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Ortho Metalation of *m*-$(Me_2NCH_2)_2C_6H_4$: Crystal Structure and Chemistry of *trans*-$Rh^{III}Cl_2[C_6H_3(CH_2NMe_2)_2$-*o*,*o'*$](H_2O)$

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From the reaction of *m*-$(Me_2NCH_2)_2C_6H_4$ with aqueous rhodium trichloride in ethanol the ortho-metalated product *trans*-$Rh^{III}Cl_2$(N-C-N)(H_2O) could be isolated in 45% yield (N–C–N = $C_6H_3(CH_2NMe_2)_2$-*o*,*o'*). Its solid-state structure was determined by an X-ray diffraction study. Crystals are monoclinic, space group $P2_1/n$, with lattice parameters a = 9.070 (1) Å, b = 17.277 (3) Å, c = 9.855 (1) Å, β = 91.34 (1)°, V = 1543.9 (4) Å^3, Z = 4, and D(calcd) = 1.648 g cm^{-3}. Refinement with 3710 observed reflections converged at R = 0.042. The structure of *trans*-$Rh^{III}Cl_2$(N-C-N)(H_2O) consists of a rhodium(III) center that is octahedrally coordinated. A *mer* arrangement of the C and two N atoms of the monoanionic N-C-N ligand (Rh–C(aryl) = 1.913 (3) Å) and a coordinated water molecule trans to C(aryl) form a planar arrangement. The two mutually trans Cl atoms sited above and below this plane complete the coordination sphere. In the solid state the molecules form infinite chains via intermolecular O–H···Cl hydrogen bonds. Metathesis of this new compound with either a large excess of alkali-metal salt or a slight excess of silver salt led to the formation of a range of new arylrhodium(III) compounds, *trans*-RhX_2(N-C-N)(H_2O) (X = Br, O_2CH, O_2CMe, NO_3, and CN). Halogen-bridged bi- and trinuclear complexes RhCl(N-C-N)$(\mu$-Cl$)_2$M(COD) (M = Rh^I, Ir^I; COD = 1,5-cyclooctadiene) and $[RhCl(N\text{-}C\text{-}N)(\mu\text{-}Cl)_2]_2M$ (M = Pd^{II}, Cu^{II}) were synthesized by mixing *trans*-$RhCl_2$(N-C-N)(H_2O) with the appropriate metal salt: $[MCl(COD)]_2$, $CuCl_2$, and $PdCl_2(COD)$ or Li_2PdCl_4, respectively. The same reaction with Li(acac) as the metal salt led to the formation of RhCl(acac)(N-C-N).

Introduction

Much work has been done in our laboratory to develop a rich organometallic chemistry based on the monoanionic ligand *o*,*o'*-$(Me_2NCH_2)_2C_6H_3$ (N-C-N). Due to its rigid geometry and potential for terdentate bonding it has been possible to synthesize many compounds incorporating both transition and main-group metals. Some platinum complexes have served as model systems for a detailed study of oxidative-addition/reductive-elimination processes.[1-4] Oxidation of MX(N-C-N) (M = Ni^{II} or Pt^{II}) by halogens or copper(II) salts to compounds with higher metal valencies (M = Ni^{III} or Pt^{IV}) succeeds without cleavage of the metal–carbon (N-C-N) bond. The first true organonickel(III) compounds were synthesized in such reactions.[1] Starting from $Pt^{II}X$(N-C-N) the reaction with chlorine and bromine afforded $Pt^{IV}X_3$(N-C-N).[2] The reaction with iodine, however, stopped at the stage of the unique coordination complex $Pt^{II}I$(N-C-N)$(\eta^1$-$I_2)$,[4] which contains an end-on-coordinated iodine molecule with a linear Pt–I–I arrangement.

Recently we reported the syntheses and characterization of N-C-N complexes of representatives of the neighboring cobalt triad, i.e. square-pyramidal $Co^{II}X$(N-C-N)(L) (X = halogen, L = pyridine or phosphine).[5] The electronic configuration of these paramagnetic compounds is similar to that of the isoelectronic nickel(III) analogues. However, the extreme air sensitivity of $Co^{II}X$(N-C-N)(L) species has limited the ready exploration of their chemistry. In view of this we felt it necessary to extend our research to the heavier homologues of the cobalt triad: rhodium and iridium. In the first paper on this subject we now present initial results on the development of rhodium(III) N-C-N chemistry.[6]

Experimental Section

General Considerations. $RhCl_3(\gamma$-pic$)_3$[7] (γ-pic = γ-picoline), $[RhCl(COD)]_2$[8a] (COD = 1,5-cyclooctadiene), $[IrCl(COD)]_2$,[8b] and $[RhCl(COT)_2]_2$[8c] (COT = cyclooctene) were synthesized by literature procedures. ^{1}H and ^{13}C NMR spectra were recorded on Varian T60 and XL100 and Bruker AC100 and WM250 spectrometers. The IR spectra were measured on a Perkin-Elmer 283 instrument. FD mass spectra were measured on a Varian MAT711 spectrometer; in the case of isotope patterns the value given is for the most intense peak. Elemental analyses were carried out at the Analytical Department of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands.

Reaction of Li_2(N-C-N)$_2$ with $RhCl_3$. Li_2(N-C-N)$_2$ was prepared from (N-C-N)Br (1.33 g, 4.9 mmol) and metallic lithium shavings (0.4 g, excess) in diethyl ether under an atmosphere of dry nitrogen.[9] The ether was removed in vacuo, and Li_2(N-C-N)$_2$ was extracted with benzene (10 mL) in order to separate it from lithium bromide formed in the synthesis. The benzene extract was added at room temperature to a suspension of anhydrous $RhCl_3$ (0.93 g, 4.3 mmol) in benzene (15 mL). After 2 h no reaction was apparent and the mixture was refluxed for $^1/_2$ h. Filtration and subsequent evaporation of solvent yielded a pale orange oil, identified by ^{1}H NMR as pure (N-C-N)$_2$ (yield 1.0 g, 100%) (see Table IV and ref 20).

Reaction of Li_2(N-C-N)$_2$ with $RhCl_3(\gamma$-pic$)_3$. The procedure followed was as for anhydrous $RhCl_3$ above. Unreacted Li_2(N-C-N)$_2$ was observed by ^{1}H NMR after 1-h reflux in benzene.

Attempted Reaction of Rhodium(I) Compounds with (N-C-N)Br or (N-C-N)H: General Procedure. Equimolar amounts of a rhodium(I) complex (vide infra) and either (N-C-N)Br or (N-C-N)H were stirred for several hours at room temperature. No reaction took place, and the reaction mixture was subsequently refluxed for a few hours, but only unchanged starting compounds were identified. Attempts included the following: $[RhCl(CO)_2]_2$ with (N-C-N)H in benzene; $RhCl(PPh_3)_2(CO)$ with (N-C-N)Br in benzene; $[RhCl(COD)]_2$ with (N-C-N)Br in hexane or ethanol and with (N-C-N)H in acetone or ethanol; $[RhCl(cyclooctene)_2]_2$ with (N-C-N)Br in benzene or ethanol.

