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Conversion of *N*-Allylaniline Promoted by Rh(I):[1] Synthesis and Molecular Structure of 2-Ethyl-1,2,3,4-tetrahydro-3-methyl-4-anilinoquinoline

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N-Allylaniline (1) is converted catalytically into 2-ethyl-1,2,3,4-tetrahydro-3-methyl-4-anilinoquinoline (7) by Rh(I). The first step of the N-heterocycle ring synthesis is the isomerization of 1 into *trans*-*N*-prop-1-enylaniline (3). The cis isomer could be neither isolated nor detected in the reaction mixture. 1 and 3 undergo an intermolecular double-bond addition reaction promoted by Rh(I) to afford (*Z*)-2-methyl-1,3-dianilinopent-1-ene (6). A rhodium complex containing 6 as a chelate was isolated in combination with other complexes, and the diamine was displaced and characterized. The ring closure reaction to afford 7 goes most probably through ortho metalation of a phenyl ring. The nature of 7 was established from a single-crystal X-ray study; the molecular structure of 7 in solution was determined by NMR spectroscopy.

Introduction

Quinoline derivatives possess interesting therapeutic properties;[3] in particular the 1,2,3,4-tetrahydroquinoline derivatives are used as schistosomicidal agents.[4] While several methods of synthesis of these rings are described in the literature,[5-9] most are multistep stoichiometric processes with low overall yields but a few are based on catalytic reactions.[8,9]

Although nucleophilic attack by an amino group on a coordinated double bond is a reaction of long standing,[10] only recently has it been developed as a useful method for a synthesis of N-containing compounds,[11] including N-containing heterocycles.[12] We found that 2-allylaniline in boiling benzene in the presence of Rh(I) undergoes intramolecular nucleophilic attack by the NH_2 group on the coordinated double bond to afford 2,3-dihydro-2-methylindole.[13] The first step of the cyclization reaction is the isomerization of the allylamine into *trans*-*N*-prop-1-enylaniline. In this reaction the behavior of the Rh(I) catalyst is different from that of Pd(II); with Pd(II), production of 2-methylindole occurs with loss of HCl and reduction of Pd(II) to Pd(0).[14] This different behavior is also encountered when *N*-allylaniline is considered. In fact, while Pd(II) cleaves the C–N bond to afford aniline and allene or methylacetylene,[15] Rh(I) is able to convert *N*-allylaniline without extensive hydrogen extraction and HCl elimination, at least at room temperature,[16] and reduction of the catalyst to metal does not occur.

In view of the potential utilization of these properties in synthetic chemistry we decided to investigate further

(1) Metal-Assisted N-Heterocycle Synthesis. 5. For part 4, see ref 13.
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(16) This is true when the reaction is carried out below 50 °C. At higher temperatures H-transfer processes and olefin metathesis reactions are observed.

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Table I. Conversion of *N*-Allylaniline versus Time[a]

product	time, h						
	0	2	6	10	24	48	72
naa	100	99	92	70	50	30	10
npa		1	6	25	24	27	23
6		0	0	2	10	10	18
7		0	0	0	1	7	15

[a] The number of millimoles of each species present in the reaction mixture is indicated for the given time.

the action of Rh(I) as $[RhCl(C_2H_4)_2]_2$[17] on *N*-allylaniline (**1**) itself. Here we report the resultant synthesis of 2-ethyl-1,2,3,4-tetrahydro-3-methyl-4-anilinoquinoline (**7**).

Experimental Section

All reactions were carried out in an atmosphere of pure and dry dinitrogen (99.99%). Solvents were dried, distilled from sodium–benzophenone, and stored under argon. ^1H and ^{13}C NMR spectra were obtained with a Varian XL 200 instrument. IR spectra were recorded on a Perkin-Elmer 598 instrument. A Perkin-Elmer Sigma 3 apparatus was used for GC analyses (OV 17 and SE 30 columns, 2 m, N_2 40 mL min^{-1}). Flash gas chromatography was carried out under dinitrogen pressure (2.0 atm). The solvents used in flash chromatography were distilled before use.

Isolation of $[RhCl(PhN(H)CH_2CH{=}CH_2)]_2$ ($[RhCl(naa)]_2$, 2). A solution of $[RhCl(C_2H_4)_2]_2$[17] (380 mg, 1.0 mmol) and naa (264 mg, 2.0 mmol) in tetrahydrofuran (40 mL) was stirred for 1 h at room temperature under dinitrogen. The resulting yellow solid was filtered off, washed with pentane, and dried under vacuum. The complex isolated had the correct elemental analyses and its spectral features (IR, UV–visible, NMR) were identical with those of a sample obtained from $Rh_2Cl_2(naa)_3$.[13]

Catalytic Conversion of *N*-Allylaniline (naa, 1). In the catalytic conversion of *N*-allylaniline a molar ratio amine/rhodium higher than 100 was usually used. Toluene and tetrahydrofuran were used as solvents. In a typical run *N*-allylaniline (12.0 g, 90 mmol) was dissolved in the solvent (40 mL) and $[RhCl(C_2H_4)_2]_2$ (35.0 mg, 0.18 mmol) or $(RhCl(naa)]_2$ (**2**) (50 mg, 0.18 mmol) was added. The solution was stirred under dinitrogen, and samples (2 μL) were withdrawn each hour and analyzed by gas chromatography. The reaction was stopped when no further conversion of the starting amine was observed. The solution was concentrated under vacuum at 0 °C to 15 mL, and the mixture of amines was separated by flash chromatography. Benzene–pentane (1:5) was used as the eluent. The different fractions (25 mL) were collected under dinitrogen and analyzed by GC techniques. The fractions containing the same amines were mixed, the solvent was evaporated, and the pure amines were analyzed by IR, ^1H NMR, and ^{13}C NMR spectroscopy. The isolated pure products were aniline, *N*-allylaniline (**1**), *N,N*-diallylaniline, *trans*-*N*-prop-1-enylaniline (npa, **3**), (*Z*)-2-methyl-1,3-dianilinopent-1-ene (map, **6**), and 2-ethyl-1,2,3,4-tetrahydro-3-methyl-4-anilinoquinoline (**7**). Other poorly characterized products were obtained as low melting solids; these probably formed through polymerization of the intermediate diamine. A typical product distribution as a funtion of the reaction time is reported in Table I.

