

Carbon–Hydrogen and Carbon–Carbon Bond Activation of Cyclopropane by a Hydridotris(pyrazolyl)borate Rhodium Complex

Douglas D. Wick, Todd O. Northcutt, Rene J. Lachicotte, and William D. Jones*

Department of Chemistry, University of Rochester, Rochester, New York 14627

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Generation of the 16-electron fragment $\{[\text{HB}(3,5\text{-dimethylpyrazolyl})_3]\text{Rh}(\text{CNCH}_2\text{CMe}_3)\}$ (Tp'RhL) in the presence of cyclopropane results in C–H activation of the hydrocarbon. The cyclopropyl hydride complex rearranges in benzene solvent to the metallacyclobutane complex $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{CH}_2\text{CH}_2\text{CH}_2)$. Thermolysis of the rhodacyclobutane complex produces an η^2 -propylene complex. The related complex $\text{Tp}'\text{Rh}(\text{CN-2,6-xylyl})(\text{C}_2\text{H}_4)$ has been structurally characterized and displays η^3 -Tp' coordination, both in the solid state and in solution. Thermolysis of the rhodacyclobutane complex in the presence of neopentyl isocyanide leads to insertion of isocyanide into both Rh–C bonds of the metallacycle. Cyclobutane undergoes C–H but not C–C bond cleavage.

Introduction

Cracking and re-forming alkanes via carbon–carbon bond activation using heterogeneous catalysts is an important industrial process.¹ While intermolecular activation of alkane C–H bonds using homogeneous transition-metal complexes is well-established,² activation of unstrained alkane C–C bonds under similar conditions has not been reported. The selectivity for alkane C–H bond activation over C–C bond activation has been attributed to both kinetic and thermodynamic factors:^{1,3} i.e., the greater accessibility of the C–H bond vs the C–C bond within an alkane and the greater strength of a M–H bond vs a M–C bond⁴ formed in the activation step, respectively. The kinetic and thermodynamic barriers to C–C bond cleavage can be overcome by using strained hydrocarbons,^{1,5} ligands containing unstrained C–C bonds to direct intramolecular activation,^{3,6} or highly electrophilic metals.⁷ Cyclopropane has

been a particularly useful substrate, given the relief of ring strain⁸ that results from rupturing a C–C bond of the hydrocarbon.

The studies most relevant to the results presented here are those by Bergman¹ and Ghosh,^{5a} in which C–C bond cleavage of cyclopropane is accomplished via the rearrangement of a rhodium(III) cyclopropyl hydride complex to a rhodacyclobutane complex. These rearrangements occur in benzene solvent without significant production of phenyl hydride complexes; thus, they are considered intramolecular in nature, given the greater kinetic and thermodynamic selectivity of the metal fragment for benzene versus cyclopropane.⁹ Intermolecular C–C bond activation of cyclopropane is known to occur in the reaction of Zeise's dimer, $[\text{PtCl}_2(\text{C}_2\text{H}_4)_2]_2$, with cyclopropane, which produces a polymeric Pt(IV) complex; the polymer can be cleaved to a monomer with the addition of pyridine.¹⁰ An edge complex between platinum and cyclopropane is thought to form prior to insertion of the metal into the C–C bond.^{5d} Metallacyclobutane complexes¹¹ are typically more stable than their dialkyl analogues.¹² However, this stability does not preclude interesting reactivity such as the formation of alkene,¹³ ylide,¹⁴ and π -allyl hydride¹⁵ complexes. Metallacyclobutane complexes can also be formed and

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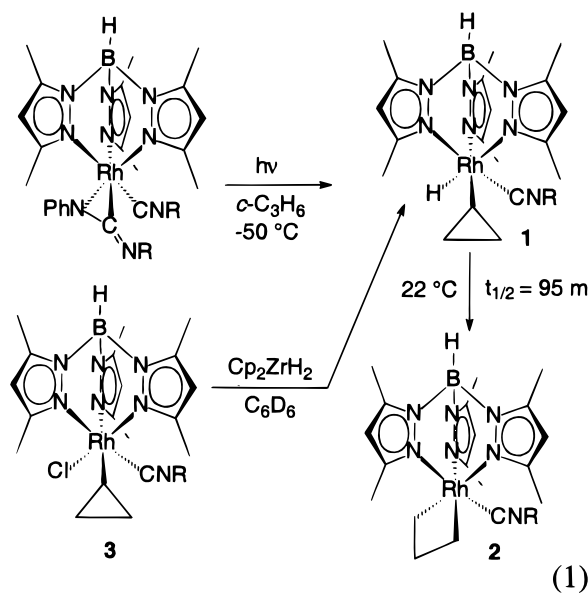
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fragmented by cycloaddition reactions, such as those involved in catalytic olefin metathesis reactions.¹⁶

We report here that the cyclopropyl hydride complex $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(c\text{-C}_3\text{H}_5)\text{H}$ (**1**, where $\text{Tp}' = \text{HB}(3,5\text{-dimethylpyrazolyl})_3$) rearranges intramolecularly in benzene solution at ambient temperature to the ring-opened rhodacyclobutane complex, (**2**). Complex **2** has been fully characterized and its rearrangement and isocyanide insertion reactions investigated. The ring-opening process does not occur from the cyclobutyl hydride complex, $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{H})(c\text{-C}_4\text{H}_7)$ (**7**).

Results and Discussion

Preparation and Characterization of $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(c\text{-C}_3\text{H}_5)\text{H}$ (1**) and $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{CH}_2\text{CH}_2\text{CH}_2)$ (**2**).** The cyclopropyl hydride complex $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(c\text{-C}_3\text{H}_5)\text{H}$ (**1**) can be prepared by photolysis ($\lambda > 345$ nm) of a cyclopropane solution of $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{PhN}=\text{C}=\text{NCH}_2\text{CMe}_3)$ or by reaction of the cyclopropyl chloride complex $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(c\text{-C}_3\text{H}_5)\text{Cl}$ (**3**)¹⁷ with Cp_2ZrH_2 in benzene (eq 1). In the ¹H NMR spectrum of **1** in C_6D_6



a doublet at $\delta -14.892$ is assigned to the hydride ligand and four multiplets from $\delta 0.9$ to 2.1 in a 2:1:1:1 ratio are assigned to the five protons of the cyclopropyl ring. The resonances for the neopentyl isocyanide ligand of **1** are shifted upfield from those in **3**. Resonances for the Tp' ligand are in a pattern that is consistent with tridentate coordination of the ligand to a chiral octahedral $\text{Rh}(\text{III})$ center, i.e., a 3:3:3:3:3:1:1:1 ratio of the distinct methyl and methine group singlets.

The cyclopropyl hydride complex rearranges to the rhodacyclobutane complex $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{CH}_2\text{-}$

$\text{CH}_2\text{CH}_2)$ (**2**) at ambient temperature in benzene (eq 1). The yield of **2** as shown by ¹H NMR spectroscopy is 95%, the remaining 5% being $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{C}_6\text{D}_5)\text{D}$. This result indicates that the rearrangement is intramolecular, since reductive elimination of cyclopropane would lead to activation of the phenyl C–D bond and not activation of the cyclopropane C–C bond. The rearrangement of **1** to **2** in C_6D_6 at 22°C was monitored by ¹H NMR spectroscopy and found to be first order in **1** with a rate constant of $[1.26(24)] \times 10^{-4} \text{ s}^{-1}$. This rate constant is approximately half that for the rearrangement of $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{H})(c\text{-C}_3\text{H}_5)$ to $(\text{C}_5\text{Me}_5)\text{-Rh}(\text{PMe}_3)(\text{CH}_2\text{CH}_2\text{CH}_2)$ at -20°C in toluene-*d*₈ ($k = [2.1(2)] \times 10^{-4} \text{ s}^{-1}$),¹ which indicates the greater stability of **1** compared to that of its Cp^* analogue. The rhodacyclobutane complex is air-stable and has been fully characterized by NMR (¹H and ¹³C{¹H}) and IR spectroscopy and elemental and single-crystal X-ray diffraction analyses.

