Synthesis and Characterization of (Tris(3,5-dimethylpyrazolyl)borato)rhodium Alkyl and Vinyl Chloride Complexes

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A series of complexes of the type Tp′Rh($CNCH_2CMe_3$)(R)Cl, where R = CH_3, CD_3, *n*-propyl, isopropyl, cyclopropyl, and vinyl and Tp′ = tris(3,5-dimethylpyrazolyl)borate have been synthesized and fully characterized. The complexes are prepared by reaction of the corresponding Grignard reagent with Tp′Rh($CNCH_2CMe_3$)Cl_2, which in turn is synthesized from Tp′Rh($NCCH_3$)Cl_2. The complex Tp′Rh($CNCH_2CMe_3$)(isopropyl)Cl crystallizes in orthorhombic space group *Pbcn* (No. 60) with a = 27.8224(1) Å, b = 14.2541(2) Å, c = 14.5549(2) Å, Z = 8, and V = 5772.23(9) Å^3. The complex Tp′Rh($CNCH_2CMe_3$)(cyclopropyl)Cl crystallizes in monoclinic space group $P2_1/c$ (No. 14) with a = 9.573(2) Å, b = 18.933(3) Å, c = 17.873(14) Å, β = 103.70(4)°, Z = 4, and V = 3147(3) Å^3. The complex Tp′Rh(PMe_3)Cl_2 crystallizes in monoclinic space group $P2_1/n$ (No. 14) with a = 10.9384(6) Å, b = 17.3111(9) Å, c = 13.5132(7) Å, β = 111.536(1)°, Z = 4, and V = 2378.5(2) Å^3.

Introduction

Transition-metal alkyl, alkyl halide, and aryl halide complexes serve as invaluable precursors to alkyl and aryl hydride complexes for mechanistic studies of alkane and arene reductive elimination.[1] The halide derivatives can readily be converted to their hydrido counterparts using a variety of hydride-donating reagents. As part of our investigation of the mechanism of alkane reductive elimination from complexes of the type Tp′Rh($CNCH_2CMe_3$)(X)(alkyl), where X = H or D and Tp′ = tris(3,5-dimethylpyrazolyl)borate, we required a simple preparative route to the corresponding chloride complexes Tp′Rh($CNCH_2CMe_3$)(alkyl)Cl, the details of which are reported herein.

Previously we have prepared Tp′Rh($CNCH_2CMe_3$)(R)Cl (R = aryl, *n*-alkyl, and cycloalkyl) by the reaction of CCl_4 with the corresponding hydride complexes made by photolysis of a hydrocarbon solution of the carbodiimide complex Tp′Rh($CNCH_2CMe_3$)(PhN═C═NCH_2CMe_3).[2] However, the usefulness of this method is limited by a lengthy preparative route to the required hydride complexes,[3] poor economy of starting materials, and yield-reducing side reactions. Additionally, secondary derivatives of normal alkanes cannot be prepared by this method. Ghosh and Graham have reported that the reaction of Tp′Rh$(CO)_2$ with CH_3I produces Tp′Rh(CO)(I)(CH_3).[4] While the analogous reaction of Tp′Rh($CNCH_2CMe_3$)$_2$[3a] with a haloalkane is feasible, it is not economical due to the sacrifice of 1 equiv of neopentyl isocyanide. Chambron and co-workers have reported the preparation of TpRh(PPh_3)(I)(CH_3) from the reaction of TpRh(PPh_3)$(I)_2$ and CH_3I.[5] Preparation of complexes of the type Tp′Rh($CNCH_2CMe_3$)(X)(alkyl) using this method were not pursued because attempts to prepare the required dihalide complexes, Tp′Rh($CNCH_2CMe_3$)$(X)_2$, where X = Br or I, from the reaction of Tp′Rh($CNCH_2CMe_3$)$_2$ with bromine or iodine were not successful. Instead, this reaction gives complexes of the type [Tp′Rh($CNCH_2CMe_3$)$_2$(X)][X].

A convenient and reliable method for the introduction of organic ligands into transition-metal compounds is the reaction of a transition-metal halide complex with a Grignard or lithium reagent. Surprisingly, reactions of complexes of the type Tp′Rh(L)$(X)_2$ (X = halide and L = CO, CNR, or PR_3) with Grignard reagents to give complexes of the form Tp′Rh(L)(X)(alkyl) have not been generally investigated. Powell and co-workers have reported a method for synthesizing a wide range of air-stable Rh(III) dichloride complexes from the general precursor Tp′Rh(MeOH)Cl_2.[6] Unfortunately, repeated attempts to reproduce the preparation of this compound failed in our hands.

This report begins with an alternate high-yield synthesis of the previously characterized Tp′Rh(CH_3CN)Cl_2,[6] which is an excellent precursor to the complex Tp′Rh($CNCH_2CMe_3$)Cl_2 (**1**). The report continues with the synthesis and characterization of **1** and complexes of the type Tp′Rh($CNCH_2CMe_3$)(R)Cl, where R = CH_3 (**2a**), CD_3 (**3a**), *n*-C_3H_7 (**4a**), *i*-C_3H_7 (**5a**), *c*-C_3H_5 (**6a**), and $CHCH_2$ (**7a**), via the reaction of alkyl and vinyl Grignard reagents with **1**.

Results and Discussion

Alternate Preparation of Tp′Rh(CH_3CN)Cl_2. The successful preparation of Tp′Rh(CH_3CN)Cl_2 in good yield is dependent on the purity of KTp′. The dominant side product when using crude KTp′ is Tp′Rh(3,5-dimethylpyrazolyl)Cl_2,[6] which is not formed if recrystallized KTp′ is used. Tp′Rh(CH_3CN)Cl_2 is prepared by the addition of solid KTp′ to an acetonitrile solution of RhCl_3(CH_3CN)$_3$ (eq 1). The tridentate

$$Rh(Cl)_3(CH_3CN)_3 \xrightarrow[-\ 2\ CH_3CN\ ,\ -\ KCl]{KTp',\ CH_3CN} Tp'Rh(CH_3CN)(Cl)_2 \quad (1)$$

and anionic nature of the Tp′ ligand lead to a chelate effect and

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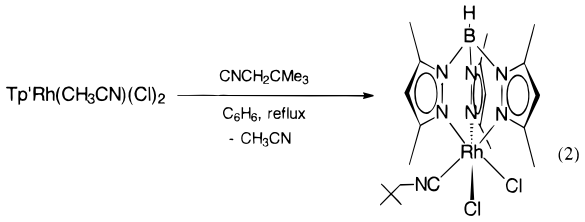
metathesis reaction, respectively. The formation of KCl provides the thermodynamic driving force for this reaction. After filtration of the reaction mixture and removal of solvent, air-stable Tp′Rh(CH_3CN)Cl_2 is obtained in nearly quantitative yield and can be used without further purification.

Synthesis and Characterization of Tp′Rh($CNCH_2CMe_3$)Cl_2 (1). Tp′Rh(CH_3CN)Cl_2 is an excellent precursor to **1**. The labile nature of the acetonitrile ligand allows for substitution of acetonitrile with neopentyl isocyanide by refluxing Tp′Rh(CH_3CN)Cl_2 in benzene in the presence of a slight excess of neopentyl isocyanide (eq 2). Compound **1** may be purified by



(2)

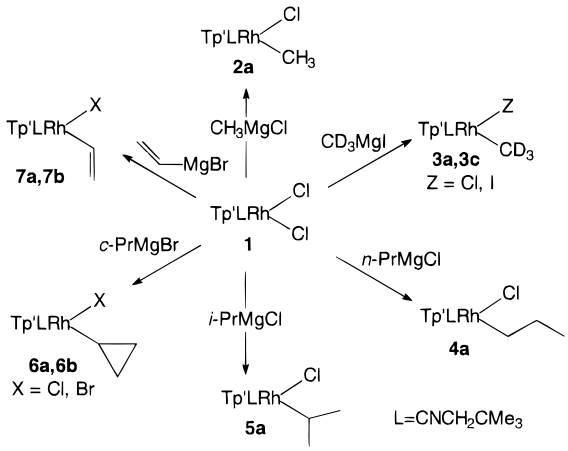
1

recrystallization at −20 °C from a methylene chloride solution layered with hexanes or by chromatography on silica gel plates using 8:1 (v/v) THF−$CHCl_3$ as the mobile phase. Compound **1** is air stable, soluble in THF and methylene chloride, slightly soluble in benzene, and has been fully characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopies and elemental analysis. X-ray diffraction studies of single crystals to determine the solid-state structure of **1** have produced solutions, but the collected data are of such poor quality that the solutions do not refine well. The data do indicate that the Tp′ ligand is η^3 coordinated and the isonitrile is linear (173°).