Synthesis of *trans*-$RhCl_2$(N-C-N)(H_2O). A mixture of $RhCl_3 \cdot 3H_2O$ (1.93 g, 7.3 mmol) and (N-C-N)H (2.12 g, 11.0 mmol) in ethanol (40 mL) was heated under reflux for 45 min. After the mixture was cooled to 0 °C, the resultant brown precipitate was isolated by filtration and washed with cold ethanol (3 × 3 mL) and diethyl ether (3 × 3 mL). This dry solid was extracted with acetone (3 × 20 mL), leaving behind a gray solid residue. The orange acetone extract was evaporated in vacuo, and the resultant solid was washed once with pentane (30 mL). This yielded 1.2 g (45%) of the golden yellow product *trans*-$RhCl_2$(N-C-N)(H_2O).

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Anal. Calcd for $C_{12}H_{21}Cl_2N_2ORh$: C, 37.6; H, 5.5; N, 7.3; Cl, 18.5. Found: C, 38.3; H, 5.6; N, 7.1; Cl, 17.9. Calcd mol wt for *trans*-$RhCl_2$(N-C-N)(H_2O): 383.11. FD mass found: $m/e = 366$ (M – H_2O). Orange crystals of *trans*-$RhCl_2$(N-C-N)(H_2O) suitable for a single-crystal X-ray diffraction study were grown by slow evaporation of a saturated acetone solution.

Synthesis of *trans*-$RhBr_2$(N-C-N)(H_2O). Solid *trans*-$RhCl_2$(N-C-N)(H_2O) (104 mg, 0.27 mmol) was treated with a solution of NaBr (20 equiv) in water (5 mL) for 5 h. The *trans*-RhX_2(N-C-N)(H_2O) was separated from the reaction mixture by extraction with CH_2Cl_2 (10 mL) and the extract evaporated to dryness. The residue was treated with a solution of NaBr (30 equiv) in water (5 mL) for 15 h and the resulting reaction mixture extracted with CH_2Cl_2 (10 mL). The red CH_2Cl_2 extract was dried over Mg_2SO_4, filtered, and evaporated to dryness and the residue washed with pentane (2 × 10 mL) to afford a brick red solid: *trans*-$RhBr_2$(N-C-N)(H_2O) (yield 104 mg, 80%). Anal. Calcd for $C_{12}H_{21}Br_2N_2ORh$: C, 30.5; H, 4.5; Br, 33.9; N, 5.9; O, 3.4. Found: C, 30.5; H, 4.5; Br, 32.8; N, 5.7; O, 3.5. Calcd mol wt for *trans*-$RhBr_2$(N-C-N)(H_2O): 472.03. FD mass found: $m/e = 454$ (75%, M – H_2O), 373/375 (100%, M – H_2O – Br), 294 (100%, M – H_2O – 2 Br).

Synthesis of *trans*-$Rh(O_2CH)_2$(N-C-N)(H_2O). A solution of *trans*-$RhCl_2$(N-C-N)(H_2O) (132 mg, 0.35 mmol) in CH_2Cl_2 was treated with a 30-fold excess of NaO_2CH for 24 h. The solution was filtered and again treated with excess NaO_2CH for 24 h. The solution was filtered, dried over Mg_2SO_4, and refiltered and the filtrate evaporated to dryness. Pale yellow *trans*-$Rh(O_2CH)_2$(N-C-N)(H_2O) was obtained in 80% yield. Anal. Calcd for $C_{14}H_{23}N_2O_5Rh$: C, 41.8; H, 5.8; N, 7.0; O, 19.9. Found: C, 41.6; H, 5.7; N, 6.9; O, 18.9.

Synthesis of *trans*-$Rh(O_2CMe)_2$(N-C-N)(H_2O). A solution of *trans*-$RhCl_2$(N-C-N)(H_2O) (54 mg, 0.14 mmol) and KO_2CMe (15 equiv) in methanol was stirred for 3 h. The solvent was removed in vacuo and the residue extracted with acetone (7 mL). This yellow solution was evaporated to dryness and washed with diethyl ether and pentane, yielding light yellow *trans*-$Rh(O_2CMe)_2$(N-C-N)(H_2O) (yield 34 mg, 55%). Calcd mol wt for $Rh(O_2CMe)_2$(N-C-N)(H_2O): 430.31. FD mass found: $m/e = 412$ (M – H_2O).

Reaction of *trans*-$RhCl_2$(N-C-N)(H_2O) with NaOH. To a solution of *trans*-$RhCl_2$(N-C-N)(H_2O) (30 mg, 0.08 mmol) in wet methanol (1 mL) was added excess NaOH. Stirring for 10 min resulted in decolorization of the solution and deposition of a black substance. Filtration and evaporation of the reaction mixture yielded an oil that was identified by ^1H NMR as nearly pure (N-C-N)H (see Table IV).

Synthesis of *trans*-$Rh(NO_3)_2$(N-C-N)(H_2O). To a solution of *trans*-$RhCl_2$(N-C-N)(H_2O) (102 mg, 0.27 mmol) in acetone (10 mL) was added $AgNO_3$ (115 mg, 0.68 mmol) and the resulting mixture stirred for 18 h. The solvent was removed in vacuo and the residue extracted with CH_2Cl_2 (10 mL). The extract was filtered several times through Celite to remove silver salts and subsequently evaporated to dryness. The residue was washed with pentane (5 mL), affording yellow *trans*-$Rh(NO_3)_2$(N-C-N)(H_2O) (yield 75 mg, 65%). Anal. Calcd for $C_{12}H_{21}N_4O_7Rh$: C, 33.0; H, 4.8; N, 12.8; O, 22.0. Found: C, 33.9; H, 4.7; N, 11.1; O, 23.2. IR (KBr): $\nu(NO_3)$ 966, 986, 1284, 1502 cm^{-1}.

Synthesis of *trans*-$Rh(CN)_2$(N-C-N)(H_2O). To a solution of *trans*-$RhCl_2$(N-C-N)(H_2O) (105 mg, 0.27 mmol) in benzene (10 mL) was added AgCN (80 mg, 0.60 mmol). The reaction mixture was stirred for 18 h and filtered. The filtrate was dried in vacuo, yielding a yellow brown residue, which was then washed with pentane to afford yellow *trans*-$Rh(CN)_2$(N-C-N)(H_2O) (yield 40 mg, 40%). IR (KBr): ν(CN) 2140 cm^{-1}. Calcd mol wt: 364.25. FD mass found: $m/e = 364$ (M).

Synthesis of RhCl(acac)(N-C-N) (acac = Acetylacetonate). To a solution of *trans*-$RhCl_2$(N-C-N)(H_2O) (250 mg, 0.65 mmol) in benzene (25 mL) was added an excess of solid Li(acac) (277 mg, 2.4 mmol). After it was stirred for 1 h, the reaction mixture was filtered. The filtrate was evaporated to dryness and the yellow residue washed with pentane; yield 225 mg (80%). Anal. Calcd for $C_{17}H_{26}ClN_2O_2Rh$: C, 47.6; H, 6.1; N, 6.5; O, 7.5. Found: C, 47.0; H, 6.0; N, 6.3; O, 7.2. Calcd mol wt for RhCl(acac)(N-C-N): 428.77. FD mass found: $m/e = 428$ (M).