The ¹H NMR spectrum of **2** in C_6D_6 shows resonances for the Tp' methyl groups and methine protons in a 2:1 ratio, which indicates that two of the three pyrazolyl rings are equivalent by a plane of symmetry containing a pyrazolyl ring, rhodium, and C_β of the rhodacyclobutane ring. Four multiplets at $\delta 1.626, 2.050, 3.340,$ and 3.620 in a 2:2:1:1 ratio are assigned to $\text{H}_\alpha, \text{H}_{\alpha'}, \text{H}_\beta,$ and $\text{H}_{\beta'}$, respectively, of the rhodacyclobutane moiety. Two singlets at $\delta 0.680$ and 2.612 in a 9:2 ratio are assigned to the *tert*-butyl and methylene protons of the neopentyl isocyanide ligand, the latter being equivalent due to the C_s symmetry of the molecule. The IR spectrum of **2** shows an absorption for the isocyanide CN stretch at 2161 cm^{-1} , which is significantly lower than that for the isocyanide stretch in **3** (2211 cm^{-1}) and $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{C}_6\text{H}_5)\text{H}$ (2178 cm^{-1})¹⁸ but is still consistent with the isocyanide ligand being coordinated to a $\text{Rh}(\text{III})$ center. The ¹³C{¹H} NMR spectrum of **2** displays two doublets at $\delta -16.39$ and 35.61 for C_α and C_β , respectively, of the metallacyclobutane moiety. The NMR data are comparable to those for previously characterized platinacyclobutanes¹⁹ and two rhodacyclobutane complexes $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{CH}_2\text{CH}_2\text{CH}_2)$ ¹ and $\text{Tp}'\text{Rh}(\text{CO})(\text{CH}_2\text{CH}_2\text{CH}_2)$ ^{5a} (Table 1).

The solid-state structure of **2** as determined by single-crystal X-ray analysis is fully consistent with the NMR data (Figure 1). Selected bond angles and distances are listed in Table 2. The nonbonded contact distance of 2.42 \AA between C_1 and C_3 of the ring indicates that the cyclopropane ring is cleaved, not intact, as in an edge-bound complex with C–C bond distances similar to those in free cyclopropane (1.52 \AA).¹¹ For other metallacyclobutane complexes the range of distances for this nonbonded contact is between 2.37 and 2.6 \AA .¹¹ The geometrical structure of **2** is a distorted octahedron, and the rhodacyclobutane ring is nearly planar. The minimal puckering of the ring is indicated by a dihedral angle of 9.1° for the intersecting planes $\text{Rh}-\text{C}_1-\text{C}_3$ and $\text{C}_1-\text{C}_2-\text{C}_3$ and a dihedral angle of 9.2° for planes $\text{Rh}-$

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(19) ¹³C{¹H} NMR data for C_α and C_β of the metallacyclobutane ligand: $\text{Pt}(\text{C}_3\text{H}_6)(\text{Cl})_2(\text{C}_5\text{H}_5\text{N})_2$, $\delta -15.2$ and 30.0 ;^{5d} $\text{Pt}(\text{C}_3\text{H}_6)(\text{Br})_2(\text{C}_5\text{H}_5\text{N})_2$, $\delta -17.9$ and 30.4 .^{5d}

Table 1. Selected ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR Data for the Rhodacyclobutane Complexes

compd	H_α	H_β	C_α (J_{RhC} , Hz)	C_β (J_{RhC} , Hz)
$\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{CH}_2\text{CH}_2\text{CH}_2)^a$	m, 1.63; m, 2.05	m, 3.34; m, 3.62	d, -16.39 (16)	d, 35.61 (5)
$\text{Tp}'\text{Rh}(\text{CO})(\text{CH}_2\text{CH}_2\text{CH}_2)^b$	m, 1.40; m, 1.65	m, 2.82; m, 3.15	d, -13.31 (15.0)	d, 35.50 (3.7)
$(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{CH}_2\text{CH}_2\text{CH}_2)^c$	m, 0.20; m, 0.38	m, 3.20; m, 3.48	tdd, -22.85 (19.1)	dt, 31.33 (5.8)

^a C_6D_6 solvent. ^b CD_2Cl_2 solvent.

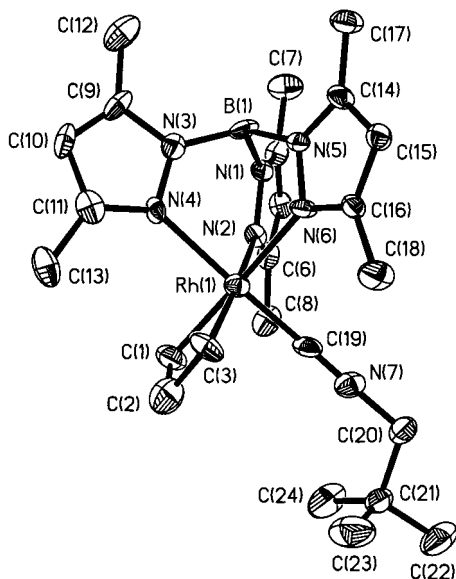


Figure 1. ORTEP drawing of $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{CH}_2\text{CH}_2\text{CH}_2)$ (**2**). Ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

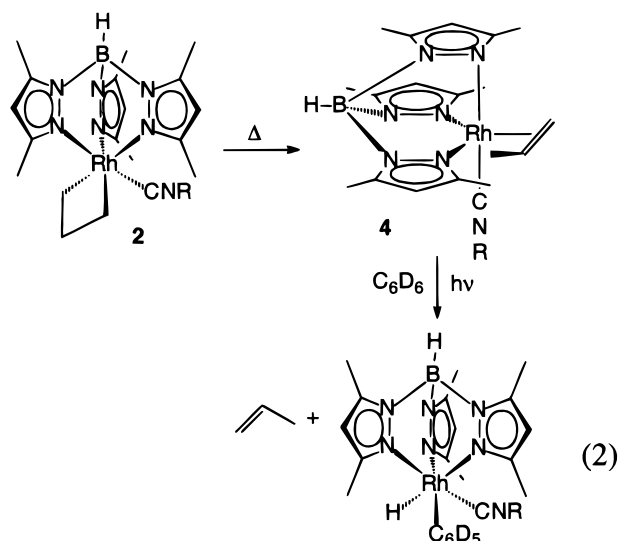
Table 2. Selected Bond Angles (deg) and Distances (Å) for $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{CH}_2\text{CH}_2\text{CH}_2)$ (**2**)

C1-C2-C3	103(1)	C3-Rh-N6	100.7(4)
Rh-C1-C2	93.6(8)	C3-Rh-C19	87.3(5)
Rh-C3-C2	91.6(7)	C19-Rh-N4	177.7(4)
C1-Rh-C3	71.0(5)	C19-Rh-N2	93.0(4)
C1-Rh-N4	92.8(4)	C19-Rh-N6	94.1(4)
C1-Rh-N2	101.0(4)	C19-N7-C20	177(1)
C1-Rh-N6	171.2(4)	Rh-C19-N7	179(1)
C1-Rh-C19	88.4(5)	N4-Rh-N2	84.9(3)
C3-Rh-N4	94.8(4)	N4-Rh-N6	85.0(4)
C3-Rh-N2	171.9(4)	N6-Rh-N2	87.4(3)
Rh-C1	2.05(1)	C19-N7	1.15(1)
Rh-C3	2.11(1)	Rh-N2	2.209(8)
C1-C2	1.55(2)	Rh-N4	2.182(9)
C2-C3	1.54(2)	Rh-N6	2.176(9)
Rh-C19	1.88(1)		

C1-C2 and Rh-C2-C3. The two angles of the rhodacyclobutane moiety with C_α as the vertex (93.6° and 91.6°) are notably smaller than the same angles in $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{CH}_2\text{CH}_2\text{CH}_2)$ (99.5 and 96.6°).¹ However, these differences are not correlated to significant differences in the Rh-C and C-C bond lengths of the metallacycle between the two complexes.