Isolation of $RhCl(PhN(H)CH_2CH{=}CH_2)(PhN(H)CH{=}CHCH_3)$ (RhCl(naa)(npa), 4). $[RhCl(naa)]_2$ (**2**) (270 mg, 0.5 mmol) was suspended in toluene in the presence of the free naa (530 mg, 4 mmol), and the solution was stirred under dinitrogen until GC analysis of the solution revealed the presence of npa. The solution was filtered and concentrated under vacuum, and pentane was added. The solid was filtered and recrystallized from toluene–pentane twice to afford 100 mg of yellow RhCl(naa)(npa) (**4**) that decomposes at 120 °C. It is diamagnetic and a nonelectrolyte in nitrobenzene (Λ_M = 1.5 S mol^{-1} cm^2) and acetone (Λ_M = 2.0 S mol^{-1} cm^2); yield 25%. Anal. Calcd for $C_{18}H_{22}ClN_2Rh$: C, 53.5; H, 5.40; Cl, 8.77; N, 6.92. Found: C, 53.4; H, 5.40; Cl, 8.8; N, 6.95.

The solid shows characteristic absorption bands (in Nujol) at 3395, 3270, and 3235 cm^{-1} (ν(NH)) and at 1000, 990, 970, 950, 910, and 890 cm^{-1} (attributed to the bending of the coordinated double bonds). The ^1H NMR spectrum (deuteriochloroform) shows signals at δ 7.30 (m, H arom, 10 H), 6.69 (d, 1 H, =CHN, J = 19.8 Hz), 6.65 (m, 1 H, =C(*H*)CH_3), 5.94 (m, 1 H, CH=), 5.80 (br, 2 H, NH), 5.27 (d, 1 H, C=CH(trans), J = 16.5 Hz), 5.165 (d, 1 H, C=CH(cis), J = 9.7 Hz), 3.77 (d, 2 H, CH_2, J = 5.5 Hz), and 1.24 (d, 3 H, CH_3, J = 5.3 Hz). Solid **4** was reacted with D_2O. The bands at 3390 and 3235 cm^{-1} disappeared rapidly while the band at 3270 cm^{-1} persisted for some time. We ascribe this persistence to the presence of an N–H···Cl bond. At 3270 cm^{-1} it is in the right range for a bond of modest strength.[18] The decreased lability of the H atom involved in this bond can play an important role in control of the stereochemistry in the heterocycle synthesis.

Isolation of the Complex $RhCl(PhN(H)CH{=}C(CH_3)C(H)(C_2H_5)N(H)Ph)$ (RhCl(map), 5). The conversion of naa was stopped when the quinoline derivative was formed in solution. The solvent was evaporated to 20 mL under vacuum at 0 °C, and pentane was added to the residual oil. The resultant precipitate was recrystallized twice from tetrahydrofuran–pentane to yield 60 mg of yellow RhCl(map) (**5**) that decomposes at 105 °C under dinitrogen. Anal. Calcd for $C_{18}H_{22}ClN_2Rh$: C, 53.5; H, 5.40; Cl, 8.77; N, 6.92. Found: C, 53.6; H, 5.6; Cl, 8.8; N, 6.7. IR (in Nujol): 3390, 3160, 3120 cm^{-1} (ν(NH)), 340 cm^{-1} (ν(RhCl)). ^1H NMR: δ 7.10–6.70 (m, 9 H, H arom), 6.60 (s, 1 H, NC(H)=), 6.30 (br, 2 H, NH), 4.25 (t, 1 H, NC(H)Et), 1.78 (d, 3 H, =C(CH_3), J = 0.70 Hz), 1.69 (m, 2 H, CH_2), 1.27 (t, 3 H, CH_3CH_2, J = 7.40 Hz), -2.67 (s, ~1 H, agostic H).

Crystallization of 2-Ethyl-1,2,3,4-tetrahydro-3-methyl-4-anilinoquinoline (7). The amine was isolated by chromatography (see above) from the reaction solution. The amine (300 mg) was dissolved in benzene (10 mL), and pentane (5 mL) was added. The solution was kept at 10 °C for 1 day, and the white crystals that separated were filtered off, washed with pentane, and dried under vacuum. Anal. Calcd for $C_{18}H_{22}N_2$: C, 81.16; H, 8.32; N, 10.52. Found: C, 81.2; H, 8.33; H, 10.51.

The Role of Rh(I) in the Synthesis of the Isoquinoline Ring. In order to exclude that other species, such as Lewis acids, casually present in the reaction medium might play a role in the synthesis of the heterocycle, we have studied the conversion of naa in toluene in the presence of $AlCl_3$ or $MoCl_4$ or SiO_2 or Rh(I) supported over silica. In a typical run 0.1 mol of the Lewis acid was added to 1.0 mL of naa in toluene (10 mL), and the suspension was stirred under dinitrogen. Samples (1 μL) were withdrawn each hour for the first 12 h and analyzed by GC with the use of two columns (SE30 and OV17). The GC analysis shows that even for long reaction times no conversion of naa occurs in the presence of the Al, Mo, and Si compounds. Only Rh/SiO_2 was able to convert naa; the main reaction was the very slow intermolecular transfer of an allyl group to afford aniline and *N,N*-diallylaniline. We thus conclude that all the processes observed and described here are promoted by Rh(I).

Spectroscopic Data for the Free Amines. The ^1H NMR spectra of *N*-allylaniline (naa) and of *N,N*-diallylaniline were identical with those of authentic samples.[15,19,20] *trans*-*N*-Prop-1-enylaniline (npa, **3**): δ 7.20–6.50 (m, 5 H, H arom), 5.80 (dq, 1 H, NC(H)=, J_{trans} = 13.6, J_{H-CH_3} = 1.2 Hz), 4.19 (dq, 1 H, =C(H)CH_3, J_{H-CH_3} = 6.2 Hz), 4.05 (s, 1 H, NH), 1.27 (dd, 3 H, CH_3). (*Z*)-2-Methyl-1,3-dianilinopent-1-ene (map, **6**): δ 7.20–6.70