Synthesis of RhCl(N-C-N)(μ-Cl)$_2$Rh(COD). A solution of $[RhCl(COD)]_2$ (32.5 mg, 0.066 mmol) in toluene (2 mL) was added to a solution of *trans*-$RhCl_2$(N-C-N)(H_2O) (48 mg, 0.125 mmol) in toluene (6 mL). The yellow solid that separated within a few minutes was filtered off and washed with toluene (2 × 5 mL) and pentane (2 × 5 mL) and then dried in vacuo; yield 39 mg (50%). Anal. Calcd for $C_{20}H_{31}N_2Cl_3Rh_2$: C, 34.3; H, 4.5; N, 4.0; Cl, 15.2. Found: C, 34.3; H, 4.5; N, 3.9; Cl, 15.0. Calcd mol wt for Rh_2Cl_3(N-C-N)(COD): 611.65. FD mass found: $m/e = 610$ (M).

Synthesis of RhCl(N-C-N)(μ-Cl)$_2$Ir(COD). This yellow product was obtained in 75% yield as described above. Anal. Calcd for $C_{20}H_{31}N_2Cl_3RhIr$: C, 39.3; H, 5.1; N, 4.6; Cl, 17.4. Found: C, 39.2; H, 5.4; N, 4.8; Cl, 17.8. Calcd mol wt for $RhIrCl_3$(N-C-N)(COD): 700.97. FD mass found: $m/e = 700$ (M).

Table I. Crystal Data and Details of the Structure Determination

a. Crystal Data

formula	$C_{12}H_{21}Cl_2N_2ORh$	D(calcd), g cm^{-3}	1.648
mol wt	383.12		
space group	$P2_1/n$	$F(000)$, e	776
cryst syst	monoclinic	μ(Mo Kα), cm^{-1}	13.1
a, Å	9.070 (1)		
b, Å	17.277 (3)	min and max abs cor	0.626, 1.333
c, Å	9.855 (1)		
β, deg	91.34 (1)	approx cryst size, mm	0.33 × 0.48 × 0.63
V, Å^3	1543.9 (4)		
Z	4		

b. Data Collection

radiation	Mo Kα (Zr filtered), 0.71073 Å
T, K	295
θ_{max}, deg	30
data set	$-12 \leq h \leq 12, 0 \leq k \leq 24, 0 \leq l \leq 13$
$\omega/2\theta$ scan, deg	$\Delta\omega = 0.70 + 0.35 \tan \theta$
horiz and vert aperture, mm	3.0, 4.0
max time/rfln, s	60
ref rflns	444 ($\sigma = 0.7\%$), $\bar{3}54$ ($\sigma = 0.5\%$)
total no. of rfln data	4845
total no. of unique rflns	4169
no. of obsd data ($I > 2.5\sigma(I)$)	3710
X-ray exposure, h	90

c. Refinement

no. of params	228
weighting scheme	$w^{-1} = \sigma^2(F)$
final R values	$R_F = 0.042$, $R_{wF} = 0.065$
S	1.16
$(\Delta/\sigma)_{max}$	0.839, x [H(1)]
$(\Delta/\sigma)_{av}$	0.1
min and max residual density, e Å^{-3}	−1.42, 1.14

Synthesis of [RhCl(N-C-N)(μ-Cl)$_2$]$_2$Pd. A solution of *trans*-$RhCl_2$(N-C-N)(H_2O) (63 mg, 0.164 mmol) in benzene (10 mL) was treated with $PdCl_2$(COD) (23.5 mg, 0.082 mmol; Li_2PdCl_4 may also be used). The reaction mixture was refluxed for a few minutes, and the warm red solution was filtered. This solution was concentrated to 3 mL, and diethyl ether was added (10 mL). The rust-colored solid that separated was filtered off, washed with diethyl ether, and dried in vacuo; yield 53.5 mg (70%). Anal. Calcd for $C_{24}H_{38}N_4Cl_6PdRh_2$: C, 31.8; H, 4.2; N, 6.2; Cl, 23.4. Found: C, 32.1; H, 4.3; N, 5.9; Cl, 22.3.

Synthesis of [RhCl(N-C-N)(μ-Cl)$_2$]$_2$Cu. Under an atmosphere of dry nitrogen a solution of *trans*-$RhCl_2$(N-C-N)(H_2O) (36 mg, 0.094 mmol) in CH_2Cl_2 (10 mL) was treated with anhydrous $CuCl_2$ (140 mg, excess). The dark green solution that was instantly formed was filtered and evaporated to dryness. The green residue was washed once with pentane (10 mL) and dried in vacuo; yield 41 mg (100%). The complex is moisture sensitive and should be stored under nitrogen. Anal. Calcd for $C_{24}H_{38}N_4Cl_6CuRh_2$: C, 33.3; H, 4.4; N, 6.5; Cl, 24.6. Found: C, 33.3; H, 4.5; N, 6.3; Cl, 25.9.

Structure Determination and Refinement of *trans*-$RhCl_2$(N-C-N)(H_2O). An orange-brown transparent crystal of the title compound was mounted on a glass fiber and a data set collected on an Enraf-Nonius CAD4F diffractometer. Crystal data and numerical details of data collection and refinement are given in Table I. The scan speed was selected to obtain $\sigma(I)/I < 1\%$. The intensities of two standard reflections, measured every 1 h of the X-ray exposure time, showed no significant decay effects. The space group, $P2_1/n$, was determined from observed systematic absences [$0k0$ ($k = 2n + 1$); $h0l$ ($h + l = 2n + 1$)]. Cell dimensions were determined from the setting angles of 14 reflections ($13 < \theta < 18°$) as described by de Boer and Duisenberg.[10] Data were corrected for Lorentz and polarization effects and standard deviations calculated by following ref 11: $\sigma^2(I) = \sigma_{cs}^2(I) + (0.005I)^2$. Coordinates for rhodium were deduced from a Patterson synthesis. The positions of the remaining non-hydrogen atoms were derived from subsequent difference Fourier maps. Full-matrix least-squares refinement (on F) with isotropic thermal parameters converged to $R = 0.114$. At this stage the data were corrected for absorption by using the empirical model described by Walker and Stuart.[12] Anisotropic thermal parameters were intro-