Thermal Reactions of 2. The formation of olefins from the thermolysis of platinacyclobutanes has been the subject of numerous studies.^{5d,12-14,20} Since few rhodacyclobutane complexes have been isolable^{1,5a,21} it

was of interest to examine the products from thermolysis of **2**. Two products are observed in a ^1H NMR spectrum of a sample of **2** in C_6D_6 that had been heated to 55°C for 2.5 h (eq 2). Two sets of Tp' and neopentyl



isocyanide resonances are observed in a 2:1 ratio. The spectrum displays a pattern for each set of Tp' resonances (six methyl resonances + three methine resonances), indicating that the ligand is in an asymmetric environment. Resonances for free cyclopropane or hydride ligands are not observed. The resonance for the *tert*-butyl group of the neopentyl isocyanide ligand for each species is upfield of that for known Rh(III) complexes of the type $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{R})\text{Cl}$.¹⁷ This upfield shift has been observed for the Rh(I) complex $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{C}_2\text{H}_4)$, formed upon irradiation of $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{PhN}=\text{C}=\text{NCH}_2\text{CMe}_3)$ in the presence of ethylene.²² A number of overlapping multiplet resonances are observed in the ^1H NMR spectrum of the thermolysis sample but could not be properly assigned to olefin protons for the two products using homonuclear decoupling experiments. The two products are assigned as isomers of the propylene complex $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\eta^2\text{-propylene})$ (**4**).

Further evidence for the formulation of **4** as the η^2 -propylene complex comes from substitution experiments. Continued heating of the same sample at 90°C for an additional 12 h converts $\sim 3\%$ of the starting material to $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{C}_6\text{D}_5)\text{D}$ and propylene. The ratio of the starting rhodium complexes still present remains 2:1. Using a Hg/Xe light source, photolysis of the sample for 80 min at room temperature converts all of the starting material to $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)$ -

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Table 3. Summary of Crystallographic Data for $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{C}_3\text{H}_6)$ and $\text{Tp}'\text{Rh}(\text{CN-2,6-xylyl})(\text{C}_2\text{H}_4)$

	$\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{C}_3\text{H}_6)$, (2)	$\text{Tp}'\text{Rh}(\text{CN-2,6-xylyl})(\text{C}_2\text{H}_4)$
Crystal Parameters		
chem formula	$\text{C}_{24}\text{H}_{39}\text{BN}_7\text{Rh}$	$\text{C}_{26}\text{H}_{35}\text{BN}_7\text{Rh}$
fw	539.33	559.33
cryst syst	monoclinic	triclinic
space group (No.)	$P2_1/n$ (14)	$P\bar{1}$ (2)
Z	4	2
a , Å	9.828(21)	8.178(5)
b , Å	25.995(11)	10.465(4)
c , Å	10.986(12)	16.348(10)
α , deg	90	77.61(4)
β , deg	106.00(15)	84.23(3)
γ , deg	90	84.88(3)
vol., Å ³	2698(6)	1356.3(13)
ρ_{calcd} , g cm ⁻³	1.328	1.370
cryst dimens, mm	$0.34 \times 0.26 \times 0.23$	$0.02 \times 0.04 \times 0.08$
temp, °C	-30	-90
Measurement of Intensity Data		
diffractometer	Enraf-Nonius CAD4	Siemens SMART
radiation (λ , Å)	Mo (0.710 73)	Mo (0.710 73)
2θ range, deg	4–50	4–46.5
data collected	$+h,+k,\pm l$	$-7 \leq h \leq 9, -11 \leq k \leq 11, -18 \leq l \leq 14$
no. of data collected	5153	5541
no. of unique data	5071	3565
agreement between equiv data	0.0502	0.0499
no. of obsd data	2453 ($I > 3\sigma(I)$)	2633 ($I > 2\sigma(I)$)
no. of params varied	298	316
μ , cm ⁻¹	6.56	6.57
abs cor	differential (DIRDIF)	empirical (SADABS)
range of transmission factors	0.46–1.00	0.81–0.93
$R1(F_o)$, $wR2(F_o^2)$ ($I > 2\sigma(I)$)		0.0788, 0.1401
$R1(F_o)$, $wR2(F_o^2)$ (all data)		0.1133, 0.1576
$R1(F_o)$, $R_w(F_o)$ ($I > 3\sigma(I)$)	0.06448, 0.06325	
goodness of fit	1.842	1.082

(C_6D_5)D (90% of total rhodium products), propylene²³ and the rhodacyclobutane complex **2** (10% of total rhodium products). No further changes are observed with continued irradiation for 3.5 h.

The structure of **4** could be either square-planar (η^2 -Tp')Rh(CNR)(propylene), as seen in the X-ray structures of (η^2 -Tp')Rh(CNR)₂ (R = Me, 2,6-xylyl, neopentyl),²⁴ [B(pyrazolyl)₄]Rh(cod),²⁵ and Tp'Rh(PMe₃)(CO),²⁶ or pseudo-trigonal-bipyramidal (η^3 -Tp')Rh(CNR)(propylene), as seen in the X-ray structure of (η^3 -Tp')Rh(CNtolyl)(η^2 -tolyl-N=C=N-xylyl).¹⁸ A recent structure determination of hydridotriss(3,5-diisopropylpyrazolyl)borate–rhodium(norbornadiene) shows both η^2 - and η^3 -Tp groups in two distinct molecules within the asymmetric unit.²⁷ The former possible structure would be associated with a d⁸ Rh(I) configuration, whereas the latter would be associated with a d⁶ Rh(III) configuration. While neither **4** nor the ethylene complex Tp'Rh(CNCH₂CMe₃)(C₂H₄) provided X-ray-quality crystals, the derivative Tp'Rh(CN-2,6-xylyl)(C₂H₄) did, and it was able to be structurally characterized. The complex was isolated by thermal ligand exchange of 2,6-xylyl isocyanide with Tp'Rh(C₂H₄)₂.

Tp'Rh(CN-2,6-xylyl)(C₂H₄) crystallizes in space group $P\bar{1}$ ($Z = 2$) with one molecule in the asymmetric unit. The structure shows an η^3 -Tp' ligand occupying one

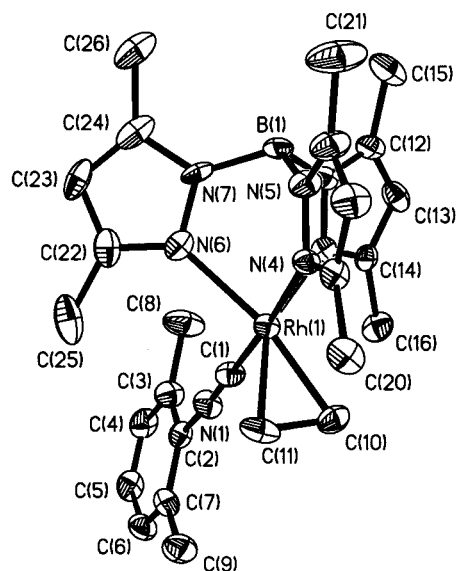


Figure 2. ORTEP drawing of $\text{Tp}'\text{Rh}(\text{CN-2,6-xylyl})(\text{C}_2\text{H}_4)$. Ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

axial and two equatorial sites of a trigonal bipyramid in which one pyrazolyl ring is trans to the axial isocyanide and the remaining two pyrazole rings are trans to the ethylene carbons (Figure 2). The compound could also be described as containing significant d⁶ Rh(III) character. Selected distances and angles are given in Table 4. The IR spectrum shows a strong band at 2110 cm⁻¹ in KBr, which shifts only slightly in hexane solution (2105 cm⁻¹), indicating similar solid-state and solution structures. On the basis of this structure, **4** is also believed to contain an η^3 -Tp' ligand.

(23) ¹H NMR (C_6D_6): δ 1.540 (dt, $J = 6.2$ and 1.6 Hz, 3 H, $\text{CH}_2\text{-CHCH}_3$), 4.929 (dm, 1 H, CH_2CHCH_3), 5.000 (dm, 1 H, CH_2CHCH_3), 5.708 (dd, $J_{\text{cis}} = 10$ Hz, $J_{\text{trans}} = 17$ Hz, 1 H, CH_2CHCH_3).