The spectroscopic data in solution are consistent with **1** having an octahedral coordination geometry with two of the three Tp′ pyrazolyl rings being equivalent by a reflection plane containing the third pyrazolyl ring which bisects the angle formed by the chloride ligands and the rhodium center. The ^{1}H NMR spectrum of **1** in C_6D_6 shows resonances at δ 2.035, 2.107, 2.732, 3.241, 5.488, and 5.524 in a 6:3:6:3:2:1 ratio which are assigned to the Tp′ methyl groups and methine protons. The resonances for the neopentyl methyl and methylene protons of **1** appear downfield of the free ligand at δ 0.789 and 2.671 in a 9:2 ratio. The IR spectrum of **1** displays an absorption at 2241 cm^{-1}, corresponding to the CN stretching mode for the neopentyl isocyanide ligand which is greater than that of the free isocyanide (2155 cm^{-1}). This fact is indicative of little back-bonding of the d orbitals on rhodium to the π^* orbitals on the isocyanide ligand and is consistent with a d^6, electron-deficient Rh(III) center which prefers an octahedral geometry. For comparison, the Rh(I) complex Tp′Rh($CNCH_2CMe_3$)$_2$ has IR absorptions for the CN stretching mode at 2158 and 2106 cm^{-1},[3a] which is consistent with increased back-bonding by an electron-rich metal and identifies the rhodium center as d^8, Rh(I) which prefers a square planar geometry. Indeed, the solid-state structure of Tp′Rh($CNCH_2CMe_3$)$_2$ is known to be square planar from single-crystal X-ray diffraction analysis.[3a]

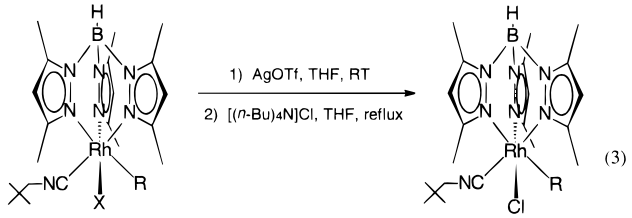
Synthesis of Tp′Rh($CNCH_2CMe_3$)(R)Cl (2a−7a). Synthesis of the alkyl chloride complexes (R = CH_3 (**2a**), CD_3 (**3a**), *n*-Pr (**4a**), *i*-Pr (**5a**), *c*-Pr (**6a**)) and the vinyl chloride complex (**7a**) is accomplished by the dropwise addition of 1.2 equiv of the corresponding alkyl or vinyl Grignard reagent as a dilute THF solution to a stirring THF solution of **1** (Scheme 1). The

Scheme 1. Products from the Reaction of **1** with Various Grignard Reagents



reaction is complete within 10 min at RT (room temperature), and there is an attendant color change from yellow to green-yellow for **2a**, **4a**, and **5a,** yellow to orange for **6a** and **7a,** and yellow to orange-brown for **3a**. The products are isolated by quenching of the excess Grignard followed by column chromatography. Use of bromo and iodo Grignards leads to halide exchange and gives mixtures of alkyl halide complexes that are highly colored. Preparative TLC allows for separation of the vinyl chloride derivative, **7a**, from the vinyl bromide derivative, **7b**.

A two-step halide exchange reaction converts the alkyl halide mixtures made in the synthesis of **3a** and **6a** to alkyl chloride complexes (eq 3).[4] It should be noted that refluxing an acetone



(3)

X = Cl, Br, I

solution of a mixture of alkyl halide complexes in the presence of NaBr or $MgBr_2$ for many days does not convert the mixture to a single alkyl bromide product. The recrystallized alkyl halide mixtures are reacted with excess AgOTf in THF, filtered to remove precipitated AgX (X = Cl, Br, I), and then quenched with a 2−4-fold excess of (*n*-Bu)N_4Cl. Further purification of all of the alkyl chloride complexes is achieved by chromatography and recrystallization at −20 °C from a THF solution (minimum volume) layered with hexanes. The air-stable crystals are typically platelike in form and green-yellow in color. A variety of reaction conditions ranging from temperature changes, to addition rates, to amounts of Grignard reagent have been examined, and the conditions detailed in the Experimental Section have proven to be optimal.

Characterization of Tp′Rh($CNCH_2CMe_3$)(R)Cl (2a−7a). Complexes **2a**−**7a** have been fully characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopies and elemental analysis. The ^{1}H NMR spectrum of **2a** in C_6D_6 in shows nine singlets from δ 2−6 in a 3:3:3:3:3:3:1:1:1 ratio, a pattern which is also characteristic of **3a**−**7a**. These resonances correspond to the six methyl groups and the three methine protons of the Tp′ ligand, respectively. This pattern is expected for an octahedral Tp′ complex with each 3,5-dimethylpyrazolyl ring *trans* to a

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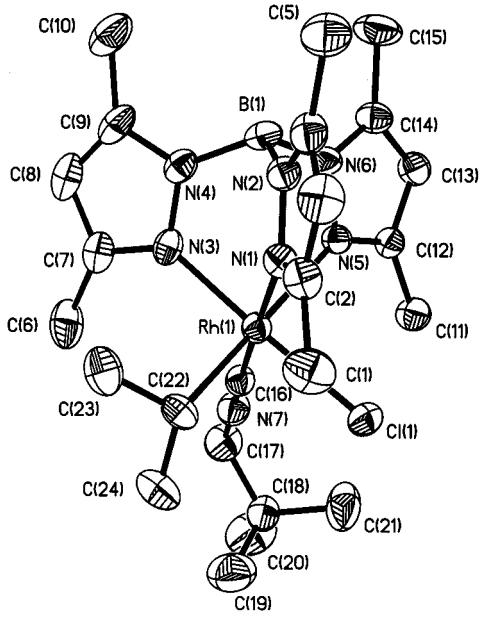


Figure 1. ORTEP drawing of Tp′Rh(CNCH$_2$CMe$_3$)(CH(CH$_3$)$_2$)Cl, **5a**. Ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

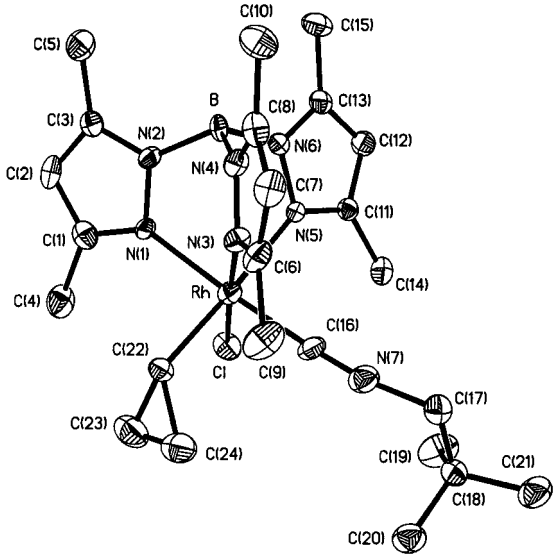


Figure 2. ORTEP drawing of Tp′Rh(CNCH$_2$CMe$_3$)(*c*-C$_3$H$_5$)Cl·THF, **6a**·THF. Ellipsoids are shown at the 50% probability level. The THF molecule and hydrogen atoms have been omitted for clarity.

different ligand. The diastereotopic methylene protons of the isocyanide ligand appear as an AB quartet ($\delta \sim 2.6$), rather than a singlet. The IR spectrum for each complex displays an absorption at $\sim$2200 cm^{-1} corresponding to the CN stretching mode of the neopentyl isocyanide ligand. These data support the description of **2a**−**7a** as octahedral Rh(III) complexes.

