown in Scheme II.[30] The essentials of the process are the cyclometalation step, for which there is adequate literature precedent,[1] and the dehydrogenation step, which has also been observed elsewhere.[23] The order of the steps and the apparent effect of temperature (rather than structure) in bringing them about are subjects for further study.

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(30) We are indebted to R. B. King for suggesting this mechanism.