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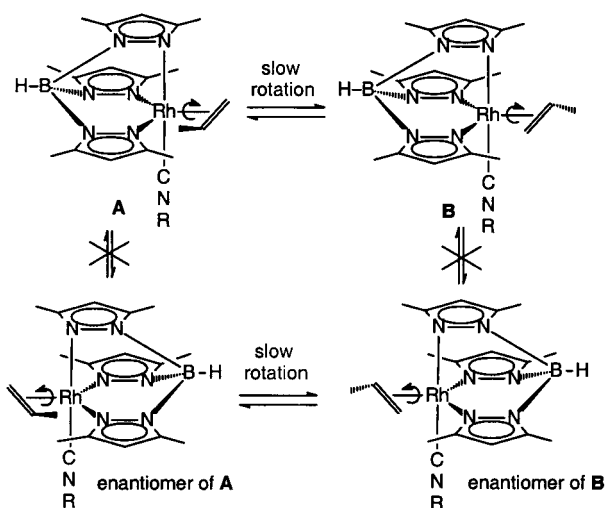
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Table 4. Selected Bond Angles (deg) and Distances (Å) for Tp'Rh(CN-2,6-xylyl)(C₂H₄)

C1–Rh–N4	176.2(4)	C10–Rh–N4	95.2(4)
C10–Rh–N6	164.9(4)	C11–Rh–N4	95.7(4)
C11–Rh–N2	151.4(4)	C11–Rh–N6	123.9(4)
C1–Rh–N6	92.9(4)	C10–Rh–N2	110.3(4)
C1–Rh–N2	94.3(4)	C1–Rh–C11	84.9(4)
C10–Rh–C11	41.1(4)	C1–Rh–C10	87.7(4)
Rh–N2	2.195(7)	Rh–C10	2.098(10)
Rh–N4	2.178(7)	Rh–C11	2.088(10)
Rh–N6	2.187(8)	C10–C11	1.469(14)
Rh–C1	1.845(11)		

Scheme 1

In addition, the recent paper by Akita et al. demonstrated that the frequency of the B–H stretch could be used to reliably assign the hapticity of the trispyrazolylborate ligand.²⁷ η^3 -Coordination was associated with $\nu_{\text{B-H}} > 2500 \text{ cm}^{-1}$, whereas η^2 -coordination was associated with $\nu_{\text{B-H}} < 2500 \text{ cm}^{-1}$. We have found a similar trend for Tp'Rh(CNR) complexes for which we have X-ray structural data. The η^2 -Tp'-containing complexes Tp'Rh(CNR)₂ (R = 2,6-xylyl, methyl) both display a $\nu_{\text{B-H}}$ value of 2471 cm^{-1} in their IR spectra (benzene solution). The complexes Tp'Rh(CNR)(C₂H₄) (R = neopentyl, 2,6-xylyl) display $\nu_{\text{B-H}}$ values of 2519 and 2521 cm^{-1} , respectively, indicating η^3 -Tp' coordination in hexane solution. The propylene complex **4** displays a $\nu_{\text{B-H}}$ of 2520 cm^{-1} in hexane solution, again consistent with η^3 -Tp' coordination. It is likely, however, that the η^3 -Tp' complex is involved in a facile, uphill equilibrium with the η^2 -Tp' form, as has been seen in other cases.²⁸

The experimental observation of inequivalent amounts of two isomers of **4** is consistent with an η^3 -Tp' complex with a static (nonrotating) propylene ligand. Were the olefin rotating rapidly, one would expect to observe only one isomer (Scheme 1). By comparison, several other TpM(olefin) complexes are believed to be static.^{29,30}

Ghosh and Graham have reported that thermolysis of the related complex Tp'Rh(CO)(CH₂CH₂CH₂) in C₆D₆

at $75 \text{ }^\circ\text{C}$ yields the η^2 -propylene complex Tp'Rh(CO)(η^2 -CH₂=CHCH₃) and free cyclopropane in a 3:1 ratio.^{5a} Only one isomer of the propylene complex was reported, which showed nine pyrazolyl resonances at $-60 \text{ }^\circ\text{C}$. On the basis of NMR and IR data they suggest that at ambient temperature the propylene complex is square planar (sp) and that the pyrazolyl ring resonances are averaged by a rapid fluxional process. Additionally, they have proposed that at low temperature the fluxional process is slowed to allow for the intermediacy of a trigonal-bipyramidal structure. The production of the η^2 -propylene complex was proposed to occur by way of an unobserved propylenyl hydride complex, which is known to be thermally unstable and to rearrange to the η^2 -propylene complex.^{5a} They also report that thermolysis of the methyl substituted rhodacyclobutane

complex Tp'Rh(CO)(CH₂CHMeCH₂) yields an η^2 -isobutylene complex (not observed but assumed due to the presence of free isobutylene) and free methylcyclopropane in a ratio of 1:4. The β -methyl group appears to block β -hydride elimination from the face of the ring containing the methyl group. Reductive elimination thus becomes the preferred pathway.

The formation of olefins and olefin complexes^{13a} from thermolysis of metallacycles is well-known. Olefin formation is generally thought to occur by abstraction of a β -hydrogen from the ring to give an allyl hydride complex which reductively eliminates olefin, commonly referred to as β -hydride elimination. Whitesides and co-workers have provided evidence for β -hydride elimination from Pt(II) metallacyclopentanes following phosphine association.^{12a} Johnson and Cheng found that alkyl-substituted platinacyclobutanes (Pt(IV)) form olefins via β -hydride elimination following ligand dissociation.^{13b} While allyl hydride species have been proposed as intermediates in the above systems, they have not been observed.

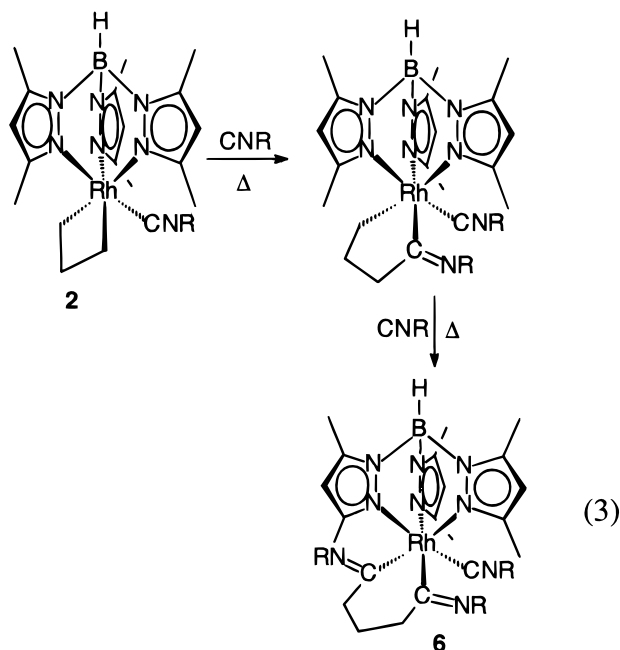
The above results from the thermolysis of **2** suggest that if β -hydride elimination is occurring to form the η^2 -propylene complex **4**, it proceeds much faster than reductive elimination of cyclopropane. Thus, the propylenyl hydride complex **5** is implicated as an intermediate in a β -hydride elimination to form the olefin complex.²²

Reaction of 2 with Isocyanide. Thermolysis of a C₆D₆ solution of **2** in the presence of 2 equiv of neopentyl isocyanide between 55 and $90 \text{ }^\circ\text{C}$ gives the first examples of insertion of neopentyl isocyanide into a Rh–C bond of a complex of the type Tp'Rh(CNCH₂CMe₃)(R)(R'), where R = H or alkyl and R' = alkyl. The rhodacyclobutane complex is almost fully reacted after 2.5 h of heating at $55 \text{ }^\circ\text{C}$. Two products are observed initially by ¹H NMR spectroscopy, and with continued heating one of the products is fully converted to the other with the simultaneous disappearance of free isocyanide (eq 3). The ¹H NMR spectrum of the final product exhibits resonances for the Tp' ligand in a 2:1 pattern, which indicates that two of the three pyrazolyl rings are equivalent. The singlets at δ 0.623 and 0.999 in a 9:18 ratio are assigned to the *tert*-butyl group of a rhodium-bound neopentyl isocyanide ligand and those of two neopentyl isocyanide ligands which have inserted into the α -Rh–C bonds of **2**, respectively. The structure of the metallacyclohexane complex **6** contains a plane