The solid-state structures for **5a** and **6a**·THF were obtained by single-crystal X-ray diffraction (Figures 1 and 2, respectively) and clearly support the structural conclusions made from the spectroscopic data. Selected bond angles and distances are listed in Tables 1 and 2, respectively. The remainder of the crystallographic data can be found in the Supporting Information. The octahedral geometry of both complexes is slightly distorted. For **5a** and **6a**·THF the 90° interactions deviate from ideal with ranges of 85.0(2)−95.6(2)° and 86.9(3)−92.8(2)°, respectively. The respective 180° interactions are at most 4 and 3.5° less than ideal. The CNC angle of the isocyanide ligands of both structures is nearly 180° which is indicative of decreased back-

Table 1. Selected Bond Angles (deg) and Distances (Å) for Tp′Rh(CNCH$_2$CMe$_3$)(CH(CH$_3$)$_2$)Cl, **5a**

	Angles		
C23−C22−C24	112.9(5)	C16−Rh1−N3	91.6(2)
C24−C22−Rh1	118.0(4)	C16−Rh1−N5	91.8(2)
C23−C22−Rh1	113.6(4)	N1−Rh1−N3	89.0(2)
C22−Rh1−Cl	87.5(2)	N1−Rh1−N5	86.8(2)
C22−Rh1−C16	92.2(2)	N3−Rh1−N5	85.0(2)
C22−Rh1−N1	89.2(2)	C16−N7−C17	178.4(6)
C22−Rh1−N3	95.6(2)	Cl1−Rh1−N1	92.1(1)
C22−Rh1−N5	176.0(2)	Cl1−Rh1−N3	176.7(1)
C16−Rh1−Cl1	87.2(2)	Cl1−Rh1−N5	92.0(1)
C16−Rh1−N1	178.4(2)		
	Distances		
C22−C23	1.509(8)	C16−N7	1.138(7)
C22−C24	1.505(8)	N7−C17	1.436(8)
Rh1−C22	2.110(5)	Rh1−N1	2.129(4)
Rh1−Cl1	2.353(2)	Rh1−N3	2.047(4)
Rh1−C16	1.891(7)	Rh1−N5	2.250(4)

Table 2. Selected Bond Angles (deg) and Distances (Å) for Tp′Rh(CNCH$_2$CMe$_3$)(*c*-C$_3$H$_5$)Cl·THF, **6a**·THF

	Angles		
C22−C23−C24	61.0(8)	C16−Rh−N1	176.5(4)
C22−C24−C23	60.5(8)	C16−Rh−N3	89.0(4)
C23−C22−C24	58.5(7)	C16−Rh−N5	90.6(4)
C22−C23−Rh	127.4(8)	N1−Rh−N3	88.5(3)
C22−C24−Rh	126.9(7)	N1−Rh−N5	86.9(3)
C22−Rh−Cl	91.5(3)	N3−Rh−N5	87.5(3)
C22−Rh−C16	92.1(4)	C16−N7−C17	172(1)
C22−Rh−Nl	90.4(3)	C1−Rh−N1	92.8(2)
C22−Rh−N3	90.9(4)	Cl−Rh−N3	177.3(2)
C22−Rh−N5	176.8(3)	Cl−Rh−N5	90.2(2)
C16−Rh−Cl	89.6(3)		
	Distances		
C22−C23	1.48(1)	C16−N7	1.15(1)
C22−C24	1.49(1)	N7−C17	1.49(1)
C23−C24	1.45(2)	Rh−N1	2.088(7)
Rh−C22	2.050(9)	Rh−N3	2.044(8)
Rh−Cl	2.349(3)	Rh−N5	2.177(7)
Rh−C16	1.89(1)		

bonding of an electron-deficient Rh(III) center. The isopropyl ligand of **5a** is tilted having one methyl group above and below the plane formed by C22−N3−N5−Cl1−Rh. The cyclopropyl ring of **6a**·THF is stretched slightly, having two of its C−C bonds (C22−C23 and C22−C24) longer than third (C23−C24). The plane of the cyclopropyl ring forms an angle with the Rh−C22 bond of 103°. These data are consistent with the solid-state structural data of a previously reported Rh(III) cyclopropyl bromide complex, (Cp*)Rh(PMe$_3$)(Br)(*c*-C$_3$H$_5$).[7] A substantial trans-influence is seen in **5a**, with the isopropyl ligand having the largest effect and the chloride ligand the smallest effect ($\Delta D_{Rh-N} = 0.20$ Å). The trans-influences in **6a** are smaller but follow the same trend as in **5a**.

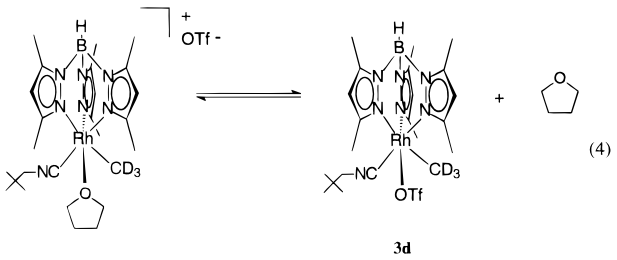
It should be noted that NMR spectroscopy is an excellent means for identification of these compounds. In the $^{13}C\{^1H\}$ NMR spectra of the alkyl chloride complexes the resonance for C$_\alpha$ of the alkyl ligand is identified as a downfield doublet (19−27 Hz) due to coupling to rhodium. A *J*-modulated spin echo experiment allowed for the distinction of the methyl carbons of Tp′ from the C$_\beta$ carbons of the cyclopropyl ring of **6a**. The expected doublet of septets in the $^{13}C\{^1H\}$ NMR of **3a** in C$_6$D$_6$ is not resolved, but a broad singlet at δ 2.27 in a ^2H NMR spectrum identifies the methyl-d_3 group for this complex.

In a ^1H NMR spectrum of **2a** in C$_6$D$_6$ a doublet with 2 Hz rhodium coupling at δ 2.369 corresponds to the rhodium-bound methyl ligand. The multiplets observed in the ^1H NMR spectra

(7) Periana, R. A.; Bergman, R. G. *Organometallics* **1984**, *3*, 508−510.

of **4a**, **5a**, and **7a** were distinguished by homonuclear decoupling experiments. Decoupling experiments were not helpful for distinguishing the multiplets of **6a**. The spectra for both **4a** and **5a** show resonances for the alkyl ligand with H_α downfield of H_β. For **4a**, the resonance pattern of a triplet (δ 1.262) and two pairs of multiplets (δ 1.8−3.5) is consistent with that expected for the *n*-propyl ligand. The four multiplets of **4a** are in a ratio of 1:1:1:1, which indicates that the protons of each methylene group are diastereotopic. For **5a**, a pair of broad doublets (δ 1.041 and 1.936) and a broad multiplet (δ 5.102) in a 3:3:1 ratio identify the isopropyl ligand. Rhodium−proton coupling constants for H_α of the isopropyl ligand of **5a** and H_α of the propyl ligand of **4a** could not be determined due to inefficient decoupling; they are likely on the order of 2−3 Hz on the basis of the RhH coupling constant for the methyl protons in **2a**. In **7a** a larger *trans* coupling (17 Hz) and a *cis* coupling (9 Hz) distinguishes the two geminal vinyl hydrogens (H_β) at δ 5.837 and 5.976, respectively. A doublet of doublets of doublets at δ 7.909 is assigned to H_α. The RhH coupling constant for H_α is 3 Hz.