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Table II. Positional and Equivalent Isotropic Thermal Parameters of *trans*-$RhCl_2[C_6H_3(CH_2NMe_2)_2$-*o,o'*$](H_2O)$

atom	*x*	*y*	*z*	*U*(eq),[a] Å^2
Rh	0.24063 (2)	0.11829 (1)	0.05056 (2)	0.0247 (1)
Cl(1)	0.4986 (1)	0.11877 (5)	0.0301 (1)	0.0467 (3)
Cl(2)	−0.0167 (1)	0.11256 (5)	0.0740 (1)	0.0422 (3)
O	0.2522 (3)	−0.0113 (1)	0.0865 (3)	0.0383 (6)
N(1)	0.2242 (3)	0.1219 (1)	−0.1684 (3)	0.0333 (6)
N(2)	0.2529 (3)	0.1509 (2)	0.2613 (3)	0.0367 (6)
C(1)	0.2357 (3)	0.2282 (2)	0.0273 (3)	0.0291 (6)
C(2)	0.2620 (3)	0.2583 (2)	−0.0998 (3)	0.0346 (6)
C(3)	0.2629 (4)	0.3379 (2)	−0.1147 (4)	0.043 (1)
C(4)	0.2400 (5)	0.3846 (2)	−0.0029 (6)	0.051 (1)
C(5)	0.2137 (4)	0.3536 (2)	0.1247 (4)	0.045 (1)
C(6)	0.2105 (3)	0.2737 (2)	0.1398 (3)	0.0335 (8)
C(7)	0.2938 (5)	0.1989 (2)	−0.2061 (4)	0.044 (1)
C(8)	0.1773 (5)	0.2290 (2)	0.2666 (4)	0.045 (1)
C(9)	0.0716 (5)	0.1213 (3)	−0.2243 (4)	0.048 (1)
C(10)	0.3055 (6)	0.0574 (2)	−0.2348 (4)	0.050 (1)
C(11)	0.4068 (5)	0.1609 (3)	0.3156 (5)	0.060 (2)
C(12)	0.1746 (6)	0.0960 (3)	0.3520 (4)	0.057 (1)
H(1)	0.198 (5)	−0.038 (3)	0.054 (5)	0.056 (3)
H(2)	0.313 (5)	−0.032 (3)	0.058 (5)	0.056 (3)

[a] $U(\mathrm{eq}) = {}^1/_3\sum_{ij}U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$.

duced. After further refinement all hydrogen atoms could be located in a difference map. The full-matrix refinement converged to $R = 0.0427$ after introducing weights and an empirical extinction correction, which corrects F_c by following $F_c{}^* = F_c(1 - 0.0001XF_c{}^2/\sin\theta)$, $X = 0.0068$ (1). The positions of the hydrogen atoms were refined with one common isotropic temperature factor. Table II lists the final positional parameters. The scattering factors were taken from ref 13 and the anomalous dispersion corrections from ref 14. The final difference map only shows some artifacts near the heavy atoms, ascribed to residual absorption effects. The calculations were carried out on the CDC Cyber 175 computer of the University of Utrecht using the SHELX-76[15] and the EUCLID packages.[16]

Results and Discussion

Synthesis of a Rhodium(III) N-C-N Complex. The transfer of an organo group from an organolithium or -magnesium compound to a transition or main group metal salt is a common synthetic route for the preparation of new metal-carbon bonds. The procedure has been used in our laboratory to prepare a variety of metal N-C-N compounds (see eq 1). This route is unsuccessful

$$^{1}/_{2}\mathrm{Li_2(N\text{-}C\text{-}N)_2} + \mathrm{MX}_m\mathrm{L}_n \rightarrow \mathrm{M(N\text{-}C\text{-}N)X}_{m-1}\mathrm{L}_{n-p} + \mathrm{LiX} + p\mathrm{L} \quad (1)$$

$$\mathrm{MX}_m\mathrm{L}_n = \mathrm{FeCl_3},^{17}\ \mathrm{CoX_2L_2},^{5}\ \mathrm{PdCl_2(NCPh)_2},^{9}\ \mathrm{PtBr_2(SEt_2)_2},^{9}\ \mathrm{HgCl_2},^{18}\ \mathrm{TlCl_3},^{18}\ \text{and}\ \mathrm{SnBr_2R_2}^{19}$$

for the preparation of rhodium(III) N-C-N compounds. Reaction of $Li_2(N\text{-}C\text{-}N)_2$ in benzene with anhydrous $RhCl_3$ led to the quantitative formation of the C–C coupling product $(N\text{-}C\text{-}N)_2$ instead of the expected $Rh^{III}Cl_2(N\text{-}C\text{-}N)$ complex. The structure of the biphenyl compound $(N\text{-}C\text{-}N)_2$ was deduced from its ^1H and ^{13}C NMR spectra as well as from a preliminary X-ray structure analysis of its hydrochloride salt, $(N\text{-}C\text{-}N)_2(HCl)_4$.[20] Not only anhydrous $RhCl_3$, but also $TaCl_5$ and VCl_3 react with $Li_2(N\text{-}C\text{-}N)_2$ to afford quantitatively the biaryl compound (N-C-N).[20] The selectivity of these C–C couplings, leading to $(N\text{-}C\text{-}N)_2$, is most likely a result of a direct electron transfer of the organolithium aggregate to $RhCl_3$, followed by an intramolecular C–C coupling within the activated organolithium aggregate.[21] This mechanism is made plausible by NMR measurements on $Li_2(N\text{-}C\text{-}N)_2$[22a] as well as by a recent X-ray structure determination of a related compound, $Li_2[C_6H(CH_2NMe_2)_4$-*o,o',m,m'-C,N,N'*$]_2$,[22b] which show that these organolithium compounds have a dimeric structure in which both three-center/two-electron-bonded ipso carbon atoms are already close to one another. An alternative mechanism, involving the formation of $[RhCl_2(N\text{-}C\text{-}N)]_n$, is less likely, since cleavage of a Rh^{III}–C bond in this situation would be expected to produce not only $(N\text{-}C\text{-}N)_2$ but also (N-C-N)H and (N-C-N)Cl. In another attempt we reacted $Li_2(N\text{-}C\text{-}N)_2$ with monomeric $RhCl_3(\gamma\text{-pic})_3$ in benzene. The failure to react probably stems from the hard donor character of γ-picoline, stabilizing the rhodium(III) center to such an extent that even electron transfer from the lithium reagent is unfavorable.

Other approaches for the synthesis of d^6 transition-metal compounds with an M–C bond are the oxidative addition of an organic reagent RX to an appropriate d^8 species and the cyclometalation reaction involving rhodium(III).[23,24] The former approach was followed in the synthesis of NiBr(N-C-N)[25] (see eq 2). In the present case this synthetic approach would imply

$$\mathrm{(N\text{-}C\text{-}N)Br} + \mathrm{Ni^0(COD)_2} \rightarrow \underset{70\%}{\mathrm{Ni^{II}Br(N\text{-}C\text{-}N)}} + \underset{\text{traces}}{\mathrm{Ni^{III}Br_2(N\text{-}C\text{-}N)}} \quad (2)$$

the use of a rhodium(I) complex that would produce a Rh^{III}-(N-C-N) compound on reaction with either (N-C-N)Br or (N-C-N)H. However, although numerous reactions of this type were attempted (see Experimental Section for details), no evidence for Rh(III) N-C-N compounds was ever found and starting compounds were recovered. For the dimeric rhodium(I) complexes $[RhClL_2]_2$, where L is CO or cyclooctene and L_2 is 1,5-cyclooctadiene, there was even no sign of a chloride bridge splitting through N-coordination of either (N-C-N)Br or (N-C-N)H. This bridge splitting can be accomplished with a variety of ligands,[26] and in the case of azobenzene, for example, this leads to metalation of the coordinated ligand.[27] Shaw et al.[24c] reacted a related diphosphorus ligand, 1,5-bis(di-*tert*-butylphosphino)-2-methylpentane, (P-C-P')H, with $[M^ICl(COT)_2]_2$, to give the metalated product $M^{III}H(Cl)(P\text{-}C\text{-}P')$, where M = Rh or Ir. It appears that initial coordination of heteroatoms, within the organic molecule, to the metal is a prerequisite for metalation.