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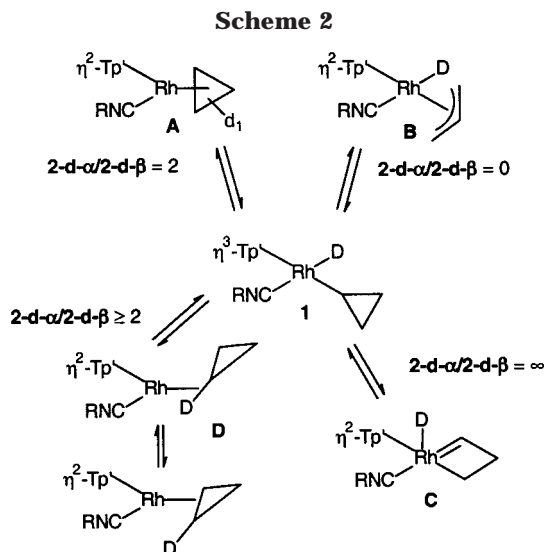
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of symmetry which accounts for the equivalence of two of the three pyrazolyl rings. An AB quartet of doublets at δ 1.722 which is integrated as four protons relative to the singlet at δ 0.623 is assigned to the pairs of diastereotopic methylene protons of the inserted isocyanide ligands. The doublet has a coupling constant of 2 Hz, which corresponds to a four-bond Rh–H coupling. The ^1H NMR data for the intermediate mono-inserted compound indicate that all three pyrazolyl rings of its Tp' ligand are inequivalent. The spectrum also shows two singlets at δ 0.592 and 1.056 in a ratio of 1:1, which are assigned to the rhodium-bound and inserted neopentyl isocyanide groups, respectively. Continued heating at 90 °C for 12 h leads to decomposition of **6** and generation of $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{C}_6\text{D}_5)\text{D}$ as the dominant organometallic species (30%). No organic product(s) of the reaction could be identified. The related rhodacyclobutane complex $\text{Tp}'\text{Rh}(\text{CO})(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)$ inserts CO to give the mono-inserted rhodacyclopentane complex after 1 week at ambient temperature under 950 psi of CO.^{5a} The di-inserted rhodacyclohexane complex results after heating the mono-inserted product to 75 °C under 1000 psi of CO for 8 days. No organic products via reductive elimination of the cycloalkane rings were observed for this system.

Mechanistic Considerations for the Rearrangement of 1 to 2. It was stated earlier that the rearrangement of **1** to **2** was intramolecular in nature. To more rigorously examine this process, the rearrangement of $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(c\text{-C}_3\text{H}_5)\text{D}$ (**1-d**; prepared from the reaction of **3** with Cp_2ZrD_2 in C_6H_6) to the labeled rhodacyclobutane complex **2-d** was monitored by ^1H NMR (with presaturation of the solvent resonance) and $^2\text{H}\{^1\text{H}\}$ NMR spectroscopy at 22 °C. The metallacyclobutane products formed in ~98% yield (NMR).

In the rearrangement of **1-d** to **2-d** the deuterium label is found to reside in both the α - and β -carbon positions of **2-d**. The ratio of $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)-$



$(\text{CHDCH}_2\text{CH}_2\text{CH}_2)$ (**2-d- α**) to $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{CH}_2\text{CHDCH}_2)$ (**2-d- β**) was 2.2:1 as determined by the ratio of the integral values of the multiplets at δ 1.63 and 2.05 (H_α) to the multiplets at δ 3.34 and 3.60 (H_β) in a ^1H NMR spectrum of the sample. Only a minor amount of isomerization of **1-d** to $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{CDCH}_2\text{CH}_2)\text{H}$ is indicated by the observation of a doublet at δ -14.9. This process is extremely slow compared to the ring-opening reaction as $\text{Tp}'\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{CDCH}_2\text{CH}_2)\text{H}$ constitutes no more than 2% of the total mixture.

Periana and Bergman have presented results of an experiment using the related ^{13}C -labeled cyclopropyl hydride complex $\text{Cp}^*\text{Rh}(\text{PMe}_3)(^{13}\text{CHCH}_2\text{CH}_2)\text{H}$, which gave insight into the mechanism of C–C bond cleavage of cyclopropane via the cyclopropyl hydride complex.¹ In their study they found that the ^{13}C label resided predominantly at the α -carbon position in the rhodacyclobutane complex. The ratio of α - to β -labeled compounds was 5.6:1, which is greater than the statistical value of 2:1 predicted by random scrambling of the label, suggesting that the rearrangement proceeded by regiospecific insertion of the C–C bond α to the rhodium atom. Isomerization of $\text{Cp}^*\text{Rh}(\text{PMe}_3)(^{13}\text{CHCH}_2\text{CH}_2)\text{H}$ to $\text{Cp}^*\text{Rh}(\text{PMe}_3)(\text{CH}^{13}\text{CH}_2\text{CH}_2)\text{H}$, which would then rearrange to the β -labeled rhodacyclobutane, was determined to be a slow process compared to the ring-opening reaction. This result further supported the predominance of the α - ^{13}C -labeled metallacyclobutane complex.

Periana and Bergman considered a number of mechanisms to account for the results from their study of the rearrangement of $\text{Cp}^*\text{Rh}(\text{PMe}_3)(^{13}\text{CHCH}_2\text{CH}_2)\text{H}$ to $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(^{13}\text{CH}_2\text{CH}_2\text{CH}_2)$. These are applicable to the discussion of the results from the present study; the intermediates for each mechanism are depicted in Scheme 2, which is an adaptation from their work.¹ Each intermediate could rearrange to give metallacyclobutane **2**. A value for $2\text{-d-}\alpha/2\text{-d-}\beta$ of 2.0 would be expected for random scrambling of the deu-

terium label, as shown for intermediate A of Scheme 2. The intermediate is a "symmetrically coordinated" cyclopropane complex in which random C–C bond insertion can occur. This type of coordination is thought to occur on metal surfaces,^{1,5e} but there is no precedent in homogeneous solution. Given that the experimental value of **2-d- α /2-d- β** is ~ 2 , mechanism A cannot be ruled out.

Intermediate B, a π -allyl hydride complex, could form by the labilization of one of the Tp' pyrazolyl rings, generating a bidentate Tp' complex. This type of labilization has been implicated in the mechanism of reductive elimination of benzene from Tp'Rh(CNCH₂CM₃)(C₆H₅)H³¹ and of methane from Tp'Rh(CNCH₂CM₃)(CH₃)H.²² Formation of the rhodacyclobutane complex would then occur by hydride attack at the β -carbon of the π -allyl ligand, and the expected value of the ratio of **2-d- α /2-d- β** would be close to zero. Periana and Bergman have shown that the π -allyl cation Cp*Rh(PMe₃)(η^3 -CH₂CHCH₂)⁺, which is formed by halide abstraction from Cp*Rh(PMe₃)(I)(*c*-C₃H₅), is attacked by hydride preferentially at the β -carbon of the π -allyl ligand. Independent studies show that halide abstraction from Tp'Rh(CNCH₂CM₃)(Br)(*c*-C₃H₅) followed by chloride addition yield only unrearranged Tp'Rh(CNCH₂CM₃)(Cl)(*c*-C₃H₅), (**3**).¹⁷ The results from the present labeling study are not consistent with intermediate B. The **2-d- α /2-d- β** ratio of ~ 2 indicates that a substantial quantity of the deuterium label resides at the α -position.

Formation of a metal–carbene species by α -elimination, intermediate C, requires coordinative unsaturation of the metal, which could be achieved by detaching one of the three arms of the Tp' ligand. Arguing against intermediate C, however, is the fact that deuterium should *only* appear at the α -carbon of **2**. The observed ratio of ~ 2 for **2-d- α /2-d- β** is therefore inconsistent with this pathway.

Intermediate D invokes the intermediacy of an alkane complex in which a C–H or C–C bond of cyclopropane interacts weakly with a rhodium(I) metal center. Independent evidence convincingly argues for the existence of alkane intermediates in the reductive elimination of methane from Tp'Rh(CNCH₂CM₃)(CH₃)H in benzene and the isomerization of Tp'Rh(CNCH₂CM₃)(*i*-Pr)H to Tp'Rh(CNCH₂CM₃)(*n*-Pr)H in benzene,²² and in alkane activation by Tp'Rh(CO)₂.³² Furthermore, if the migration from the σ -C–H bond to the σ -C–C bond is reversible, then incorporation of label into the β -carbon positions of **2** can be accommodated by a series of reversible migrations. The observed ratio for **2-d- α /2-d- β** of 2.2 indicates that the rate of C–C insertion in the σ -C–C complex must be slower than back-migration to the σ -C–H complex, unlike the example studied by Periana and Bergman. Intermediate D best explains the observed results in a consistent and simple manner.