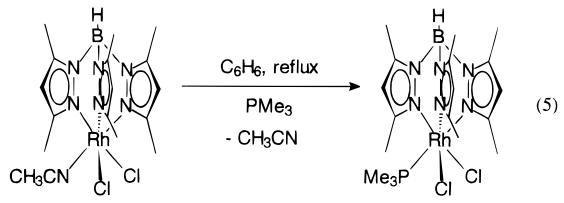
The ^{1}H NMR spectrum of a purified mixture of alkyl halides from the synthesis of **3a** shows two sets of resonances having the same pattern which corresponds to two octahedral methyl halide complexes, **3a** and the iodo derivative, **3c**. Following the halide abstraction step the ^{1}H NMR spectrum of the reaction mixture in THF-d_8 shows, presumably, an equilibrium mixture of a cationic alkyl THF complex and a neutral alkyl triflate complex, **3d**, both of which are thermally stable in solution at RT (eq 4). When the THF-d_8 solvent is replaced with C_6D_6,



3d

the ^{1}H NMR spectrum of the resulting solution shows the presence of only one product, presumably, **3d**. Replacement of a polar solvent with a nonpolar solvent drives the equilibrium in eq 4 to the right favoring **3d**. The resonance pattern is similar to that observed for an alkyl chloride complex. Due to their lability, no additional investigations of the chemistry or characterization of **3d** and the cationic alkyl THF complex were pursued.

Synthesis and Characterization of Tp′Rh(PMe$_3$)Cl$_2$ (8). The preparation of Tp′Rh(PMe$_3$)Cl$_2$ (**8**) is accomplished by refluxing a benzene suspension of Tp′Rh(CH$_3$CN)Cl$_2$ in the presence of 1.5 equiv of trimethylphosphine under nitrogen atmosphere for 1 h (eq 5). Compound **8** may be purified by



recrystallization from CH_2Cl_2/hexane, giving large orange prisms in 85% yield. The phosphine dichloride complex is air-stable, soluble in THF and CH_2Cl_2, slightly soluble in benzene, and has been fully characterized by ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{31}P{^{1}H} NMR, and IR spectroscopies and elemental and single-crystal X-ray analyses. The ^{1}H NMR spectrum of **8** in C_6D_6 displays a doublet at δ 1.265 (J = 11 Hz) that is assigned to the rhodium-bound PMe$_3$ ligand. The spectrum also shows six singlet resonances between δ 2.1 and 5.5 in a ratio of 3:6:6:3:2:1 for the methyl and methine protons of the Tp′ ligand. The ^{31}P{^{1}H} NMR spectrum of **8** in C_6D_6 displays a doublet at δ 1.642 with a Rh−P coupling constant of 106 Hz for the phosphine ligand. The magnitude of the Rh−P coupling constant is significantly smaller than that of the Rh(I) complex Tp′Rh(CO)(PMe$_3$) (148 Hz)[4a] and is consistent with the changes in coupling constants observed in Cp*Rh(PMe$_3$)(L$_n$) systems with Rh(I) and Rh(III) centers.[8] The ^{13}C{^{1}H} NMR spectrum of **8** in C_6D_6 shows resonances for the ring carbons of the pyrazolyl ring *trans* to PMe$_3$ as doublets ($J \approx 4$ Hz) assigned to long-range coupling to phosphorus. As no such coupling was observed in the ^{13}C{^{1}H} NMR spectrum of Tp′Rh(CNCH$_2$-CMe$_3$)(Cl$_2$) (**1**) in C_6D_6, the coupling observed for **8** is not believed to be due to rhodium.

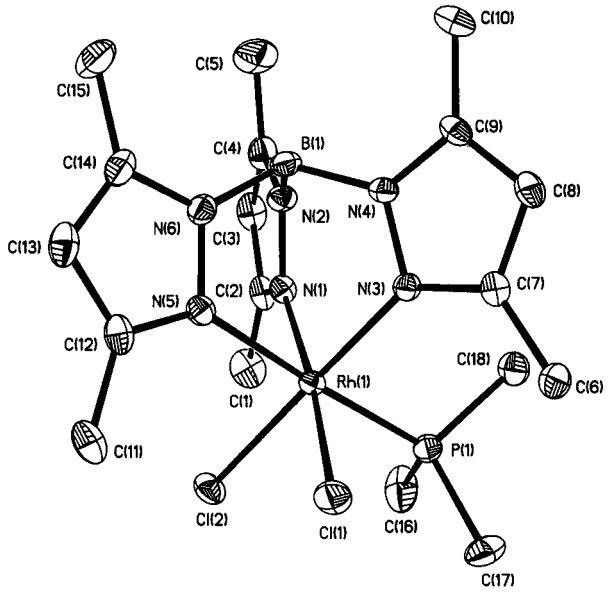


Figure 3. ORTEP drawing of Tp′Rh(PMe$_3$)Cl$_2$. Ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Angles (deg) and Distances (Å) for Tp′Rh(PMe$_3$)Cl$_2$, **8**

Angles			
P−Rh−Cl1	90.89(3)	Cl1−Rh−N5	89.23(6)
P−Rh−Cl2	90.10(3)	Cl2−Rh−N1	90.72(6)
P−Rh−N1	93.62(6)	Cl2−Rh−N3	175.70(6)
P−Rh−N3	91.95(6)	Cl2−Rh−N5	93.33(6)
P−Rh−N5	176.56(6)	N1−Rh−N3	92.92(8)
Cl1−Rh−Cl2	86.59(3)	N1−Rh−N5	86.43(8)
Cl1−Rh−N1	174.76(6)	N3−Rh−N5	84.62(8)
Cl1−Rh−N3	89.60(6)		
Distances			
Rh−Cl1	2.3182(7)	Rh−N1	2.151(2)
Rh−Cl2	2.3512(7)	Rh−N3	2.087(2)
Rh−P	2.2859(8)	Rh−N5	2.145(2)

The solid-state structure of **8** as determined by single-crystal X-ray analysis is fully consistent with the NMR data (Figure 3). Selected bond angles and distances are listed in Table 3 with the crystallographic data being located in Table 4. The structure of **8** is fairly unremarkable as it is similar to that of Tp′Rh(CNCH$_2$CMe$_3$)(*i*-Pr)Cl (**5a**) discussed above. The Rh−P

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Table 4. Summary of Crystallographic Data for **5a**, **6a**, and **8**

cryst params	**5a**	**6a**·THF	**8**
chem formula	$C_{24}H_{40}BN_7ClRh$	$C_{24}H_{38}BClN_7Rh\cdot C_4H_8O$	$C_{18}H_{31}BCl_2N_6PRh$
fw	575.80	645.90	547.08
space group (No.)	*Pbcn* (No. 60)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	27.8224(1)	9.573(2)	10.9384(6)
b (Å)	14.2541(2)	18.933(3)	17.3111(9)
c (Å)	14.5549(2)	17.873(14)	13.5132(7)
β (deg)	90	103.70(4)	111.536(1)
V (Å^3)	5772.23(9)	3147(3)	2378.5(2)
Z	8	4	4
ρ_{calc} (g cm^{-3})	1.325	1.376	1.528
T (°C)	22	-40	−50
λ (Å)	0.71073	0.71073	0.71073
μ (cm^{-1})	7.07	6.59	1.02
$R_1(F_o)$, $wR_2(F_o^2)$ ($I > 2\sigma(I)$)[a]	0.0442, 0.0924		0.0238, 0.0553
$R_1(F_o)$, $wR_2(F_o^2)$, all data[a]	0.0735, 0.1075		0.0301, 0.0581
$R_1(F_o)$, $R_w(F_o)$ ($I > 3\sigma(I)$)[b]		0.0521, 0.0441	

[a] Using the SHELX95 package, $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$, $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [f(\text{max of 0 or } F_o^2) + (1 - f)F_c^2]$. [b] Using the TEXSAN package, $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2]^{1/2}/\sum w|F_o|^2$, where $w = [\sigma^2(F_o) + (\rho F_o^2)^2]^{1/2}$ for non-Poisson contribution weighting scheme. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$.

bond distance of 2.29 Å is quite normal for this type of molecule.