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Table II. Crystallographic Details for 2-Ethyl-1,2,3,4-tetrahydro-3-methyl-4-anilinoquinoline (7)

formula	$C_{18}H_{22}N_2$
fw	266.39
a, Å	8.226 (3)
b, Å	9.081 (3)
c, Å	20.236 (8)
β, deg	103.94 (1)
V, Å^3	1467
Z	4
d_{calcd}, g/cm^3	1.205 (123 K)
space group	C_{2h}^5—$P2_1/c$
μ, cm^{-1}	0.66
radiatn	graphite-monochromated Mo Kα (λ(Mo Kα_1) = 0.7093 Å)
takeoff angle, deg	2.5
receiving aperture	2 mm wide by 3 mm high; 20 cm from crystal
scan mode	θ–2θ
scan speed, deg θ/min	4°, with rescan of $I < 3\sigma(I)$ up to 40 s
scan width	0.70° below Kα_1 to 0.70° above Kα_2
bkgd counts	extension of $^1/_4$ scan range on each side
data collected	$\pm h,k,l$, $2.5° \leq \theta \leq 30°$
no. of unique data	4251
p for calculation of $\sigma(F_o^2)$	0.03
no. of unique data with $F_o^2 > 3\ \sigma(F_o^2)$	2906
no. of variables	270
R on F_o^2	0.079
R_w on F_o^2	0.121
R on F_o ($F_o^2 > 3\sigma(F_o^2)$)	0.057
R_w on F_o ($F_o^2 > 3\sigma(F_o^2)$)	0.058
error observn unit wt	1.34

(m, 10 H, H arom), 6.65 (s, 1 H, NC(H)=), 5.60 (s. br, 2 H, NH), 4.10 (t, 1 H, C(*H*)Et, J_{H-CH_2} = 6.35 Hz), 1.70 (complex doublet, 3 H, =C(CH_3), J = 0.95 Hz), 1.69 (m, 2 H, CH_2), 1.25 (t, 3 H, CH_3C, $J_{CH_3-CH_2}$ = 7.45 Hz).

Crystallographic Study of 7. A suitable crystal of 7 was mounted directly in the cold stream (123 K) of a Nonius CAD4 X-ray diffractometer. Crystallographic details are presented in Table II.

In the solution and refinement of the structure, procedures, and programs standard in this laboratory were employed.[21] The structure was solved with the use of direct methods and a combination of refinement and difference electron density syntheses. No correction for absorption effects was necessary. The structure was refined by full-matrix least-squares methods. The final cycle was carried out on F_o^2 and involved the refinement of the positional parameters of all 42 atoms in the molecule, anisotropic thermal parameters for the non-hydrogen atoms, and isotropic thermal parameters for the hydrogen atoms. Details on the refinement, including agreement indices, are given in Table II. Final positional and isotropic or equivalent isotropic thermal parameters are given in Table III. Table IV[22] presents the anisotropic thermal parameters while Table V lists structure amplitudes (×10^2).[22] A negative entry in Table V indicates that $F_o^2 < 0$.

Results and Discussion

As we have previously described,[13] *N*-allylaniline (naa, **1**) in the presence of $[RhCl(C_2H_4)_2]_2$ at room temperature in toluene or tetrahydrofuran under dinitrogen affords different complexes depending upon the reaction time and the ligand-to-Rh molar ratio. We have now found that one of the Rh–naa complexes catalyzes the conversion of naa into other amines. In order to obtain more information about the reaction pathway, we have monitored by chromatographic techniques the naa conversion and we have isolated complexes formed at various reaction times.

(21) See, for example: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273–3277.

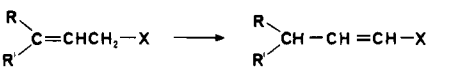
Table III. Positional Parameters and *B*(eq) for 2-Ethyl-1,2,3,4-tetrahydro-3-methyl-4-anilinoquinoline (7)

atom	x	y	z	B, Å^2
N(1)	0.88166 (16)	−0.12453 (14)	1.093225 (63)	1.69 (3)
N(2)	0.75620 (16)	0.17645 (15)	0.935524 (64)	1.78 (3)
C(1)	0.81235 (18)	0.01384 (16)	1.112520 (72)	1.55 (3)
C(2)	0.82455 (18)	0.13016 (16)	1.059239 (71)	1.50 (3)
C(3)	0.71817 (18)	0.08418 (16)	0.989194 (70)	1.48 (3)
C(4)	0.74068 (17)	−0.07802 (16)	0.974521 (73)	1.55 (3)
C(5)	0.68607 (19)	−0.13316 (19)	0.908244 (80)	2.04 (4)
C(6)	0.70687 (21)	−0.27963 (20)	0.893255 (93)	2.50 (4)
C(7)	0.78538 (22)	−0.37397 (19)	0.944930 (95)	2.48 (5)
C(8)	0.84241 (20)	−0.32232 (18)	1.010462 (86)	2.05 (4)
C(9)	0.81912 (18)	−0.17463 (16)	1.026240 (74)	1.60 (3)
C(10)	0.90679 (22)	0.05621 (20)	1.184405 (78)	2.11 (4)
C(11)	0.90660 (28)	−0.06240 (24)	1.237705 (92)	2.97 (5)
C(12)	0.77168 (23)	0.28274 (18)	1.077719 (87)	2.08 (4)
C(13)	0.63684 (18)	0.25094 (16)	0.887086 (73)	1.56 (3)
C(14)	0.49115 (19)	0.31002 (17)	0.900841 (79)	1.80 (4)
C(15)	0.38027 (20)	0.38965 (18)	0.851644 (86)	2.14 (4)
C(16)	0.40973 (21)	0.41486 (21)	0.788033 (90)	2.60 (4)
C(17)	0.55431 (22)	0.35798 (22)	0.774392 (85)	2.62 (4)
C(18)	0.66594 (20)	0.27699 (19)	0.822528 (79)	2.07 (4)
HN(1)	0.8805 (24)	−0.1947 (22)	1.1213 (10)	1.9 (4)
HN(2)	0.8425 (27)	0.1433 (24)	0.9209 (10)	2.6 (5)
HC(1)	0.6871 (19)	0.0003 (17)	1.11220 (72)	1.3 (3)
HC(2)	0.9447 (21)	0.1330 (19)	1.05685 (79)	1.4 (4)
HC(3)	0.5988 (19)	0.1034 (16)	0.98916 (69)	1.2 (3)
HC(5)	0.6299 (22)	−0.0635 (19)	0.87362 (87)	2.5 (4)
HC(6)	0.6684 (24)	−0.3136 (22)	0.84891 (98)	2.8 (5)
HC(7)	0.8030 (23)	−0.4720 (22)	0.93612 (90)	2.3 (4)
HC(8)	0.8964 (20)	−0.3877 (19)	1.04700 (80)	2.0 (3)
H1C(10)	0.8544 (22)	0.1458 (20)	1.19800 (84)	2.2 (4)
H2C(10)	1.0235 (24)	0.0819 (21)	1.18455 (90)	3.2 (4)
H1C(11)	0.9522 (24)	−0.0274 (22)	1.28397 (98)	3.4 (4)
H2C(11)	0.7920 (25)	−0.0984 (22)	1.23547 (93)	3.4 (4)
H3C(11)	0.9727 (26)	−0.1500 (25)	1.23157 (98)	4.0 (5)
H1C(12)	0.7628 (23)	0.3515 (21)	1.03809 (93)	2.7 (4)
H2C(12)	0.8489 (24)	0.3253 (21)	1.11751 (97)	3.0 (4)
H3C(12)	0.6589 (23)	0.2796 (21)	1.08935 (87)	2.8 (4)
HC(14)	0.4722 (20)	0.2990 (19)	0.94585 (82)	2.1 (4)
HC(15)	0.2836 (22)	0.4319 (20)	0.86347 (83)	2.3 (4)
HC(16)	0.3293 (23)	0.4714 (21)	0.75366 (89)	3.2 (4)
HC(17)	0.5731 (24)	0.3749 (22)	0.73041 (98)	3.6 (4)
HC(18)	0.7654 (26)	0.2343 (22)	0.81244 (96)	3.1 (5)