Is the Ring-Opening Mechanism General for Other Strained Hydrocarbons? Given that C–H

activation of cyclopropane was followed by C–C activation, it was of interest to determine if this process was general for other strained-ring hydrocarbons such as cyclobutane. Photolysis ($\lambda > 345$ nm) of a cyclobutane solution of the Rh–carbodiimide complex for 30 min at -15 °C followed by evaporation of the solvent gives a red solid. The ¹H NMR spectrum of a C₆D₆ solution of the solid shows a doublet at $\delta -15.531$ with a RhH coupling constant of 25 Hz. The chemical shift and coupling constant are characteristic of known cycloalkyl hydride complexes.³³ The pattern and relative intensities of the resonances for the Tp' and neopentyl isocyanide ligands are consistent with an octahedral chiral Rh(III) complex containing a tridentate Tp' ligand. This complex is identified as the cyclobutyl hydride complex Tp'Rh(CNCH₂CM₃)(*c*-C₄H₇)H (**7**). At 22 °C **7** in C₆D₆ does not rearrange to the C–C bond-cleaved rhodacyclopentane complex but rather reductively eliminates cyclobutane with a first-order rate constant of $[5(1)] \times 10^{-4} \text{ s}^{-1}$; growth of a singlet at $\delta 1.881$ for free cyclobutane is observed in the ¹H NMR spectrum of this sample. This rate constant corresponds to a half-life of approximately 23 min, which is intermediate between that for reductive elimination of cyclopentane from Tp'Rh(CNCH₂CM₃)(*c*-C₅H₉)H (**7** min at 23 °C in C₆H₆) and that for reductive elimination of pentane from Tp'Rh(CNCH₂CM₃)(*n*-C₅H₁₁)H (54 min at 23 °C in C₆H₆).³³

Conclusions

The reaction of Tp'Rh(CNCH₂CM₃)(*c*-C₃H₅)Cl (**3**) and Cp₂ZrH₂ in C₆D₆ gives Tp'Rh(CNCH₂CM₃)(*c*-C₃H₅)H (**1**) in quantitative yield. The cyclopropyl hydride complex rearranges to the rhodacyclobutane complex

Tp'Rh(CNCH₂CM₃)(CH₂CH₂CH₂) (**2**) with a half-life of 1.6 h at 22 °C in C₆D₆. A single-crystal X-ray analysis of **2** confirms the characterization of **2** as a metallacycle. A deuterium labeling study in which **1-d** rearranges to **2-d** shows that rhodium inserts randomly into the C–C bonds of cyclopropane following deuteride migration from the metal to the ring. The rhodacyclobutane complex is thermally unstable and rearranges to the photolabile propylene complex, (η^3 -Tp')Rh(CNCH₂CM₃)(η^2 -H₂C=CHCH₃) (**4**). Neopentyl isocyanide inserts into both Rh–C α bonds of **2** when a C₆D₆ solution of **2** is heated in the presence of neopentyl isocyanide. The cyclobutyl hydride complex **7** in C₆D₆ does not undergo a rearrangement similar to **1**; rather, it reductively eliminates cyclobutane.

Experimental Section

General Considerations. All reactions, recrystallizations, chromatography, and routine manipulations, unless otherwise noted, were carried out at ambient temperature under a nitrogen atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corp. Dri-lab. All hydrocarbon solvents were distilled under nitrogen or vacuum from dark purple solutions of sodium benzophenone ketyl. Chlorinated solvents were distilled under vacuum from calcium hydride suspensions. Silica gel (200–400 mesh, 60 Å) for column chromatography was purchased

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from Aldrich Chemical Co. and dried under vacuum at 200 °C. Silica gel plates (2 mm) used in preparative thin-layer chromatography contained a fluorescent indicator and were purchased from Analtech. Cyclopropane (CP grade) was purchased from Matheson and used as received. Cyclobutane was prepared according to a literature method.³⁴ TpRh(CNCH₂CMe₃)(PhN=C=NCH₂CMe₃),¹⁸ Cp₂ZrH₂,³⁵ 3,¹⁷ neopentyl isocyanide,³⁶ and Tp'Rh(C₂H₄)₂³⁷ were prepared as described in the literature.

¹H (400 MHz), ²H (61 MHz), and ¹³C (100 MHz) NMR spectra were recorded on a Bruker AMX-400 spectrometer. All chemical shifts are reported in ppm (δ) relative to tetramethylsilane and referenced to the chemical shifts of residual solvent resonances (C₆D₆, δ 7.15). Chemical shifts for ¹³C NMR were measured in ppm relative to the deuterated solvent resonance (C₆D₆, δ 128.0). Chemical shifts for ²H NMR were measured in ppm relative to the deuterated solvent resonance of added C₆D₆, δ 7.15. Elemental analyses were performed by Desert Analytics. An Enraf-Nonius CAD4 diffractometer and a Siemens SMART (CCD) diffractometer were used for X-ray crystal structure determination of complexes **2** and Tp'Rh(CN-2,6-xylyl)(C₂H₄), respectively. Infrared spectra were recorded by a Mattson Instruments 6020 Galaxy Series FTIR and processed with First:Aquire v1.52 software. Photolysis experiments were performed using a 200 W Hg(Xe) arc lamp (Oriol). High-resolution MS were obtained by the UIUC mass spec laboratory.

Synthesis of Tp'Rh(CNCH₂CMe₃)(CH₂CH₂CH₂) (2**) via Rearrangement of Tp'Rh(CNCH₂CMe₃)(H)(c-C₃H₅) (**1**).**
Method 1. A 5 mL quartz bomb containing a stirbar was charged with 60 mg (0.088 mmol) of Tp'Rh(CNCH₂CMe₃)(PhN=C=NCH₂CMe₃). The bomb was sealed under nitrogen with an O-ring joint containing a valve and vacuum line adapter. The bomb was evacuated and filled with approximately 2 mL of cyclopropane by condensation at 77 K. The sample was warmed to -50 °C and was irradiated (λ > 345 nm) for 45 min while being stirred constantly. Removal of the cyclopropane at low temperature gave an orange-yellow solid. This solid was dissolved in cyclohexane, and a ¹H NMR analysis of an aliquot of the solution showed two products in an approximate ratio of 2:1. The dominant product was the cyclopropyl hydride **1**. Approximately 1 mL of CCl₄ was added to the cyclohexane solution at -20 °C to convert **1** to the cyclopropyl chloride complex **3**. Preparative TLC using 9:1 hexanes-THF as the mobile phase gave two bands which were extracted with THF. The upper band gave 10 mg of **2** as a pale yellow solid, and the lower band gave 15 mg of **3**. The combined yield based on starting material was 52%. ¹H NMR for **1** (C₆D₆): δ -14.892 (d, J_{RhH} = 25 Hz, 1 H), 0.592 (s, 9 H, C(CH₃)₃), 0.890 (m, 2 H, RhC₃H₅), 1.153 (m, 1 H, RhC₃H₅), 1.913 (m, 1 H, RhC₃H₅), 2.116 (m, 1 H, RhC₃H₅), 2.213 (s, 3 H, pzCH₃), 2.225 (s, 3 H, pzCH₃), 2.295 (s, 3 H, pzCH₃), 2.306 (s, 3 H, pzCH₃), 2.578 (s, 2 H, NCH₂), 2.779 (s, 3 H, pzCH₃), 2.800 (s, 3 H, pzCH₃), 5.655 (s, 1 H, pzH), 5.679 (s, 1 H, pzH), 5.872 (s, 1 H, pzH). The instability of **1** precluded obtaining satisfactory analytical data.