Conclusions

The reaction of KTp′ with $RhCl_3(CH_3CN)_3$ provides an alternate synthesis of Tp′Rh(CH_3CN)Cl_2 in 88% yield. The acetonitrile ligand of Tp′Rh(CH_3CN)Cl_2 can be substituted with neopentyl isocyanide to prepare **1** in 80% yield. Complex **1** reacts with alkyl and vinyl Grignard reagents to give the alkyl and vinyl chloride complexes **2a**−**7a** in moderate yield. Complexes **2a**−**7a** are new, air-stable, octahedral rhodium(III) alkyl (vinyl) chloride complexes which contain a tridentate Tp′ ligand and a neopentyl isocyanide ligand.

Experimental Section

General Methods. All reactions, recrystallizations, and routine manipulations, unless otherwise noted, were carried out at RT under a nitrogen atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corp. dri-lab. Unless otherwise noted dry solvents were used in all reactions and recrystallizations. Hexanes were stirred over concentrated sulfuric acid for 24 h and washed successively with potassium permanganate in 10% aqueous sulfuric acid, water, and saturated aqueous sodium carbonate. The resulting olefin-free hydrocarbon was predried over anhydrous calcium chloride before being distilled under nitrogen from a dark purple solution of sodium benzophenone ketyl. Acetonitrile and chloroform-d_1 were stirred over calcium hydride for 24 h, degassed using three freeze−pump−thaw cycles, and distilled under vacuum. Benzene, diethyl ether, and tetrahydrofuran were distilled under nitrogen from dark purple solutions of sodium benzophenone ketyl. Benzene-d_6, cyclohexane-d_{12}, and tetrahydrofuran-d_8 were degassed using three freeze−pump−thaw cycles and distilled under vacuum from dark purple solutions of sodium benzophenone ketyl. The dry, proteo solvents were stored in screw-cap glass bottles in the dri-lab, and the dry, deutero solvents were stored in ampules with Teflon-sealed vacuum line adapters. Anisole (99%), silver trifluoromethanesulfonate (99+%), and silica gel (200−400 mesh, 60 Å) for column chromatography were purchased from Aldrich Chemical Co. and used without further purification. Chloroform, methylene chloride, hexanes (for chromatography), and tetrahydrofuran (for chromatography) were purchased from Fischer Chemical and used without further purification. All Grignard reagents (diethyl ether or THF solutions) with the exception of cyclopropylmagnesium bromide were purchased from Aldrich Chemical Co. Cyclopropylmagnesium bromide was prepared according to a published procedure.[9] All Grignard reagents were titrated before use with 2-propanol in *p*-xylene using 1,10-phenanthroline as the indicator.[10] Tetrabutylammonium chloride was recrystallized according to a published purification technique[11] and stored in the dri-lab. Potassium tris(3,5-dimethyl)pyrazolylborate,[12] neopentyl isocyanide,[13] and $RhCl_3(CH_3CN)_3$[14] were synthesized as previously reported. Silica gel plates (2 mm) used in preparative thin-layer chromatography contained a fluorescent indicator and were purchased from Analtech. All chromatography was executed in air at RT using solvents as received.

^{1}H (400 MHz), ^{2}H (61 MHz), and ^{13}C (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 (C_6D_6, δ 7.15; C_6D_{12}, δ 1.38; THF-d_8, δ 1.73, 3.58; $CDCl_3$, δ 7.24). Chemical shifts for ^{13}C NMR were measured in ppm relative to the deuterated solvent resonance (C_6D_6, δ 128.0; C_6D_{12}, δ 26.4). Chemical shifts for ^{2}H NMR were measured in ppm relative to the deuterated solvent resonance of added C_6D_6, 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 **6a**·THF and **5a** and **8**, respectively. Infrared spectra were recorded by a Mattson Instruments 6020 Galaxy Series FTIR and processed with First:Aquire v1.52 software.

Purification of Potassium Tris(3,5-dimethyl)pyrazolylborate (KTp′). The following improvement over Trofimenko's recrystallization procedure[12b] was used. Crude KTp′ (1.0 g) was washed with chloroform (2 × 50 mL), filtered, and added to an Erlenmeyer flask containing 200 mL of anisole. The suspension was brought to a vigorous boil until a clear solution was obtained. Approximately 5 mL of anisole was added to a 500 mL filter flask and brought to a boil. The KTp′ solution was hot vacuum filtered into the preheated filter flask fitted with a Büchner funnel and a Whatman filter disc (*caution: extreme bumping of solution can occur*). The filtrate was evenly divided into two preheated 250 mL Erlenmeyer flasks and heated to boiling. The volume of the filtrate was reduced by evaporation to a total of 100 mL (2 × 50 mL) or to the point at which the solution's appearance was slightly cloudy or with the appearance of crystals. The flasks were immediately stoppered and cooled to −20 °C for 24 h. The recrystallized product was harvested, washed with ice cold hexanes (3 × 25 mL), and dried under high vacuum to give 0.5 g as colorless microcrystals. The purified KTp′ was stored under nitrogen.

Synthesis of Tp′Rh(CH_3CN)Cl_2. To a stirred solution of 316 mg (0.951 mmol) of $RhCl_3(CH_3CN)_3$ in 50 mL of acetonitrile was added all at once 326 mg (0.969 mmol) of KTp′. The clear orange solution quickly became a cloudy suspension, and after 10 min of stirring its color changed to yellow. The suspension was stirred for 3 h and was filtered through a glass frit funnel to remove precipitated potassium chloride and unreacted KTp′. The filtrate was evaporated *in vacuo* to give 427 mg (88%) of crude Tp′Rh(CH_3CN)Cl_2 as a yellow powder. The ^{1}H NMR spectrum of the crude product in $CDCl_3$ was consistent with that previously reported by Powell.[6] The crude product was used in subsequent reactions (it may be purified by preparative TLC using acetonitrile−methylene chloride (1:1, v/v) as the mobile phase; acetonitrile can be used for extraction). ^{1}H NMR ($CDCl_3$): δ 2.331 (s, 3 H, RhNCCH_3), 2.352 (s, 6 H, pzCH_3), 2.513 (s, 3 H, pzCH_3),

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2.612 (s, 6 H, pzCH_3), 2.772 (s, 3 H, pzCH_3), 5.796 (s, 1 H, pzH), 5.823 (s, 2 H, pzH).

Synthesis of Tp′Rh(CNCH$_2$CMe$_3$)Cl$_2$ (1). To a stirred suspension of 944 mg (1.844 mmol) of Tp′Rh(CH_3CN)Cl_2 in 75 mL of benzene was added a solution of 300 μL (2.316 mmol) of neopentyl isocyanide in 2 mL of benzene. The resulting suspension was refluxed under positive nitrogen pressure for 4 h giving a clear bright yellow solution. The solvent was removed *in vacuo* to give a bright orange-yellow powder. The solid was recrystallized at −20 °C from a methylene chloride solution layered with hexanes. The crystals were washed with ice-cold hexanes and dried under vacuum to give 836 mg (80%) as orange-yellow plates. ^{1}H NMR (C_6D_6): δ 0.789 (s, 9 H, C(CH_3)$_3$), 2.035 (s, 6 H, pzCH_3), 2.107 (s, 3 H, pzCH_3), 2.671(s, 2 H, NCH_2), 2.732 (s, 6 H, pzCH_3), 3.241 (s, 3 H, pzCH_3), 5.488 (s, 2 H, pzH), 5.524 (s, 1 H, pzH). ^{13}C{^{1}H} NMR (C_6D_6): δ 12.18, 12.44, 15.41, 15.64 (s, pzCH_3), 26.54 (s, C(*C*H$_3$)$_3$), 32.34 (s, *C*(CH$_3$)$_3$), 56.38 (s, NCH_2), 108.36, 108.88 (s, pzCH), 142.60, 144.22, 153.12, 155.42 (s, pzC_q). IR (KBr): 2538 cm^{-1} (B−H), 2241 cm^{-1} (CNR). Anal. Calcd (found) for $C_{21}H_{33}BCl_2N_7Rh$: C, 44.39 (43.91); H, 5.85 (5.94); N, 17.26 (16.82).