Isomerization of naa (1) to npa (3). The first reaction observed is the olefin double-bond migration to afford the eneamine **3** (eq 1). The catalytic isomerization of allyl-

1 **3** (1)

amine is promoted by several metal systems.[19,20,23] The tendency of Rh(I) to catalyze the inner to terminal double-bond migration in functionalized allylic systems (eq 2) is also well-documented.[24-26] The activity of the catalyst



(2)

depends on the ligands bonded to the metal and on the coordination number. Coordinatively saturated Rh(I) complexes, such as $RhCl(diphos)_2$, $Rh(diphos)_2^+$, or $[RhCl(BINAP)]_2$, show no catalytic activity in tetrahydrofuran at 40 °C,[27] while coordinatively unsaturated

(22) Supplementary material.
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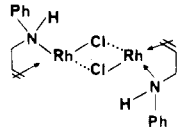
(27) (a) diphos = 1,2-bis(diphenylphosphino)ethane; BINAP = 1,1′-dinaphthyl-2,2′-bis(diphenylphosphine); COD = 1,5-cyclooctadiene. (b) Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138–1151.

complexes, such as Rh(diphos)$^+$ and Rh(diphos)(COD)$^+$, are active catalysts.[28] Moreover, Rh(I) systems with chiral phosphorus ligands are highly enantioselective catalysts for the synthesis of optically active eneamines from allylamines.[28] The availability of a vacant site on the metal for bonding the substrate or the presence of a good leaving ligand is a fundamental requisite for the activity of the catalyst, and the optical activity of coligands on the metal induces an elevated enantioselectivity.

In our case with ethylene as a good leaving group the substrate itself becomes coordinated to the metal. Thus the complex $[RhCl(naa)]_2$ (**2**) is formed. We isolated it in



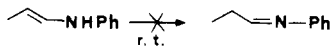
2

pure form after the reaction had proceeded for about 1 h. The naa ligand is coordinated to the Rh center through the nitrogen atom and the double bond. In strongly coordinating solvents **2** becomes monomeric.[29] Once **2** is formed the isomerization of naa (**1**) to the eneamine npa (**3**) takes place. The process is highly selective: only the *trans*-eneamine is formed, as the cis isomer **3a** (eq 3) could

(3)

3 **3a**

neither be isolated nor detected in solution. Further isomerization of **3** to the imine (eq 4) has not been detected



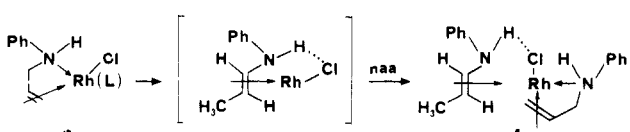
(4)

at room temperature. Above 60 °C npa-to-imine conversion occurs readily[13] in the presence of Rh(I) catalysts. When an alkyl substituent is present on the amine, the eneamine-to-imine conversion takes place smoothly.[28] Tertiary amines are not isomerized (eq 5, R = R′ = alkyl). In the present instance the phenyl group on the nitrogen atom probably decreases the isomerization rate.

(5)

R = H, R′ = alkyl

Chromatographic analyses (Table I) show that the eneamine npa does not accumulate in the reaction mixture as the unique product of conversion of *N*-allylaniline. On the other hand, Pt(II), Pd(II), and Pd(0) phosphine complexes are good catalysts for the isomerization of 2-allylaniline into *trans*-2-prop-1-enylaniline as the unique product,[20] and Rh(I) in boiling dichloromethane catalyzes the same reaction in good yield (70% in 6 h) and with high selectivity (>98%).[13] In this latter instance at the end of the catalytic run the Rh complex with the isomerized ligand could be isolated in nearly quantitative yield. In the present case npa would not behave as a bidentate ligand because of greater strain with respect to 2-allylaniline (eq 6).



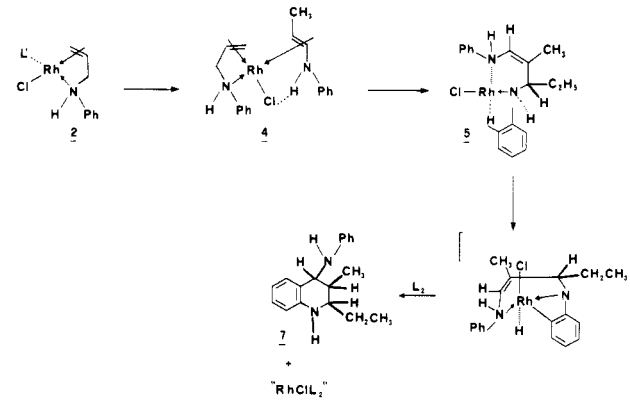
2 **4**

(6)

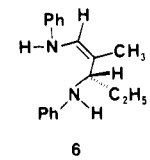
(28) Tani, K.; Yamagata, T.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R.; Otsuka, S. *J. Am. Chem. Soc.* **1984**, *106*, 5208–5217.