Method 2. To a solution of 95 mg (0.166 mmol) of **3** in 20 mL of C₆H₆ was added 34 mg (0.146 mmol) of Cp₂Zr(H)₂. The suspension was stirred for 45 min and flash-chromatographed through silica gel in a glass frit funnel using 9:1 hexanes-THF as the eluent. The pale brown filtrate was allowed to stand for 5 h to allow for complete conversion of **1** to **2**. Benzene was removed to yield 67 mg (74%) of a pale brown-

yellow solid. The solid was dissolved in a minimum volume of diethyl ether. Evaporation at ambient temperature proceeded to the point at which crystals were just beginning to form, after which the solution was cooled to -20 °C for 24 h to promote further crystallization. The white-yellow needlelike crystals were washed three times with hexanes at -20 °C, dried under vacuum, and stored under nitrogen. Data for **2** are as follows. ¹H NMR (C₆D₆): δ 0.680 (s, 9 H, C(CH₃)₃), 1.626 (m, 2 H, RhCH₂CH₂CH₂), 2.050 (m, 2 H, RhCH₂CH₂CH₂), 2.234 (s, 3 H, pzCH₃), 2.251 (s, 6 H, pzCH₃), 2.459 (s, 6 H, pzCH₃), 2.612 (s, 2 H, NCH₂), 2.683 (s, 3 H, pzCH₃), 3.340 (m, 1 H, RhCH₂CH₂CH₂), 3.620 (m, 1 H, RhCH₂CH₂CH₂), 5.630 (s, 1 H, pzH), 5.719 (s, 2 H, pzH). ¹³C{¹H} NMR (C₆D₆): δ -16.39 (d, J_{RhC} = 16 Hz, RhCH₂CH₂CH₂), 12.50, 13.34, 13.44, 14.11 (s, pzCH₃), 26.50 (s, C(CH₃)₃), 31.44 (s, C(CH₃)₃), 35.61 (d, J_{RhC} = 5 Hz, RhCH₂CH₂CH₂), 55.90 (s, NCH₂), 105.76, 108.32 (s, pzCH), 142.32, 143.31, 149.35, 150.76 (s, pzC_q). IR (KBr): 2518 (B-H), 2161 cm⁻¹ (CNR). Anal. Calcd (found) for C₂₄H₃₉BN₇Rh: C, 53.45 (53.06); H, 7.29 (7.19); N, 18.18 (17.93).

Thermolysis of **2 in C₆D₆. Characterization of Isomers of Tp'Rh(CNCH₂CMe₃)(η²-H₂C=CHCH₃) (**4**).** A resealable 5 mm NMR tube was charged with 5 mg (0.009 mmol) of **2**, and C₆D₆ was vacuum-distilled into the tube. After an initial ¹H NMR spectrum was acquired, the sample was heated to 55 °C for 2.5 h. The solution changed from colorless to light green-yellow. Two products were observed in a 2:1 ratio by ¹H NMR spectroscopy. The sample was heated to 90 °C for 2.25 h to complete the reaction. The sample was heated at 90 °C for an additional 12 h, and periodic ¹H NMR analysis of the sample showed very little decomposition and no change in the ratio of the two products. ¹H NMR for the major product (C₆D₆): δ 0.501 (s, 9 H, C(CH₃)₃), 2.166 (s, 3 H, pzCH₃), 2.179 (s, 3 H, pzCH₃), 2.305 (s, 3 H, pzCH₃), 2.323 (s, 3 H, pzCH₃), 2.621 (s, 3 H, pzCH₃), 2.649 (s, 3 H, pzCH₃), 5.302 (s, 1 H, pzH), 5.885 (s, 1 H, pzH), 5.916 (s, 1 H, pzH). ¹H NMR for the minor product (C₆D₆): δ 0.416 (s, 9 H, C(CH₃)₃), 2.066 (s, 3 H, pzCH₃), 2.109 (s, 3 H, pzCH₃), 2.270 (s, 3 H, pzCH₃), 2.377 (s, 3 H, pzCH₃), 2.404 (s, 3 H, pzCH₃), 2.413 (s, 3 H, pzCH₃), 5.205 (s, 1 H, pzH), 5.885 (s, 1 H, pzH), 5.952 (s, 1 H, pzH). Unassigned ¹H NMR resonances for the methylene protons of the neopentyl isocyanide ligand and all protons of the η²-propylene ligand: δ 1.482 (dt, J = 8, 2 Hz), 1.952 (dd, J = 7, 2 Hz), 2.556 (s), 2.839 (bm), 2.920m (bd), 3.579 (bd), 4.095 (bm), 4.227 (bm). IR (hexanes): 2520 (B-H), 2135 cm⁻¹ (C-N).

Thermolysis of **2 in the Presence of Neopentyl Isocyanide. Characterization of Tp'Rh(CNCH₂CMe₃)(C(NR)CH₂CH₂) and Tp'Rh(CNCH₂CMe₃)(C(NR)CH₂CH₂CH₂C(NR)) (**6**), R = CH₂CMe₃.** A resealable 5 mm NMR tube was charged with 5 mg (0.009 mmol) of **2**, and C₆D₆ was vacuum-transferred into the tube. After an initial ¹H NMR spectrum was acquired, 2 μL of neopentyl isocyanide was added to the sample under inert conditions. No reaction was observed after the sample had remained at room temperature for 1 h. The sample was heated to 55 °C for 3.5 h and then to 90 °C for 1 h to complete the reaction. Spectra were acquired periodically, and an intermediate, assigned as the mono-isocyanide insertion derivative, was observed to appear and then decay as a final product appeared. The color of the solution changed from colorless to a fluorescent pale orange. ¹H NMR for the intermediate (C₆D₆): δ 0.592 (s, 9 H, RhCNCH₂C(CH₃)₃), 1.056 (s, 9 H, RhC(NCH₂C(CH₃)₃), 1.722 (dd, J_{HH} = 15 Hz, J_{RhH} = 2 Hz, 2 H, RhC(NCH₂C(CH₃)₃), 2.245 (s, 3 H, pzCH₃), 2.288 (s, 3 H, pzCH₃), 2.360 (s, 3 H, pzCH₃), 2.400 (s, 3 H, pzCH₃), 2.499 (s, 3 H, pzCH₃), 3.116 (m, 2 H, RhC(NR)CH₂CH₂CH₂), 3.440 (m, 2 H, RhC(NR)CH₂CH₂CH₂), 5.618 (s, 1 H, pzH), 5.678 (s, 1 H, pzH), 5.801 (s, 1 H, pzH). The resonances for the remaining Tp' methyl protons, the methylene protons of the isocyanide ligand, and the methylene protons of rhodium-bound ring carbon were not identified due to their overlap with

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each other. $^1\text{H NMR}$ for **6** (C_6D_6): δ 0.623 (s, 9 H, $\text{RhCNCH}_2\text{C}(\text{CH}_3)_3$), 0.999 (s, 18 H, $\text{RhC}(\text{NCH}_2\text{C}(\text{CH}_3)_3)$), 1.722 ($\text{AB}_{\text{q}}\text{d}$, $J_{\text{RhH}} = 2$ Hz, 4 H, $\text{RhC}(\text{NCH}_2\text{C}(\text{CH}_3)_3)$), 2.196 (s, 3 H, pzCH_3), 2.249 (s, 6 H, pzCH_3), 2.297 (s, 6 H, pzCH_3), 2.306 (s, 3 H, pzCH_3), 2.498 (s, 2 H, $\text{RhCNCH}_2\text{C}(\text{CH}_3)_3$), 3.292 (tm, 2 H, $\text{RhC}(\text{NR})\text{CH}_2\text{CH}_2\text{C}(\text{NR})$), 3.661 (dm, 2 H, $\text{RhC}(\text{NR})\text{CH}_2\text{CH}_2\text{C}(\text{NR})$), 5.575 (s, 1 H, pzH), 5.723 (s, 2 H, pzH). The resonances for the methylene protons of the metallacycle carbon were not identified due to their overlap with each other. High-resolution FAB/MS: calcd (found) for $\text{C}_{36}\text{H}_{62}\text{BN}_9\text{Rh}$, 734.42763 (734.4276).

Photolysis of $\text{Tp}^*\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{PhN}=\text{C}=\text{NCH}_2\text{CMe}_3)$ in Neat Cyclobutane: Characterization of $\text{Tp}^*\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{c-C}_4\text{H}_7)\text{H}$ (7**).** Cyclobutane (0.6 mL) was condensed into a resealable 5 mm NMR tube that had been charged with approximately 5 mg of $\text{Tp}^*\text{Rh}(\text{CNCH}_2\text{CMe}_3)(\text{PhC}=\text{N}=\text{CCH}_2\text{CMe}_3)$ at 77 K. The sample was warmed to -15 °C using a MeOH/dry ice slurry and photolyzed ($\lambda > 345$ nm) for 30 min. After removal of cyclobutane under vacuum C_6D_6 was condensed into the tube, giving a clear red solution. $^1\text{H NMR}$ (C_6D_6): δ -15.531 (d, $J_{\text{RhH}} = 25$ Hz, 1 H), 0.683 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 2.197 (s, 6 H, pzCH_3), 2.308 (s, 3 H, pzCH_3), 2.357 (s, 3 H, pzCH_3), 2.609 (s, 3 H, pzCH_3), 2.677 (s, 3 H, pzCH_3), 2.702 (s, 2 H, NCH_2), 5.627 (s, 1 H, pzH), 5.653 (s, 1 H, pzH), 5.869 (s, 1 H, pzH). The compound was not isolated due to its instability.