In light of previous metalation studies using rhodium(III) complexes and ligands with either one[23] or two[24] chelating heteroatoms, the system $RhCl_3{\cdot}3H_2O$/(N-C-N)H has been thoroughly studied. Addition of (N-C-N)H to $RhCl_3{\cdot}3H_2O$ in ethanol at room temperature resulted in the instantaneous formation of an insoluble red solid, which gave an approximate analysis as $RhCl_{2.9}(N\text{-}C\text{-}N)_{0.8}(H_2O)_{2.5}$. The Cl/Rh and N-C-N/Rh ratios indicate that this solid is a mixture of compounds most probably

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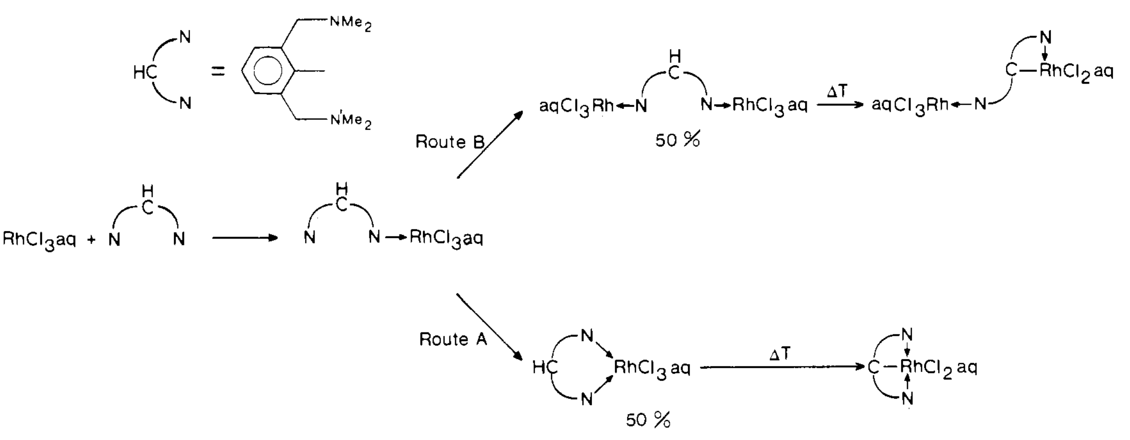
Scheme I



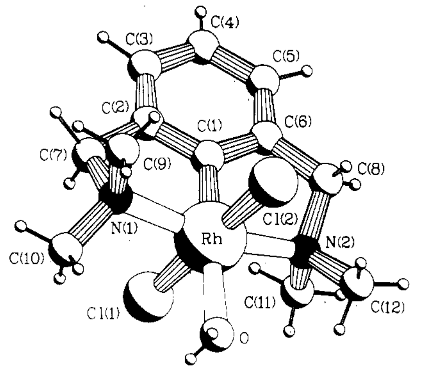


Figure 1. PLUTO drawing of *trans*-RhCl$_2$(N-C-N)(H$_2$O) illustrating the molecular structure and adopted numbering scheme.

resulting from the bidentate ligating capacity of (N-C-N)H (see Scheme I). Monodentate coordination through one of the amine sites of (N-C-N)H to rhodium can be followed by either an intramolecular bidentate coordination to the same rhodium (route A) or by intermolecular coordination to another rhodium (route B). On the basis of the elemental analyses an approximate 1/1 distribution is expected to be present. When the original reaction mixture was heated, the golden yellow ortho-metalated product *trans*-RhCl$_2$(N-C-N)(H$_2$O) was obtained in 45% yield. This octahedral complex, incorporating a terdentate-bonded N-C-N ligand, was characterized by elemental analysis, ^{1}H and ^{13}C NMR, mass spectrometry, and an X-ray structure determination, of which the main structural features will be discussed later. Although its preparation was repeated several times with different RhCl$_3$(H$_2$O)$_3$/(N-C-N)H ratios, the yield of *trans*-RhCl$_2$(N-C-N)(H$_2$O) never exceeded 45% (based on Rh). It is therefore likely that this soluble product results from metalation of only the one complex in which (N-C-N)H is bidentate-bonded to a rhodium center (route A). The gray insoluble residue obtained from this reaction, which gave an approximate analysis as RhCl$_{2.5}$(N-C-N)$_{0.65}$(H$_2$O)$_{1.45}$, is clearly a product of route B. The Cl/Rh ratio of 2.5 suggests a partly metalated nature, in accordance with the assumption that (a) the initial coordination complex of route B contains one rhodium on each amine substituent of (N-C-N)H and (b) only one rhodium side metalates (see Scheme I).

Solid-State Structure of *trans*-RhCl$_2$(N-C-N)(H$_2$O). The molecular geometry and atomic numbering scheme of *trans*-RhCl$_2$(N-C-N)(H$_2$O) is shown in Figure 1. Bond distances and angles are listed in Table III. The coordination around rhodium can be described as distorted octahedral, and in this respect there is a resemblance to the structure of Ni^{III}(NCS)$_2$(N-C-N)(py)[28] (py = pyridine) and more particularly to that of Pt^{IV}Cl$_3$(N-C-N).[2] In these complexes the principal distortions, which stem from the geometrical constraints of the N-C-N ligand, are the acute C(aryl)-M-N angles, which in *trans*-RhCl$_2$(N-C-N)(H$_2$O) are 81.4 (1)° for N(1) and 81.7 (1)° for N(2). These small changes are in concert with a Rh-C(aryl) bond of 1.913 (3) Å, which is short when compared to the normal range of 1.98-2.00 Å found for Rh-C bonds.[29-31] Both the two Rh-Cl (2.3532 (9) and 2.3528 (9) Å) and the two Rh-N distances (2.160 (3) and 2.152 (3) Å)

Table III. Selected Geometrical Data of *trans*-RhCl$_2$[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o,o'*](H$_2$O)

(a) Bond Distances (Å)

Rh-Cl(1)	2.3532 (9)	N(2)-C(12)	1.494 (6)
Rh-Cl(2)	2.3528 (9)	C(1)-C(2)	1.382 (4)
Rh-O	2.269 (2)	C(1)-C(6)	1.382 (4)
Rh-N(1)	2.160 (3)	C(2)-C(3)	1.383 (5)
Rh-N(2)	2.152 (3)	C(2)-C(7)	1.499 (5)
Rh-C(1)	1.913 (3)	C(3)-C(4)	1.385 (6)
N(1)-C(7)	1.522 (4)	C(4)-C(5)	1.393 (7)
N(1)-C(9)	1.478 (5)	C(5)-C(6)	1.389 (5)
N(1)-C(10)	1.495 (5)	C(6)-C(8)	1.505 (5)
N(2)-C(8)	1.515 (5)	O-H(1)	0.74 (5)
N(2)-C(11)	1.493 (5)	O-H(2)	0.72 (5)