(29) Aresta, M.; Quaranta, E., Unpublished results.

Scheme I



Rh(I)-Assisted Coupling of 1 and 3 To Afford 6. The GC analysis shows that the solution gets gradually richer in the eneamine **3** but that the concentration of npa eventually becomes constant when about 30% of the starting amino olefin, naa, has been converted. At this point new products are formed but their concentrations do not become high for a few hours. The reaction mixtures from several runs were separated into their components by flash chromatography under dinitrogen, and the most abundant of the new products is (*Z*)-2-methyl-1,3-dianilinopent-1-ene (map, **6**). Moreover, we have characterized the solid complexes isolated from these solutions. Elemental analyses show that the yellow solid obtained is the impure complex RhCl(map) (**5**).[30] After several crystallizations from the appropriate solvents we were able to isolate a sample that analyzed correctly for RhCl(map), but still its proton NMR spectrum clearly showed that it contained some **4** (see Scheme I). The molar ratio **5**/**4** is approximately 5/1 from integration of appropriate signals. The infrared spectrum of the solid in Nujol shows bands at 3390, 3160, and 3120 cm^{-1}. Bands at 3100 and 3075 cm^{-1} are found for $PdCl_2(naa)_2$[15] and have been assigned to ν(NH) of the N-bonded ligand. The band at 3390 cm^{-1} is in the range of a free amino group. In fact free *N*-allylaniline shows an N–H stretching mode at 3420 cm^{-1}. The far-IR spectrum of **5** shows a band of 340 cm^{-1}, a value consistent with a terminal ν(RhCl) stretch.[31]



6

Treatment of impure **5** with an excess of diphos afforded $RhCl(diphos)_2$, identical with an authentic sample, and a solution from which the free amines **1**, **3**, and **6** were isolated by chromatography under dinitrogen. These results show that eneamine **3** undergoes, with the starting amino olefin **1**, a new Rh(I)-promoted dimerization reaction that corresponds to a intermolecular double-bond addition[32] (Scheme I). This dimerization reaction does not occur in the presence of phosphine ligand such as PPh_3, PEt_2Ph, $PEtPh_2$, PEt_3, or PMe_3; rather, the isomerization **1** → **3** is the only observed process.[33] Presumably the availability

(30) Attempts to isolate pure materials by fractional crystallization failed. The best results obtained were close to the $C_{18}H_{22}ClN_2Rh$ formula, i.e. to the complex of formula RhCl(diamine).

(31) Adams, D. M. *Metal-Ligand and Related Vibrations*; Arnold Ed.: London, 1967; p 69.

(32) Rh(I) phosphine complexes readily promote olefin addition reactions. See, for example: Hughes, R. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed., Pergamon: Oxford, 1982; p 423.

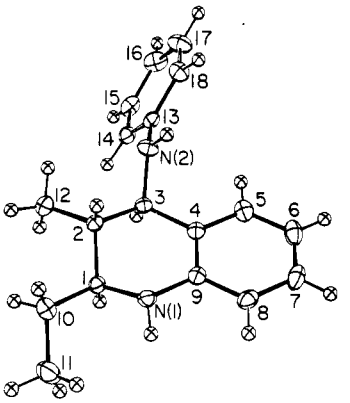


Figure 1. A drawing of the structure 2-ethyl-1,2,3,4-tetrahydro-3-methyl-4-anilinoquinoline (**7**). The thermal ellipsoids are drawn at the 50% probability level except for the H atoms which are of arbitrary size.

of vacant coordination sites on the Rh center is necessary for the coordination of 2 mol of amine and subsequent dimerization (Scheme I). The reaction is regiospecific. Only the isomer corresponding to the $NC(H)=C(CH_3)$-$C(H)(CH_2CH_3)N$ arrangement has been isolated; neither the $NCH_2C(CH_3)=C(CH_2CH_3)N$ isomer nor the imino forms have been found.[34]

There are two possibilities for the coordination of diamine **6** to the Rh center, namely, through two N atoms (six-membered ring) or through one of the N atoms and the double bond (4.5-membered ring).[35] Spectroscopic data from **5** do not enable us to decide on one of these possibilities, especially since the compound is impure. In either case a molecular model shows that the phenyl ring bonded to the N atom coordinated to the Rh center can assume a configuration in which an ortho-hydrogen atom completes the square-planar geometry about Rh. The ^1H NMR signal for the agostic proton is at −2.67 ppm.

Isolation and Characterization of 7. When the Rh complexes were not isolated from solution at this stage but the reaction was run for a longer time, a new product was formed. It was isolated by flash chromatography and shown to be **7**, 2-ethyl-1,2,3,4-tetrahydro-3-methyl-4-anilinoquinoline from an X-ray study of the solid and a spectroscopic study of a solution of **7**.

Crystallographic Study of 7. A drawing of the structure of **7**, together with the labeling scheme, is shown in Figure 1. Bond distances and angles are given in Table VI, while information on least-square planes is given in Table VII.

Our search of the literature reveals three structures for substituted 1,2,3,4-tetrahydroquinolines.[36-38] Only the latter study[38] approaches the accuracy of the present one. The same trends are seen in the quinoline rings in both structures. These include the half-chair conformation for the saturated heterocyclic ring (Table VII) and the asymmetric N–C bonds within that ring.

Structure of 7 in Solution. That the structure of **7** in $CDCl_3$ solution is the same as in the solid state has been demonstrated by ^1H and ^{13}C NMR spectroscopy. The ^1H spectrum shows one multiplet centered at 7.21–7.04 ppm (four protons) and a second centered at 6.67–6.55 ppm (five protons); these multiplets are assigned to the aromatic