Synthesis of Tp′Rh(CNCH$_2$CMe$_3$)(CH$_3$)Cl (2a). To a stirred solution of 124 mg (0.218 mmol) of **1** in 15 mL of THF was added, dropwise over a period of 1 min, a solution of 90 μL (0.243 mmol) of 2.7 M CH_3MgCl in 2 mL of THF. Upon addition of the Grignard reagent the color of the solution changed from yellow to green-yellow. The reaction mixture was stirred for 15 min. The excess Grignard reagent was quenched with a saturated solution of NH_4Cl(aq) until all had reacted to give a clear solution. This solution was filtered through cotton, reduced in volume under vacuum, and chromatographed using a 1 cm × 5 cm column of silica gel with hexanes−THF (2:1, v/v) as the mobile phase. Solvent removal *in vacuo* gave a pale green-yellow powder. The product was recrystallized at −20 °C from a THF solution layered with hexanes. The recrystallized product was washed with ice-cold hexanes and dried under vacuum to give 85 mg (71%) as green-yellow microcrystals. ^{1}H NMR (C_6D_6): δ 0.703 (s, 9 H, C(CH_3)$_3$), 2.087 (s, 3 H, pzCH_3), 2.150 (s, 3 H, pzCH_3), 2.237 (s, 3 H, pzCH_3), 2.278 (s, 3 H, pzCH_3), 2.369 (d, J_{RhH} = 2 Hz, 3 H, RhCH_3), 2.596 (AB_q, 2 H, NCH_2), 2.811 (s, 3 H, pzCH_3), 2.932 (s, 3 H, pzCH_3), 5.524 (s, 1 H, pzH), 5.533 (s, 1 H, pzH), 5.727 (s, 1 H, pzH). ^{13}C{^{1}H} NMR (C_6D_6): δ −3.11 (d, J_{RhC} = 19 Hz, RhCH_3), 12.27, 12.62, 12.90, 14.49, 14.63, 14.85 (s, pzCH_3), 26.48 (s, C(*C*H$_3$)$_3$), 31.90 (s, *C*(CH$_3$)$_3$), 56.11 (s, NCH_2), 106.70, 107.80, 108.45 (s, pzCH), 142.54, 142.62, 144.18, 150.97, 151.16, 153.05 (s, pzC_q). IR (KBr): 2526 cm^{-1} (B−H), 2202 cm^{-1} (CNR). Anal. Calcd (found) for $C_{22}H_{36}BClN_7Rh$: C, 48.24 (48.88); H, 6.62 (6.50); N, 17.90 (17.44).

Synthesis of Tp′Rh(CNCH$_2$CMe$_3$)(CD$_3$)Cl (3a). To a stirred solution of 99 mg (0.174 mmol) of **1** in 15 mL of THF was added, dropwise over a period of 1 min, 250 μL (0.200 mmol) of a solution of 0.8 M CD_3MgI in 2 mL of THF. Upon addition of the Grignard reagent the color of the solution changed from yellow to orange-brown. The reaction mixture was stirred for 10 min. The workup and recrystallization methods for **3a** were identical to those described in the synthesis of **2a**. Recrystallization yielded 64 mg (0.116 mmol, based on all chloride) of a mixture tentatively assigned by ^{1}H NMR spectroscopy (*vide infra*) as **3a** and Tp′Rh(CNCH$_2$CMe$_3$)(I)(CD$_3$) (**3c**). The mixture was dissolved in 25 mL of THF, and 42 mg (0.162 mmol) of AgOTf was added all at once. The reaction flask was covered with aluminum foil, and the reaction mixture was stirred for 5.5 h. Filtration removed precipitated AgCl and AgI giving a pale yellow solution. The filtrate contained three products tentatively assigned by ^{1}H NMR spectroscopy as **3**$^+$, **3c**, and Tp′Rh(CNCH$_2$CMe$_3$)(OTf)(CD$_3$) (**3d**) (*vide infra*). An additional 50 mL of THF and 117 mg (0.421 mmol) of (n-Bu)$_4$NCl were added to the filtrate. The reaction mixture was refluxed for 8 h under positive nitrogen pressure, filtered, reduced in volume under vacuum, and purified by preparative TLC using hexanes−THF (3:1, v/v) as the mobile phase. Extraction with THF and solvent removal *in vacuo* gave a green-yellow oil. Recrystallization at −20 °C from a THF solution layered with hexanes yielded 30 mg of **3a** (31% based on **1**) as green-yellow microcrystals. ^{1}H NMR (C_6D_6): δ 0.706 (s, 9 H, C(CH_3)$_3$), 2.088 (s, 3 H, pzCH_3), 2.151 (s, 3 H, pzCH_3), 2.239 (s, 3 H, pzCH_3), 2.274 (s, 3 H, pzCH_3), 2.609 (AB_q, 2 H, NCH_2), 2.811 (s, 3 H, pzCH_3), 2.923 (s, 3 H, pzCH_3), 5.525 (s, 1 H, pzH), 5.534 (s, 1 H, pzH), 5.728 (s, 1 H, pzH). ^{13}C{^{1}H} NMR (C_6D_6): δ 12.27, 12.62, 12.90, 14.47, 14.63, 14.83 (s, pzCH_3), 26.47 (s, C(*C*H$_3$)$_3$), 31.89 (s, *C*(CH$_3$)$_3$), 56.08 (s, NCH_2), 106.69, 107.78, 108.44 (s, pzCH), 142.53, 142.62, 144.17, 150.94, 151.14, 153.03 (s, pzC_q). ^{2}H{^{1}H} NMR (C_6H_6): δ 2.270 (bs, RhCD_3). IR (KBr): 2526 cm^{-1} (B−H), 2202 cm^{-1} (CNR). Anal. Calcd (found) for $C_{22}H_{33}D_3BClN_7Rh$: C, 48.24 (48.74); H, 6.62 (6.76); N, 17.90 (17.19). Compounds **3**$^+$ and **3d** were not isolated due to their lability.

^{1}H NMR Characterization of Tp′Rh(CNCH$_2$CMe$_3$)(I)(CD$_3$) (3c). ^{1}H NMR (C_6D_6): δ 0.745 (s, 9 H, C(CH_3)$_3$), 2.059 (s, 3 H, pzCH_3), 2.132 (s, 3 H, pzCH_3), 2.218 (s, 3 H, pzCH_3), 2.274 (s, 3 H, pzCH_3), 2.686 (AB_q, 2 H, NCH_2), 2.843 (s, 3 H, pzCH_3), 2.965 (s, 3 H, pzCH_3), 5.523 (s, 1 H, pzH), 5.563 (s, 1 H, pzH), 5.729 (s, 1 H, pzH).

^{1}H NMR Characterization of Tp′Rh(CNCH$_2$CMe$_3$)(OTf)(CD$_3$) (3d). ^{1}H NMR (C_6D_6): δ 0.648 (s, 9 H, C(CH_3)$_3$), 1.964 (s, 3 H, pzCH_3), 2.048 (s, 3 H, pzCH_3), 2.139 (s, 3 H, pzCH_3), 2.148 (s, 3 H, pzCH_3), 2.691 (s, 3 H, pzCH_3), 2.695 (s, 3 H, pzCH_3), 4.078 (AB_q, 2 H, NCH_2), 5.385 (s, 1 H, pzH), 5.448 (s, 1 H, pzH), 5.707 (s, 1 H, pzH).