(b) Bond Angles (deg)

Cl(1)-Rh-Cl(2)	177.68 (3)	Rh-N(2)-C(11)	113.8 (2)
Cl(1)-Rh-O	88.53 (7)	Rh-N(2)-C(12)	113.4 (2)
Cl(1)-Rh-N(1)	87.70 (8)	C(8)-N(2)-C(11)	107.7 (3)
Cl(1)-Rh-N(2)	93.02 (8)	C(8)-N(2)-C(12)	108.8 (3)
Cl(1)-Rh-C(1)	90.39 (8)	C(11)-N(2)-C(12)	108.2 (3)
Cl(2)-Rh-O	89.17 (7)	Rh-C(1)-C(2)	118.6 (2)
Cl(2)-Rh-N(1)	93.09 (8)	Rh-C(1)-C(6)	118.2 (2)
Cl(2)-Rh-N(2)	86.86 (8)	C(2)-C(1)-C(6)	123.2 (3)
Cl(2)-Rh-C(1)	91.89 (8)	C(1)-C(2)-C(3)	118.2 (3)
O-Rh-N(1)	100.74 (9)	C(1)-C(2)-C(7)	114.6 (3)
O-Rh-N(2)	96.1 (1)	C(3)-C(2)-C(7)	127.2 (3)
O-Rh-C(1)	177.5 (1)	C(2)-C(3)-C(4)	119.6 (4)
N(1)-Rh-N(2)	163.1 (1)	C(3)-C(4)-C(5)	121.8 (3)
N(1)-Rh-C(1)	81.4 (1)	C(4)-C(5)-C(6)	118.9 (3)
N(2)-Rh-C(1)	81.7 (1)	C(1)-C(6)-C(5)	118.4 (3)
Rh-N(1)-C(7)	104.5 (2)	C(1)-C(6)-C(8)	114.5 (3)
Rh-N(1)-C(9)	114.5 (2)	C(5)-C(6)-C(8)	127.2 (3)
Rh-N(1)-C(10)	113.1 (2)	N(1)-C(7)-C(2)	109.9 (3)
C(7)-N(1)-C(9)	107.8 (3)	N(2)-C(8)-C(6)	109.2 (3)
C(7)-N(1)-C(10)	109.4 (3)	Rh-O-H(1)	121 (4)
C(9)-N(1)-C(10)	107.4 (3)	Rh-O-H(2)	118 (4)
Rh-N(2)-C(8)	104.7 (2)	H(1)-O-H(2)	92 (5)

(c) Hydrogen Bonds[a]

D-H···A	D···A, Å	D-H, Å	H···A, Å	∠D-H···A, deg
O-H(1)···Cl(2)^{i}	3.157 (3)	0.74 (5)	2.42 (5)	173 (5)
O-H(2)···Cl(1)^{ii}	3.162 (3)	0.72 (5)	2.45 (5)	172 (5)

[a] Symmetry codes: (i) $-x, -y, -z$; (ii) $1 - x, -y, -z$.

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Table IV. ^{1}H NMR Data of N-C-N Compounds[a]

compd	solv	SF[b]	aryl[f]	CH$_2$[j]	NMe
trans-RhCl$_2$(N-C-N)(H$_2$O)	*c*	250	6.88 (t), 6.98 (d)	3.96	2.60
trans-RhBr$_2$(N-C-N)(H$_2$O)	*c*	250	6.86 (t), 6.94 (d)	4.06	2.77
trans-Rh(O$_2$CH)$_2$(N-C-N)(H$_2$O)[g]	*c*	250	7.03	3.88	2.40
trans-Rh(O$_2$CMe)$_2$(N-C-N)(H$_2$O)[h]	*c*	250	7.00	3.84	2.37
trans-Rh(NO$_3$)$_2$(N-C-N)(H$_2$O)	*c*	100	7.08	4.01	2.51
trans-Rh(CN)$_2$(N-C-N)(H$_2$O)	*d*	100	6.94	3.91	2.64
RhCl(acac)(N-C-N)[i]	*d*	100	6.93	3.66 (d), 3.99 (d)	2.07, 2.55
RhCl(N-C-N)(μ-Cl)$_2$Rh(COD)[k]	*d*	100	6.95	3.79 (d), 4.05 (d)	2.77, 3.03
RhCl(N-C-N)(μ-Cl)$_2$Ir(COD)[l]	*d*	250	6.96	3.79 (d), 4.05 (d)	2.76, 2.93
[RhCl(N-C-N)(μ-Cl)$_2$]$_2$Pd[m]	*d*	250	6.95	3.79 (d), 4.04 (d)	2.75, 3.15
[RhCl(N-C-N)(μ-Cl)$_2$]$_2$Pd[n]	*d*	250	6.92	3.72 (d), 4.03 (d)	2.77, 3.09
(N-C-N)H	*d*	250	7.15 (s, br)	3.36	2.19
(N-C-N)$_2$	*d*	100	7.39	2.90	2.09
(N-C-N)$_2$(HCl)$_4$	*e*	250	7.89 (t), 7.94 (d)	4.04	2.96

[a] Chemical shifts (in ppm) relative to external TMS. [b] Spectrometer frequency (^{1}H) in MHz. [c] Acetone-d_6. [d] Chloroform-d_1. [e] Methanol-d_4. [f] For AB$_2$ multiplet: ^3J(H–H) = 7.5 Hz. [g] O$_2$C*H*, 7.48 ppm (^3J(Rh–H) = 4.0 Hz). [h] O$_2$CC*H*$_3$, 1.70 ppm. [i] acac, 1.66 (Me), 2.11 (Me), and 5.33 (H) ppm. [j] For AB doublet: ^2J(H–H) = 13.5 Hz. [k] –10 °C; COD, olefinic protons, 4.22 and 4.42 ppm. [l] COD, olefinic protons, 3.74 and 4.19 ppm. [m] Major isomer. [n] Minor isomer.

Table V. ^{13}C NMR Data of N-C-N Compounds[a]

		aryl C					
compd	solv	ipso	ortho	meta	para	CH$_2$	NMe
trans-RhCl$_2$(N-C-N)(H$_2$O)	*b*	160.3[d]	145.0	121.1	123.2	72.6	54.1
trans-Rh(O$_2$CH)$_2$(N-C-N)(H$_2$O)[e]	*b*	*g*	144.6	121.6	123.3	72.0	51.8
trans-Rh(O$_2$CMe)$_2$(N-C-N)(H$_2$O)[f]	*b*	*g*	144.5	121.4	124.0	71.7	51.3
(N-C-N)H	*c*	127.8	138.7	127.5	129.5	64.0	45.0
(N-C-N)$_2$	*c*	168.2	140.5	126.3	127.1	61.3	45.6

[a] ^{1}H-decoupled spectra, measured at 62.89 MHz; chemical shifts (in ppm) relative to external TMS. [b] Acetone-d_6. [c] Chloroform-d_1. [d] ^1J(Rh–C) = 25.7 Hz. [e] O$_2$*C*H, 173.7 ppm (^2J(Rh–C) = 1.6 Hz). [f] O$_2$C*C*H$_3$, 24.4 ppm; O$_2$*C*CH$_3$, 182.7 ppm. [g] Not observed.