Synthesis of $\text{Tp}^*\text{Rh}(\text{C}_2\text{H}_4)(\text{CN-2,6-xylyl})$. A solution of $\text{Tp}^*\text{Rh}(\text{C}_2\text{H}_4)_2$ (67 mg, 0.147 mmol) in 25 mL of THF was cooled to -40 °C. To the stirred yellow-orange solution was added a solution of 2,6-xylyl isocyanide (19.4 mg, 0.148 mmol) in 20 mL of THF over 15 min. The resulting pale yellow solution was stirred for 1.5 h at -40 °C. Removal of solvent at room temperature afforded a pale yellow solid. The solid was dissolved in hexanes and filtered through glass wool. The solution was evaporated to dryness, yielding 56 mg (0.101 mmol, 68%) of pale yellow solid. $^1\text{H NMR}$ (C_6D_6): δ 1.90 (s, 6H, $(\text{CH}_3)_2\text{C}_6\text{H}_3$), 2.13 (s, 3H, pzCH_3), 2.18 (s, 3H, pzCH_3), 2.31 (s, 6H, pzCH_3), 2.51 (s, 6H, pzCH_3), 2.70 (bd, 2H, C_2H_4), 3.50 (bd, 2H, C_2H_4), 5.31 (s, 1H, pzH), 5.82 (s, 2H, pzH), 6.53 (d, $J_{\text{HH}} = 7.6$ Hz, 2H, $(\text{CH}_3)_2\text{C}_6\text{H}_3$), 6.63 (t, $J_{\text{HH}} = 7.6$ Hz, 1H, $(\text{CH}_3)_2\text{C}_6\text{H}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 12.20, 12.29, 13.35, 15.12 (s, pzCH_3), 18.10 (s, $(\text{CH}_3)_2\text{C}_6\text{H}_3$), 20.99 (d, $J_{\text{Rh-C}} = 15$ Hz, $\text{Rh}(\text{C}_2\text{H}_4)$), 105.10, 108.20 (pzCH), 126.54, 127.68, 133.54 (s, $(\text{CH}_3)_2\text{C}_6\text{H}_3$), 142.10, 143.00, 149.36, 151.81 (s, pzC_q). IR (KBr): 2520 ($\nu_{\text{B-H}}$), 2110 cm^{-1} ($\nu_{\text{C-N}}$). IR (hexane): 2520 ($\nu_{\text{B-H}}$), 2105 cm^{-1} ($\nu_{\text{C-N}}$). Anal. Calcd (found) for $\text{C}_{26}\text{H}_{35}\text{N}_7\text{BRh}$: C, 55.83 (56.02); H, 6.31 (6.29); N, 17.53 (17.49).

X-ray Structural Determination of **2.** Yellow prisms of **2** were obtained from a diethyl ether solution at -20 °C. A single crystal having approximate dimensions of $0.34 \times 0.26 \times 0.23$ mm^3 was mounted on a glass fiber with epoxy. Lattice constants were obtained from 25 centered reflections with values of χ between 5 and 70°. Cell reduction revealed a primitive monoclinic crystal system. Data were collected at -30 °C in accord with the parameters found in Table 3. The intensities of three representative reflections which were measured after every 60 min of X-ray exposure time remained constant throughout the data collection, indicating crystal and electronic stability. The Molecular Structure Corp. TEXSAN analysis software package was used for data reduction, solution, and refinement.³⁸ The space group was uniquely assigned

(38) $\text{R1} = (\sum ||F_o| - |F_c||) / \sum |F_o|$ and $\text{wR2} = [\sum w(|F_o| - |F_c|)^2]^{1/2} / \sum w|F_o|^2$, where $w = 1/[\sigma^2(F_o) + (pF_o)^2]^{1/2}$ for the non-Poisson contribution weighting scheme. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Source of scattering factors f_o , f' , and f'' : Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

as $P2_1/n$ on the basis of systematic absences. A Patterson map solution of the structure was used to locate the rhodium atom. The structure was expanded with the DIRDIF program to reveal all non-hydrogen atoms. An absorption correction was applied using the program DIFABS following isotropic refinement. Anisotropic refinement of all non-hydrogen atoms allowed for the use of a difference Fourier map for the location of the hydrogen atoms, whose coordinates were subsequently idealized. Full-matrix least-squares anisotropic refinement of the non-hydrogen atoms (with hydrogen atoms attached to carbon and boron atoms in idealized positions) was executed until convergence was achieved.

X-ray Structural Determination of $\text{Tp}^*\text{Rh}(\text{CN-2,6-xylyl})(\text{C}_2\text{H}_4)$. Crystals of $\text{Tp}^*\text{Rh}(\text{CN-2,6-xylyl})(\text{C}_2\text{H}_4)$ were grown by slow evaporation from cyclohexane. A pale yellow fragment of approximate dimensions $0.02 \times 0.04 \times 0.08$ mm was cut from a cluster of plates under Paratone-8277, mounted under the oil on a glass fiber, and immediately placed in a cold nitrogen stream at -90 °C on the X-ray diffractometer. The X-ray intensity data were collected on a standard Siemens SMART CCD Area Detector System equipped with a normal focus molybdenum-target X-ray tube operated at 2.0 kW (50 kV, 40 mA). A total of 1321 frames of data (1.3 hemispheres) were collected using a narrow frame method with scan widths of 0.3° in ω and exposure times of 60 s/frame using a detector-to-crystal distance of 5.094 cm (maximum 2θ angle of 56.52°). The total data collection time was approximately 26 h. Frames were integrated to a maximum 2θ angle of 46.54° with the Siemens SAINT program to yield a total of 5541 reflections, of which 3565 were independent ($R_{\text{int}} = 4.99\%$, $R_{\text{sig}} = 11.87\%$)³⁹ and 2633 were above $2\sigma(I)$. Laue symmetry revealed a triclinic crystal system, and the final unit cell parameters (at -90 °C) were determined from the least-squares refinement of three-dimensional centroids of 1939 reflections.⁴⁰ The space group was assigned as $P\bar{1}$ and the structure was solved by using direct methods and refined by full-matrix least squares on F^2 (Siemens, SHELXTL, version 5.04). It should be noted that the intensity statistics provided in the XPREP program strongly suggested the chiral space group $P1$; however, successful solution and refinement in $P\bar{1}$ proved to be the correct choice. For a Z value of 2, there is one independent molecule in the asymmetric unit. All non-hydrogen atoms were refined anisotropically with hydrogens included in idealized positions, giving a data to parameter ratio of approximately 11:1. The structure was refined to a goodness of fit (GOF) of 1.082 and final residuals⁴¹ of $\text{R1} = 7.88\%$ ($I > 2\sigma(I)$) and $\text{wR2} = 14.01\%$ ($I > 2\sigma(I)$).

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Supporting Information Available: Listings of fractional atomic coordinates, anisotropic thermal parameters, and bond distances and angles for **2** and for $\text{Tp}^*\text{Rh}(\text{CN-2,6-xylyl})(\text{C}_2\text{H}_4)$ (11 pages). Ordering information is given on any current masthead page.

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(39) $R_{\text{int}} = \sum |F_o^2 - F_o(\text{mean})^2| / \sum |F_o^2|$; $R_{\text{sigma}} = \sum [\sigma(F_o^2)] / \sum |F_o^2|$.

(40) It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, since systematic error is not included. More reasonable errors might be estimated at 10 times the listed value.

(41) $\text{GOF} = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$, where n and p denote the number of data and number of parameters, respectively. $\text{R1} = (\sum ||F_o| - |F_c||) / \sum |F_o|$; $\text{wR2} = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [f(\text{Max } 0, F_o^2) + (1 - f)F_c^2]$.