Synthesis of Tp′Rh(CNCH$_2$CMe$_3$)(CH$_2$CH$_2$CH$_3$)Cl (4a). The synthesis of **4a** was identical to that of **2a** except that 100 mg (0.176 mmol) of **1** and 70 μL (0.245 mmol) of 3.5 M *n*-PrMgCl were used. The workup and recrystallization methods for **4a** were also identical to that of **2a**. Yield: 55 mg (54%) as green-yellow plates. ^{1}H NMR (C_6D_6): δ 0.701 (s, 9 H, C(CH_3)$_3$), 1.262 (t, J = 7 Hz, 3 H, RhCH$_2$-CH$_2$C*H*$_3$), 1.756 (m, 1 H, RhCH$_2$C*H*$_2$CH$_3$), 1.937 (m, 1 H, RhCH$_2$C*H*$_2$-CH$_3$), 2.097 (s, 3 H, pzCH_3), 2.157 (s, 3 H, pzCH_3), 2.228 (s, 3 H, pzCH_3), 2.333 (s, 3 H, pzCH_3), 2.625 (AB_q, 2 H, NCH_2), 2.785 (s, 3 H, pzCH_3), 2.963 (s, 3 H, pzCH_3), 3.242 (m, 1 H, RhC*H*$_2$CH$_2$CH$_3$), 3.496 (m, 1 H, RhC*H*$_2$CH$_2$CH$_3$), 5.550 (s, 1 H, pzH), 5.601 (s, 1 H, pzH), 5.707 (s, 1 H, pzH). ^{13}C{^{1}H} NMR (C_6D_6): δ 12.27, 12.75, 12.981, 14.50, 14.54, 14.62 (s, pzCH_3), 17.08 (s, RhCH$_2$CH$_2$*C*H$_3$), 21.00 (d, J_{RhC} = 19 Hz, Rh*C*H$_2$CH$_2$CH$_3$), 26.57 (s, C(*C*H$_3$)$_3$), 27.11 (s, RhCH$_2$*C*H$_2$CH$_3$), 31.89 (s, *C*(CH$_3$)$_3$), 56.17 (s, NCH_2), 106.61, 107.68, 108.48 (s, pzCH), 142.51, 142.72, 144.26, 150.76, 151.11, 153.11 (s, pzC_q). IR (KBr): 2561 cm^{-1}, 2541 cm^{-1} (B−H), 2203 cm^{-1} (CNR). Anal. Calcd (found) for $C_{24}H_{40}BClN_7Rh$·THF: C, 51.90 (51.95); H, 7.47 (7.34); N, 15.13 (15.41).

Synthesis of Tp′Rh(CNCH$_2$CMe$_3$)(CH(CH$_3$)$_2$)Cl (5a). The synthesis of **5a** was identical to that of **2a** except that 97 mg (0.171 mmol) of **1** and 100 μL (0.200 mmol) of 2 M *i*-PrMgCl were used. The workup and recrystallization methods for **5a** were identical to that of **2a**. Yield: 30 mg (31%) as pale green-yellow plates. ^{1}H NMR (C_6D_6): δ 0.697 (s, 9 H, C(CH_3)$_3$), 1.041 (bd, J = 6 Hz, 3 H, RhCH-(C*H*$_3$)$_2$), 1.936 (bd, J = 6 Hz, 3 H, RhCH(C*H*$_3$)$_2$), 2.098 (s, 3 H, pzCH_3), 2.178 (s, 3 H, pzCH_3), 2.216 (s, 3 H, pzCH_3), 2.388 (s, 3 H, pzCH_3), 2.664 (AB_q, 2 H, NCH_2), 2.771 (s, 3 H, pzCH_3), 2.994 (s, 3 H, pzCH_3), 5.102 (bm, 1 H, RhC*H*(CH$_3$)$_2$), 5.554 (s, 1 H, pzH), 5.632 (s, 1 H, pzH), 5.693 (s, 1 H, pzH). ^{13}C{^{1}H} NMR (C_6D_6): δ 12.29, 12.92, 13.16, 14.67, 14.703, 15.89 (s, pzCH_3), 25.11 (d, J_{RhC} = 19 Hz, Rh*C*H-(CH$_3$)$_2$), 26.64, (s, RhCH(*C*H$_3$)$_2$), 26.74 (s, C(*C*H$_3$)$_3$), 31.65 (s, RhCH-(*C*H$_3$)$_2$), 31.88 (s, *C*(CH$_3$)$_3$), 56.31 (s, NCH_2), 106.60, 107.77, 109.14 (s, pzCH), 142.50, 142.74, 144.51, 150.79, 151.00, 153.00 (s, pzC_q). IR (KBr): 2525 cm^{-1} (B-H), 2214 cm^{-1} (CNR). Anal. Calcd (found) for $C_{24}H_{40}BClN_7Rh$: C, 50.06 (50.04); H, 7.00 (6.89); N, 17.03 (17.03).

Synthesis of Tp′Rh(CNCH$_2$CMe$_3$)(*c*-C$_3$H$_5$)Cl (6a). To a solution of 106 mg (0.187 mmol) of **1** in 15 mL of THF at −20 °C was added 1.1 mL (0.363 mmol) of 0.33 M *c*-PrMgBr in diethyl ether. The reaction mixture was warmed to 0 °C and stirred for 1 h under positive nitrogen pressure before being quenched with NH_4Cl(aq) at 0 °C. Preparative TLC with hexanes−THF (2:1, v/v) as the mobile phase followed by extraction with THF and solvent removal *in vacuo* gave 95 mg of crude product as a yellow oil. The crude product was assumed to be a mixture of **6a** and Tp′Rh(CNCH$_2$C(CH$_3$)$_3$)(Br)(*c*-C$_3$H$_5$) (**6b**), on the basis of a ^{1}H NMR spectrum of the crude product in C_6D_6 which showed two sets of resonances each with three inequivalent pyrazolyl rings. To a stirred solution of 95 mg (0.166 mmol, based on all chloride) of RhTp′(CNCH$_2$C(CH$_3$)$_3$)(X)(*c*-C$_3$H$_5$) in 25 mL of THF was added, all at once, 50 mg (0.195 mmol) of AgOTf. The reaction mixture was stirred for 1 h and filtered through a glass frit funnel giving a murky, yellow suspension. A large excess (129 mg, 0.464 mmol) of (n-Bu)$_4$NCl was added to the suspension and this reaction mixture was

stirred for 5 h giving a clear pale yellow solution. The solvent volume was reduced, and the remaining solution was chromatographed by preparative TLC using hexanes−THF (2:1, v/v) as the mobile phase. After extraction with THF, solvent removal *in vacuo*, and recrystallization at −20 °C from a THF solution layered with hexanes, 57 mg (62% based on **1**) as pale yellow prisms was isolated. ^{1}H NMR (C_6D_6): δ 0.626 (s, 9 H, C(CH$_3$)$_3$), 0.900 (m, 2 H, RhC*H*(CH$_2$)$_2$, RhCH(C*H*$_2$)$_2$), 1.033 (m, 1 H, RhCH(C*H*$_2$)$_2$), 1.758 (m, 1 H, RhCH(C*H*$_2$)$_2$), 2.049 (m, 1 H, RhCH(C*H*$_2$)$_2$), 2.111 (s, 3 H, pzCH$_3$), 2.167 (s, 3 H, pzCH$_3$), 2.225 (s, 3 H, pzCH$_3$), 2.567 (AB$_q$, 2 H, NCH$_2$), 2.573 (s, 3 H, pzCH$_3$), 2.724 (s, 3 H, pzCH$_3$), 3.062 (s, 3 H, pzCH$_3$), 5.601 (s, 1 H, pzH), 5.639 (s, 1 H, pzH), 5.701 (s, 1 H, pzH). ^{13}C{^{1}H}-jmod NMR (C_6D_6): δ 3.37 (d, J_{RhC} = 27 Hz, Rh*C*H(CH$_2$)$_2$), 12.31, 12.72, 12.97, 14.90, 15.21 (2 overlapping resonances) (s, pzCH$_3$,), 10.85, 14.26 (s, RhCH(*C*H$_2$)$_2$), 26.58 (s, C(*C*H$_3$)$_3$), 31.77 (s, *C*(CH$_3$)$_3$), 56.11 (s, NCH$_2$), 106.84, 107.83, 108.38 (s, pzCH), 142.70, 142.80, 144.28, 151.29, 151.62, 153.61 (s, pzC$_q$). IR (KBr): 2527 cm^{-1} (B−H), 2211 cm^{-1} (CNR). Anal. Calcd (found) for $C_{24}H_{38}BClN_7Rh$: C, 50.24 (50.32); H, 6.68 (6.57); N, 17.09 (15.45).