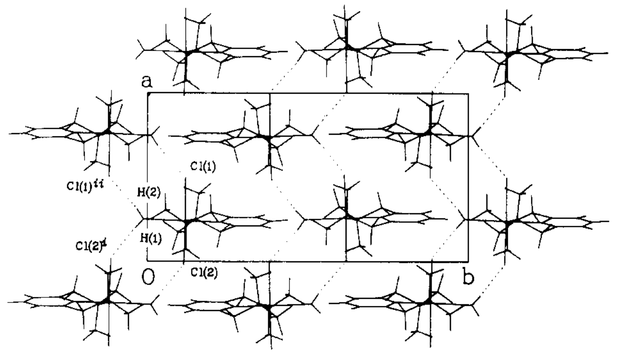

Figure 2. Projection of the crystal structure down the *c* axis. Hydrogen bonds are indicated with dashed lines.

do not differ significantly and are of normal length.[32-35] The Rh–O distance of 2.269 (2) Å lies within the range of 2.24–2.32 Å found for Rh–O bonds trans to C.[36,37] The dihedral angle between the aryl ring and the meridional plane through C(1), N(1), N(2), O, and Rh is 14.6 (1)°. The molecule exhibits noncrystallographic C_2 symmetry with respect to the line Rh–C(1). This is illustrated by the ΔC_2[Rh–C(1)] asymmetry parameter[38] of 2.9 (3)° for the eight-membered ring C(1)–C(2)–C(7)–N(1)–Rh–N(2)–C(8)–C(6). The H$_2$O molecule acts as a H-donor in intermolecular Cl···H–O bridging, as shown in Figure 2. The geometry of the hydrogen bonds is given in Table III. The Cl···H–O angles are linear within experimental error (173 (5) and 172 (5)°). Each molecule is involved in four hydrogen bonds with two other molecules. In this way infinite zigzag chains are formed in the direction of the *a* axis.

Properties and Chemistry of *trans*-RhCl$_2$(N-C-N)(H$_2$O). With respect to the free ligand (N-C-N)H the CH$_2$ and NMe$_2$ NMR signals of the title compound show a downfield coordination shift (see Tables IV and V). These signals are singlets, indicating a symmetrical coordination of the amine groups to rhodium and a trans position of the chloride atoms (C_{2v} symmetry[39]). The presence of a direct rhodium–carbon bond to the N-C-N aryl group is demonstrated by the rhodium–carbon coupling of 25.7 Hz found on the ^{13}C signal at 160.3 ppm. The FD mass spectrum of *trans*-RhCl$_2$(N-C-N)(H$_2$O) shows as the parent peak the molecular ion minus the water molecule.

trans-RhCl$_2$(N-C-N)(H$_2$O) is air-stable, as are all rhodium(III) N-C-N complexes reported here, and is even resistant to attack by dilute mineral acids. However, it does decompose in strong alkaline media into (N-C-N)H and probably rhodium oxides. It is very soluble in polar organic solvents, except alcohols, and moderately soluble in aromatic solvents. Its thermal decomposition, leading to mainly insoluble products, monitored by ^{1}H NMR in *p*-xylene-d_{10} solution and by thermometric DTA methods in the solid state, starts at ca. 125 °C.

Rhodium(III), iridium(III), and platinum(IV) complexes usually have an octahedral geometry and a favorable 18-electron configuration. Complexes of this type are often very inert, and exchange reactions take place slowly due to the high kinetic barriers.[40] Hard ligands, such as are present in *trans*-RhCl$_2$(N-C-N)(H$_2$O), will certainly help in consolidating this stable structure. Nonetheless, halide exchange in *trans*-RhCl$_2$(N-C-

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(39) The wagging in solution of the N-C-N ligand about the metal–C(aryl) bond is a feature of all four- and six-coordinate metal N-C-N complexes. It comprises the restricted back and forth rotation of the aryl ring by ca. 15° between the two twisted extremes and is accompanied by changes of the conformation of the two MNCCC five-membered rings. It has a low barrier of activation (<10 kcal mol^{-1}) and therefore becomes detectable on the ^{1}H NMR time scale only at low temperatures. In solution these N-C-N complexes appear to have an average structure that exhibits a symmetry plane that passes through the metal–C(aryl) bond and is perpendicular to the aryl plane.

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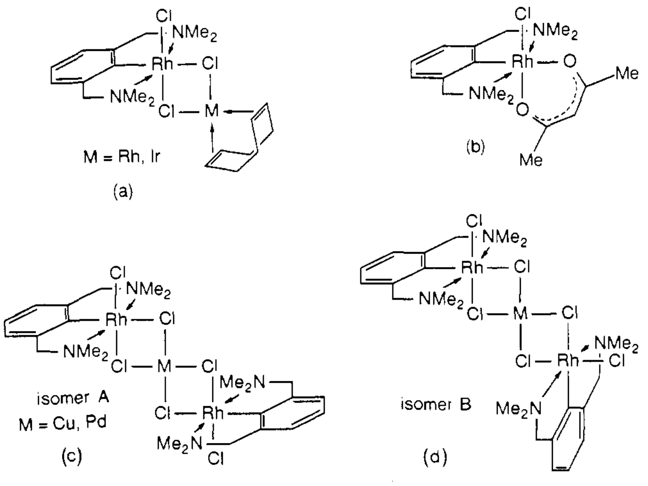

Figure 3. Proposed structures of (a) $RhCl(N\text{-}C\text{-}N)(\mu\text{-}Cl)_2M(COD)$ (M = Rh and Ir), (b) RhCl(acac)(N-C-N), (c) isomer A and (d) isomer B of $[RhCl(N\text{-}C\text{-}N)(\mu\text{-}Cl)_2]_2M$ (M = Pd and Cu).

N)(H_2O) is possible and both chlorine anions can be substituted by treatment with either excess of an alkali-metal salt or a silver salt over a period of 1 or more days. In this way the compounds *trans*-RhX_2(N-C-N)(H_2O) can be obtained, where X = Br, O_2CH, O_2CCH_3, NO_3, and CN. Their ^1H and some ^{13}C NMR data are given in Tables IV and V, respectively. All these species have spectra consistent with a symmetric N,C,N′-coordination mode as in the starting material. Only in the cases of X = Cl and Br do the three aryl protons of *trans*-RhX_2(N-C-N)(H_2O) exhibit the expected AB_2 multiplet in the ^1H NMR spectrum; all other complexes show a singlet signal as a result of coincident chemical shifts of the meta and para protons. The ^1H and ^{13}C NMR data of *trans*-$Rh(O_2CH)_2$(N-C-N)(H_2O) show clear rhodium couplings with the formate proton and carbon (^3J(Rh-H) = 4.0 Hz, ^2J(Rh-C) = 1.6 Hz) in acetone-d_6 or methanol-d_4.