Table VI. Distances (Å) and Angles (deg) in 7

N(1)-C(1)	1.471 (2)	C(13)-C(14)	1.401 (2)
N(1)-C(9)	1.405 (2)	C(14)-C(15)	1.382 (2)
N(1)-HN(1)	0.86 (2)	C(15)-C(16)	1.385 (2)
C(1)-C(2)	1.530 (2)	C(16)-C(17)	1.384 (3)
C(1)-C(10)	1.524 (2)	C(17)-C(18)	1.379 (2)
C(1)-HC(1)	1.04 (1)	C(18)-C(13)	1.404 (2)
C(2)-C(3)	1.534 (2)	C(14)-HC(14)	0.97 (2)
C(2)-C(12)	1.526 (2)	C(15)-HC(15)	0.96 (2)
C(2)-HC(2)	1.00 (2)	C(16)-HC(16)	0.98 (2)
C(3)-N(2)	1.464 (2)	C(17)-HC(17)	0.95 (2)
C(3)-C(4)	1.523 (2)	C(18)-HC(18)	0.97 (2)
C(3)-HC(3)	1.00 (1)	C(10)-C(11)	1.525 (3)
C(4)-C(5)	1.400 (2)	C(10)-H1C(10)	0.99 (2)
C(4)-C(9)	1.399 (2)	C(10)-H2C(10)	0.99 (2)
C(5)-C(6)	1.384 (2)	C(11)-H1C(11)	0.97 (2)
C(6)-C(7)	1.385 (3)	C(11)-H2C(11)	0.99 (2)
C(7)-C(8)	1.378 (2)	C(11)-H3C(11)	0.99 (2)
C(8)-C(9)	1.403 (2)	C(12)-H1C(12)	1.01 (2)
C(5)-HC(5)	0.97 (2)	C(12)-H2C(12)	0.98 (2)
C(6)-HC(6)	0.93 (2)	C(12)-H3C(12)	1.01 (2)
C(7)-HC(7)	0.93 (2)	N(1)···C(10)	2.441 (2)
C(8)-HC(8)	0.97 (2)	N(1)···H2C(10)	2.69 (2)
N(2)-C(13)	1.385 (2)	N(1)···H1C(10)	3.29 (2)
N(2)-HN(2)	0.89 (2)		

C(1)-N(1)-C(9)	117.2 (1)	N(2)-C(13)-C(14)	122.7 (1)
N(1)-C(1)-C(2)	107.9 (1)	N(2)-C(13)-C(18)	119.4 (1)
C(1)-C(2)-C(3)	110.1 (1)	C(3)-C(4)-C(5)	120.4 (1)
C(2)-C(3)-C(4)	112.0 (1)	N(1)-C(9)-C(8)	119.4 (1)
C(3)-C(4)-C(9)	121.1 (1)	C(13)-C(14)-C(15)	120.3 (1)
C(4)-C(9)-N(1)	121.0 (1)	C(14)-C(15)-C(16)	121.6 (2)
C(9)-C(4)-C(5)	118.4 (1)	C(15)-C(16)-C(17)	118.3 (2)
C(4)-C(5)-C(6)	121.7 (2)	C(16)-C(17)-C(18)	121.1 (2)
C(5)-C(6)-C(7)	119.3 (2)	C(17)-C(18)-C(13)	120.9 (2)
C(6)-C(7)-C(8)	120.3 (2)	C(18)-C(13)-C(14)	117.9 (1)
C(7)-C(8)-C(9)	120.7 (2)	C(1)-C(10)-C(11)	114.2 (2)
C(8)-C(9)-C(4)	119.6 (1)	C(3)-C(2)-C(12)	109.9 (1)
C(2)-C(3)-N(2)	110.7 (1)	C(1)-C(2)-C(12)	112.5 (1)
C(4)-C(3)-N(2)	110.6 (1)	C(2)-C(1)-C(10)	113.2 (1)
C(3)-N(2)-C(13)	124.2 (1)	N(1)-C(1)-C(10)	109.1 (1)

HC(3)-C(3)-C(2)-HC(2)[a]	−168 (1)
HC(2)-C(2)-C(1)-HC(1)	−174 (1)
HC(1)-C(1)-C(10)-H1C(10)	−56 (1)
HC(1)-C(1)-C(10)-H2C(10)	−173 (1)

[a] The torsion angle or conformation angle of a chain of atoms 1, 2, 3, and 4 is positive if when looking from 2 to 3 a clockwise motion of atom 1 would superimpose it on atom 4.

Table VII. Best-Weighted Least-Squares Planes for 7

Plane 1: $7.876x + 2.029y - 8.259z = -2.373$[a]

C(4), C(5), C(6), C(7), C(8), C(9):
0.000 (1),[b] 0.005 (2), −0.004 (2), −0.004 (2), 0.009 (2), −0.006 (1)

Plane 2: $8.027x + 1.555y - 7.434z = -1.368$

N(1), C(1), C(2), C(3), C(4), C(9):
0.124 (1), −0.361 (2), 0.314 (1), −0.090 (1), −0.053 (1), 0.042 (1)

Plane 3: $3.483x + 7.623y + 4.628z = 8.239$

C(13), C(14), C(15), C(16), C(17), C(18):
−0.002 (1), 0.004 (2), −0.003 (2), −0.002 (2), 0.005 (2), −0.001 (2)

Interplanar Angles: 1,2, 4.1°; 1,3, 58.0°; 2,3, 59.3°

[a] In monoclinic coordinates. [b] Distance (Å) of atom from the plane.

(33) We have also attempted to use optically active phosphines in order to induce an enantioselective synthesis, but under these conditions the condensation reaction does not take place. This is true also when only 1 mol of monodentate ligand/mol of rhodium is used.

(34) This diamine **6** has some allylamine–eneamine character. It might be that the $NCH_2C(CH_3)=C(CH_2CH_3)N$ isomer is not found as it could be more reactive and give rise to a polymerization process. It is known that *N,N*-dimethyl-1-methyl eneamines polymerize. See, for example: Madsen, P.; Lawesson, S.-O. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 753–756.

(35) Coordination through the eneamine part of the diamine (acting as a chelate) is less probable as the ring would be strained.

(36) Cameron, T. S.; Prout, K.; Denton, B.; Spagna, R.; White, E. *J. Chem. Soc., Perkin Trans. 1* **1975**, 176–185.

(37) Zalukaev, L. P.; Ignat'ev, N. A.; Zavalishin, E. I. *Zh. Struk. Khim.* **1974**, *16*, 237–241.

(38) Shibaeva, R. P.; Rozenberg, L. P.; Shapiro, A. B.; Povarov, L. S. *Zh. Struk. Khim.* **1981**, *22*, 140–145.