Synthesis of Tp′Rh(CNCH$_2$CMe$_3$)(CH═CH$_2$)Cl (7a). The synthesis of **7a** was identical to **2a** except that 66 mg (0.116 mmol) of **1** and 128 μL (0.128 mmol) of 1 M CH$_2$CHMgBr were reacted for 5 min. The workup and recrystallization were identical to **2a** except that preparative TLC with hexanes−THF (2:1, v/v) as the mobile phase was used for chromatography. Yield: 30 mg (46%) as pale yellow needles. ^{1}H NMR (C_6D_6): δ 0.698 (s, 9 H, C(CH$_3$)$_3$), 2.095 (s, 3 H, pzCH$_3$), 2.145 (s, 3 H, pzCH$_3$), 2.233 (s, 3 H, pzCH$_3$), 2.349 (s, 3 H, pzCH$_3$), 2.579 (AB$_q$, 2 H, NCH$_2$), 2.826 (s, 3 H, pzCH$_3$), 2.914 (s, 3 H, pzCH$_3$), 5.553 (s, 1 H, pzH), 5.578 (s, 1 H, pzH), 5.724 (s, 1 H, pzH), 5.837 (d, J = 17 Hz, 1 H, *trans*-RhCHC*H*$_2$), 5.976 (d, J = 9 Hz, 1 H, *cis*-RhCHC*H*$_2$), 7.909 (ddd, $J_{trans-HH}$ = 17, J_{cis-HH} = 9 Hz, J_{RhH} = 3 Hz, 1 H, RhC*H*CH$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 12.27, 12.57, 12.87, 14.70, 15.46, 15.57 (s, pzCH$_3$), 26.52 (s, C(*C*H$_3$)$_3$), 31.88 (s, *C*(CH$_3$)$_3$), 55.93 (s, NCH$_2$), 106.84, 107.64, 108.13 (s, pzCH), 123.69 (s, RhCH*C*H$_2$), 145.90 (d, J_{RhH} = 23 Hz, Rh*C*HCH$_2$), 142.72, 142.91, 144.27, 150.97, 151.65, 153.45 (s, pzC$_q$). IR (KBr): 2525 cm^{-1} (B−H), 2222 cm^{-1}(CNR). Anal. Calcd (found) for $C_{23}H_{36}BClN_7Rh$: C, 49.35 (49.97); H, 6.48 (6.55); N, 17.52 (17.09).

Synthesis of Tp′Rh(PMe$_3$)(Cl)$_2$ (8). To a suspension of 200 mg (0.391 mmol) of Tp′Rh(CH$_3$CN)Cl$_2$ in 40 mL of C_6H_6 was added 61 μL (0.589 mmol) of PMe$_3$ all at once. The reaction mixture was refluxed under positive N_2 pressure for 1 h. The resulting bright yellow solution was evaporated under high vacuum to give 226 mg of crude **8** as an orange-yellow powder. A sample of the crude powder (68 mg) was dissolved in a minimum of CH_2Cl_2, filtered through cotton, and layered with hexanes. After 2 weeks large orange prisms were isolated, washed with ice-cold hexanes, and dried under high vacuum to give 58 mg of **8** (90%). ^{1}H NMR (C_6D_6): δ 1.265 (d, J_{PH} = 11 Hz, 9 H, P(CH$_3$)$_3$), 2.096 (s, 3 H, pzCH$_3$), 2.115 (s, 6 H, pzCH$_3$), 2.563 (s, 6 H, pzCH$_3$), 3.206 (s, 3 H, pzCH$_3$), 5.448 (s, 2 H, pzH), 5.507 (s, 1 H, pzH). ^{31}P{^{1}H} NMR (C_6D_6): δ 1.642 (d, J_{RhP} = 106 Hz, RhP(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 12.31, 13.04, 15.29 (s, pzCH$_3$), 16.50 (d, J_{PC} = 35 Hz, P(CH$_3$)$_3$), 17.21 (s, pzCH$_3$), 108.48 (d, $^4J_{PC}$ = 4 Hz, pzCH), 110.12 (s, pzCH), 142.31 (d, $^5J_{PC}$ = 4 Hz, pzC$_q$), 144.71 (s, pzC$_q$), 154.61 (d, $^3J_{PC}$ = 5 Hz, pzC$_q$), 157.77 (s, pzC$_q$). IR (KBr): 2551 cm^{-1} (B−H). Anal. Calcd (found) for $C_{18}H_{31}BCl_2N_6PRh$: C, 39.52 (39.54); H, 5.71 (5.79); N, 15.36 (15.32).

X-ray Structural Determination of 5a. Pale green-yellow plates were crystallized from a THF solution of **5a** layered with hexanes at −20 °C. A single crystal having approximate dimensions of 0.26 × 0.15 × 0.02 mm^3 was mounted on a glass fiber with epoxy. Data were collected at 22 °C on a Siemens SMART CCD area detector system employing a 3 kW sealed tube X-ray source operating at 1.5 kW. A total of 1.3 hemispheres of data were collected over 14 h (30 s frames), yielding 23 429 observed data after integration using SAINT (see Table 4). Laue symmetry revealed an orthorhombic crystal system, and cell parameters were determined from 8192 unique reflections. (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× the listed values.) The space group was assigned as *Pbcn* on the basis of systematic absences using XPREP, and the structure was solved and refined using SHELX95. For a *Z* value of 8 there is one independent molecule within the asymmetric unit. In the final model, non-hydrogen atoms were refined anisotropically (full matrix on F^2), with hydrogens included in idealized locations. The structure was refined with R_1 = 0.0442 and wR_2 = 0.0924.[15] Fractional coordinates and thermal parameters are given in the Supporting Information.

X-ray Structural Determination of 6a·THF. Pale yellow crystals were obtained from the slow evaporation of a THF solution of **6a** at −20 °C. A single crystal having approximate dimensions of 0.30 × 0.15 × 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° on an Enraf Nonius CAD4 diffractometer. Cell reduction revealed a primitive monoclinic crystal system. Data were collected at −40 °C in accord with the parameters found in Table 4. 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. The space group was uniquely assigned as $P2_1/c$ 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. A difference Fourier map revealed significant peaks at a considerable distance from the rhodium atom which were assigned as one molecule of THF. 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 atoms in idealized positions) was executed until convergence was achieved. The structure was refined with R_1 = 0.0520 and R_w = 0.0441.[15] Fractional coordinates and thermal parameters are given in the Supporting Information.

X-ray Structural Determination of 8. Large orange prisms were crystallized by evaporation at RT of a 1:1 (v/v) CH_2Cl_2−hexanes solution of **8**. A single crystal having approximate dimensions of 0.26 × 0.22 × 0.22 mm^3 was mounted on a glass fiber with epoxy. Data were collected at −50 °C on a Siemens SMART CCD area detector system employing a 3kW sealed tube X-ray source operating at 1.5 kW. A total of 1.3 hemispheres of data were collected over 14 h (30 s frames), yielding 9264 data after integration using SAINT (see Table 4). Laue symmetry revealed a monoclinic crystal system, and cell parameters were determined from 7097 reflections. The space group was assigned as $P2_1/n$ on the basis of systematic absences using XPREP, and the structure was solved and refined using SHELX95. For a *Z* value of 4 there is one independent molecule within the asymmetric unit. In the final model, non-hydrogen atoms were refined anisotropically (on F^2), with hydrogens included in idealized locations. The structure was refined with R_1 = 0.0238 and wR_2 = 0.0553.[15] Fractional coordinates and thermal parameters are given in the Supporting Information.

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Supporting Information Available: X-ray crystallographic files in CIF format for complexes **5a**, **6a**, and **8** are available on the Internet only. Access information is given on any current masthead page.

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(15) Source of scattering factors f_o, f', and f'': Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol IV, Tables 2.2B and 2.3.1.