The water molecule in *trans*-$RhCl_2$(N-C-N)(H_2O) could be easily substituted by the addition of certain metal salts. Reaction with $[MCl(COD)]_2$ (M = Rh, Ir) yields products of stoichiometry $RhMCl_3$(N-C-N)(COD). Their ^1H NMR spectra are temperature-dependent; at the slow-exchange limit (see Table IV) they show the presence of diastereotopic C and N centers in the CH_2NMe_2 substituents of the N-C-N ligand and two vinylic resonances for the COD moiety, indicating adducts with C_s symmetry. These data suggest the compound, RhCl(N-C-N)-(μ-Cl)$_2$M(COD), with two chlorine atoms bridging the Rh^{III} and M^I centers (Figure 3), as in $Rh_2Cl_2(CO)_2(o\text{-}C_6H_4NNC_6H_5)_2$.[30] The resonances of the CH_2, NMe, and vinylic COD protons each coalesce to one singlet in a narrow temperature range (M = Rh, T = +15 (±5) °C; M = Ir, T = +40 (±5) °C). In a separate set of experiments it was found that mixtures of *trans*-$RhCl_2$(N-C-N)(H_2O) and [RhCl(COD)]2 in $CDCl_3$ at room temperature in various molar ratios (1/1 to 1/4) gave only one set of signals for both the N-C-N system and COD; the coalescence temperature was also dependent on the molar ratio. These observations are indicative of a reversible addition of the Rh^{III} and M^I moieties. The reaction of *trans*-$RhCl_2$(N-C-N)(H_2O) with $PdCl_2$(COD), Li_2PdCl_4, or $CuCl_2$, but not with $PtCl_2$(COD) or K_2PtCl_4, yields complexes with the stoichiometry $Rh_2MCl_6(N\text{-}C\text{-}N)_2$. The ^1H NMR spectrum of the palladium complex shows two nearly identical patterns with intensity ratio 3/1, indicating the presence of two isomers (see Table IV). Both patterns show diastereotopic CH_2 and NMe_2 groups for the N-C-N ligand, and this suggests an asymmetric bridging of chlorine atoms between the Rh^{III} and Pd^{II} centers. A structure consistent with these data is $[RhCl(N\text{-}C\text{-}N)(\mu\text{-}Cl)_2]_2Pd$, which contains a square-planar-coordinated palladium surrounded by four chlorine atoms bridged to the two Rh centers (Figure 3). Isomerism in this complex is due to the fact that the two N-C-N ligands can line up either mutually coplanar (isomer A in Figure 3) or perpendicular (isomer B) to each other. On the basis of steric considerations, it is anticipated that the isomer A with less repulsive interactions represents the major component of the isomer mixture.

The green copper complex is paramagnetic, and ESR data show that it is probably isostructural with the palladium analogue. The ESR spectrum (134 K, CH_2Cl_2 glass) shows one signal at $g_\perp$ = 2.075 and a further signal at $g_\parallel$ = 2.229 with a $^{63/65}Cu$ hyperfine splitting of 146 G. These data are similar to those of the square-planar $CuCl_4^{2-}$ anion measured in a K_2PdCl_4 host ($g_\perp$ = 2.049 and $g_\parallel$ = 2.232 with A_{Cu} = 175 G).[41] The existence of isomers as in the palladium analogue cannot be excluded.

The chelate effect is probably responsible for the rather fast reaction of *trans*-$RhCl_2$(N-C-N)(H_2O) with Li(acac) to afford RhCl(acac)(N-C-N). Replacement of the second chlorine, however, was not possible, even when a large excess of Li(acac) was used. The ^1H NMR spectrum of the N-C-N moiety in this compound shows two singlets for the Me and an AB pattern for the methylenic protons, indicating that the CH_2NMe_2 units are diastereotopic. The Me acac protons show up as two singlets, and this, as well as the observed temperature invariance of the ^1H NMR spectrum in the range 20–130 °C, indicates that the acac group is asymmetrically bonded to rhodium in a rigid bidentate manner. From these NMR data we conclude that the acac ligand has one oxygen atom coordinated trans to C(aryl) and one trans to the chlorine atom and this makes the environments above and below the plane of the N-C-N ligand different (Figure 3). If we neglect the "wagging" of the N-C-N ligand about its Rh–C(aryl) axis,[39] then RhCl(acac)(N-C-N) has C_s symmetry with an apparent mirror plane through rhodium, chlorine, and the acac group. The absence of water in this complex makes it a suitable precursor for studies with various organometallic reagents, and the results of those reactions leading to novel diorganorhodium(III) compounds will be the subject of a forthcoming paper.

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Registry No. (N-C-N)Br, 66479-06-9; $(N\text{-}C\text{-}N)_2$, 112576-33-7; $[IrCl(COD)]_2$, 12112-67-3; $(N\text{-}C\text{-}N)_2(HCl)_4$, 112576-34-8; *trans*-$RhCl_2$(N-C-N)($H_2O$), 112596-40-4; *trans*-$RhBr_2$(N-C-N)($H_2O$), 112596-41-5; *trans*-$Rh(O_2CH)_2$(N-C-N)($H_2O$), 112596-42-6; *trans*-$Rh(O_2CMe)_2$(N-C-N)($H_2O$), 112596-43-7; *trans*-$Rh(NO_3)_2$(N-C-N)($H_2O$), 112596-44-8; *trans*-$Rh(CN)_2$(N-C-N)($H_2O$), 112596-45-9; RhCl(acac)(N-C-N), 112596-46-0; $RhCl(N\text{-}C\text{-}N)(\mu\text{-}Cl)_2Rh(COD)$, 112596-47-1; $RhCl(N\text{-}C\text{-}N)(\mu\text{-}Cl)_2Ir(COD)$, 112596-48-2; $[RhCl(N\text{-}C\text{-}N)(\mu\text{-}Cl)_2]_2Pd$ (isomer A), 112710-07-3; $[RhCl(N\text{-}C\text{-}N)(\mu\text{-}Cl)_2]_2Pd$ (isomer B), 112596-49-3; $RhCl_3$, 10049-07-7; $RhCl_3(\delta\text{-pic})_3$, 36148-74-0; $[RhCl(CO)_2]_2$, 14523-22-9; $RhCl(PPh_3)_2(CO)$, 13938-94-8; $[RhCl(COD)]_2$, 12092-47-6; $[RhCl(cyclooctene)_2]_2$, 12279-09-3; $RhCl_3{\cdot}3H_2O$, 13569-65-8; $(N\text{-}C\text{-}N)_2Li_2$, 112576-35-9; (N-C-N)H, 19851-44-6; $PdCl_2$(COD), 12107-56-1; $CuCl_2$, 7447-39-4; $[RhCl(N\text{-}C\text{-}N)(\mu\text{-}Cl)_2]_2Cu$, 112596-50-6.

Supplementary Material Available: An ORTEP plot, a listing of all refined positional and thermal parameter values, and complete listings of bond distances, bond angles, and torsion angles for *trans*-$RhCl_2$(N-C-N)(H_2O) (6 pages); a listing of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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(41) Chow, C.; Chang, K.; Willett, R. D. *J. Chem. Phys.* **1973**, *59*, 2629.