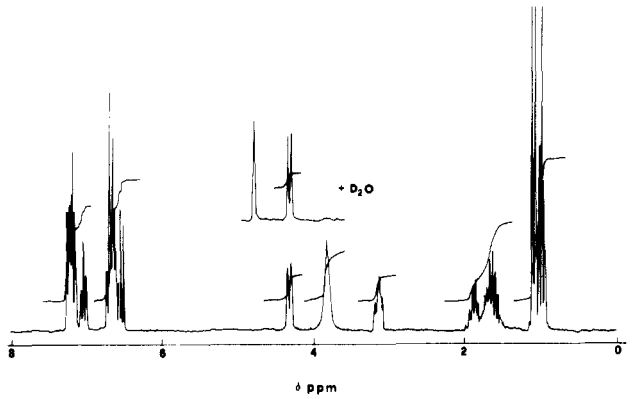


Figure 2. ^1H NMR spectrum of 7 in deuteriochloroform at 27 °C. The effect of addition of D_2O is shown. The spectrum remains unchanged in the temperature interval −20 to 50 °C.

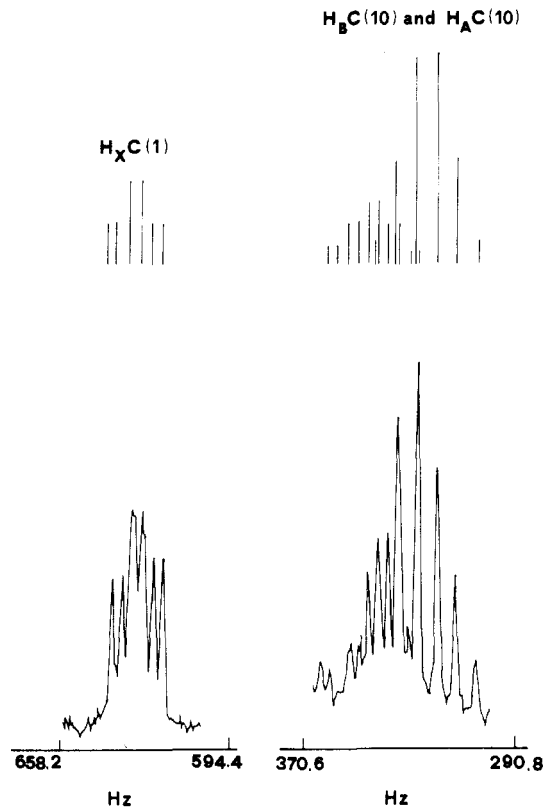


Figure 3. Calculated (upper part) and found (lower part) pattern for the $H_XC(1)$ and $H_{A,B}C(10)$ protons.

protons. The NH and the N*H*Ph signals are found as a broad singlet at 3.84 ppm. This signal disappears upon exchange with D_2O (see Figure 2).

The 5.0 ppm region of the spectrum is complex. Extended decoupling experiments were required to get information on the conformation in solution of the hydrogenated part of the quinoline ring and to obtain coupling constants. The HC(1) signal is an apparent triplet of doublets centered at 3.14 ppm (1 H). This feature suggests that the coupling constants $H_XC(1)$–$H_AC(10)$ (J_{AX}), $H_XC(1)$–$H_BC(10)$ (J_{BX}), and $H_XC(1)$–$H_{X'}C(2)$ ($J_{XX'}$) must be different where, for convenience we denote HC(1) as $H_XC(1)$ and HC(2) as $H_{X'}C(2)$. In fact, we have found that protons $H_BC(10)$ and $H_AC(10)$ give rise to two separate sets of signals centered at 1.69 (1 H, m) and 1.62 (1 H, m) ppm. Figure 3 (upper part) shows the calculated patterns for $H_XC(1)$, $H_AC(10)$, and $H_BC(10)$ (J_{AX} = 3.60, J_{BX} = 7.37, $J_{XX'}$ = 8.41, J_{AB} = 7.86 Hz). These are in good agreement with the experimental patterns (lower part). Apparently

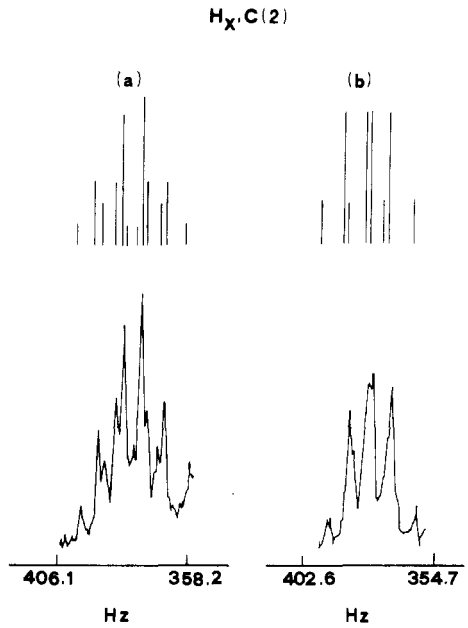


Figure 4. Calculated (upper part) and found (lower part) pattern for the $H_{X'}C(2)$ proton. In (a) HC(2) is decoupled from HC(3); in (b) HC(2) is decoupled from HC(11).

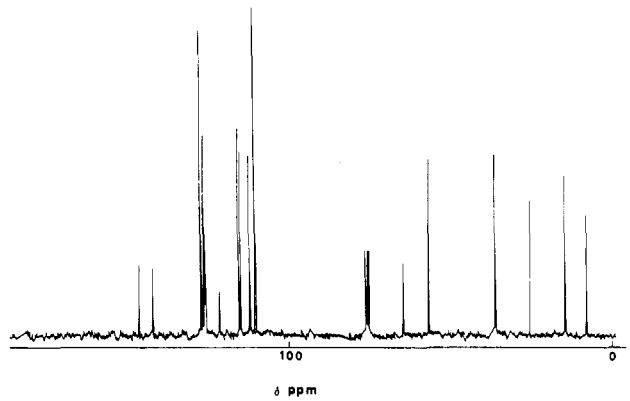


Figure 5. $^{13}C(^1H)$ NMR spectrum of 7 in deuteriochloroform at 27 °C.

the molecule in solution maintains the conformation it has in the solid state[39] with the angle HC(1)–C(1)–C(10)–H2C(10) close to −180° (axial–axial) while the angle HC(1)–C(1)–C(10)–H1C(10) is close to −60° (axial–equatorial) (Table VI).[40] On the basis of the coupling constants we assign atom $H_AC(10)$ to H1C(10) and atom $H_BC(10)$ to H2C(10). Because the H2C(10) proton can interact with the lone pair on the N(1) center, we assign the signal at 1.69 ppm to it. The CH_3CH_2 signal is at 0.99 ppm (t, 3 H, $J_{CH_3-A,B}$ = 7.57 Hz) while the $H_{X'}C(2)$ signal is at 1.88 ppm (m, 1 H, $J_{X'-CH_3}$ = 6.59, $J_{X'-3}$ = 8.80 Hz). The values of the coupling constants $J_{X-X'}$ and $J_{X'-3}$ are consistent with the $H_{X'}C(2)$–C(2)–C(1)–$H_XC(1)$ and $H_{X'}C(2)$–C(2)–C(3)–HC(3) angles (≈180°, Table VI) and are typical of axial–axial interactions.[40] Figure 4 shows the calculated and found pattern for the $H_{X'}C(2)$ proton. The CH_3 signal for

(39) A "lone pair" was placed on atom N(1) 0.95 Å toward the vertex of the tetrahedron made up of atoms HN(1), C(1), and C(9) and the lone pair. Distances from this lone pair (LP) to surrounding atoms are as follows: LP–H2C(10), 2.43 Å; LP–C(10), 2.54 Å; LP–H3C(11), 2.81 Å; LP–H1C(10), 3.45 Å; LP–H2C(11), 3.61 Å; LP–H1C(11), 3.96 Å. It is possible that this LP–H2C(10) interaction tends to stabilize the solid-state conformation in solution.

(40) The J_{H-H} in acyclic systems is around 8–10 Hz for axial–axial protons and 2–4 Hz for equatorial–equatorial or equatorial–axial protons. See for example: Becker, E. D. *High Resolution NMR*; Academic; New York, 1969; p 96.

the methyl group bonded to atom C(2) is at 1.09 ppm as a doublet (3 H). The HC(3) signal is at 4.32 ppm (d, 1 H). The values of J for some long-range couplings have also been calculated: J_{11-2} = 0.2 Hz and J_{11-1} = 0.7 Hz.

The $^{13}C(^1H)$ NMR spectrum is shown in Figure 5. The signals have been assigned[41] as follows: C(1), 57.8; C(2), 37.3; C(3), 65.8; C(4), 123.3; C(5), 116.7; C(6), 128.0; C(7), 117.3; C(8), 113.9; C(9), 148.7; C(10), 26.4; C(11), 9.07; C(12), 15.7; C(13) 144.3; C(14), 129.4; C(15), 112.5; C(16), 128.2; C(17), 112.5; C(18), 129.4 ppm (in deuteriochloroform).

Possible Mode of Formation of 7. The formation of heterocycle **7** probably proceeds according to Scheme I. The cyclometalation reaction is a well-known process, especially when transition metals stabilized by phosphine ligands are involved.[42] More specifically, both Rh(I)-promoted ortho metalation of a phenyl ring[43] and C–H bond activation in cyclopropane systems at low temperature (–60 °C) in the presence of UV radiation[44-47] are known. The resulting hydrido alkyls are usually very reactive[48] as they eliminate R–H. Despite several attempts we could neither isolate an orthometalated species nor obtain definitive information on it by ^1H NMR spectroscopy.[45] The ring closure to afford **7** can be a fast process formally equivalent to the R–H elimination from an R–Rh–H system. The steric hindrance around the two N atoms and the bulkiness of the heterocycle should make the Rh–N bond weak. As a consequence the quinoline formed should be readily displaced by the excess amino olefin present in the reaction medium. So as a result we would expect the rate-determining step for the formation of **7** to be the ortho-metalation process.[49] The role of Rh(I) in the naa conversion has been clearly demonstrated, and the action of other Lewis acids possibly present in the reaction medium can be ruled out. However, the systems used do not contain other Lewis bases in addition to the amines. The eneamine **3** seems to be primarily involved. The possible role of imines is not yet clear. Imines have not been found under the reaction conditions, but they are formed at higher temperatures.[13,16,50] This aspect and the role of the metal center in determining the stereochemistry of the reaction are currently under investigation.

Acknowledgment. This research was supported by the CNR-Rome, Progetti Finalizzati (Grant 83-00085-95 to M.A.), and the U.S. National Science Foundation (Grant CHE83-08076 to J.A.I.). We thank Delia Dell'Anna for experimental assistance.

Registry No. 1, 589-09-3; 2, 111742-35-9; (*E*)-3, 111690-87-0; 4, 111742-36-0; 5, 111717-95-4; (*Z*)-6, 111690-88-1; 7, 6590-82-5; $[RhCl(C_2H_4)_2]_2$, 12081-16-2; $PhNH_2$, 62-53-3.

Supplementary Material Available: Anisotropic thermal parameters (Table IV) (1 page) a listing of structure amplitudes (Table V) (18 pages). Ordering information is given on any current masthead page.

(41) (a) Boulton, A. J.; McKillop, A. *In Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Pergamon: Oxford, 1984; Vol. 2, p 11. (b) Johnson, C. S. *Ibid.* Vol. 2, p 117.

(42) Intramolecular C–H activation is usually slow. See: (a) Parshall, G. W.; Knoth, W. H.; Schunn, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 4990–4995. (b) Parshall, W. G. *Acc. Chem. Res.* **1970**, *3*, 139–144. (c) James, B. R.; Markham, L. D.; Wang, D. K. W. *J. Chem. Soc., Chem. Commun.* **1974**, 439–440.

(43) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Sabat, M.; Zanobini, F. *Organometallics* **1986**, *5*, 2557–2559.

(44) See, for example, the C–H activation of cyclopropane promoted by Rh(I). (a) Periana, R. A.; Bergman, R. G. *Organometallics* **1984**, *3*, 508–510. (b) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929–3939. (c) Aresta, M.; Ciccarese, A.; Quaranta, E. *C_1 Molecule Chem.* **1985**, *1*, 267–281.

(45) R–Rh–H species have been isolated at low temperatures (–60 °C) (see ref 46) and are stable in the solid state below 0 °C. In our case the metalation reaction was slowed down at low temperatures, but the N-heterocycle was not formed.

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(47) We are currently studying the effect of UV light on the synthesis of **7**.

(48) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332–338.

(49) Recently an unusual, rapid, reversible ortho metalation reaction has been reported for a Ru(II) complex: Stolzenberg, A. M.; Muetterties, E. L. *Organometallics* **1985**, *4*, 1739–1742.

(50) The fact that imines are not isolated might mean that they are more reactive and do not accumulate in the solution. But this is in contrast with the fact that they are found at temperatures higher than 60 °C.