Synthesis and Reactions of (π-Allyl)bromo-[hydrotris(3,5-dimethylpyrazolyl)borato]rhodium(III)

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$Tp^{Me2}Rh(coe)(MeCN)$ (**1**) (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borato, coe = cyclooctene) has been found to readily undergo oxidative addition of allyl bromide at room temperature to give $Tp^{Me2}Rh(\sigma$-allyl)Br(MeCN) (**4**). On prolonged reaction time or heating, complex **4** is converted to the π-allyl complex $Tp^{Me2}Rh(\pi$-allyl)Br (**5**) with liberation of MeCN. Complex **5** exhibits high reactivity toward MeMgBr and Li[$BHEt_3$], giving $Tp^{Me2}Rh(\pi$-allyl)Me (**8**) and $Tp^{Me2}Rh(\pi$-allyl)H (**9**), respectively. Deuterium-labeling experiments using Li[$BDEt_3$] indicate that complex **9** is formed mainly by nucleophilic addition of H^- to the central carbon of the π-allyl ligand, followed by β-hydrogen elimination of the resultant rhodacyclobutane intermediate. Complex **9** reacts with a variety of alkyl bromides by a radical process to afford **5** and alkanes.

Introduction

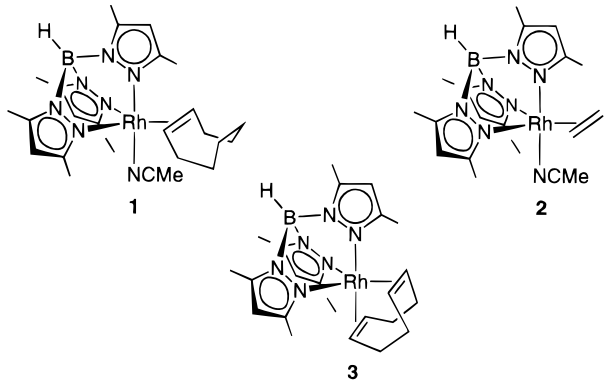
Hydrotris(pyrazolyl)borate and its derivatives (Tp^{R2}; R = H, Me, *i*-Pr, etc.) are an important class of tridentate ligands in coordination chemistry.[1] Although Tp^{R2} ligands are often likened to cyclopentadienyl ligands (Cp) because of their isoelectronic structures, Tp^{R2} ligands still have characteristic features not observed for Cp ligands: the nitrogen-based chelate structure, the C_{3v} symmetry, and the relative ease of tuning the steric factors by the selection of the substituent at the 3-position of the pyrazolyl rings. Therefore, Tp^{R2} complexes frequently exhibit unique properties and are currently of interest in organometallic chemistry.[2−7]

In this paper, we describe the synthesis and reactions of the novel (π-allyl)rhodium(III) complex $Tp^{Me2}Rh(\pi$-allyl)Br (**5**). One of the most common routes to transition-metal π-allyl complexes is oxidative addition of allylic substrates to low-valent metal species.[8] Most Tp^{R2}-coordinated π-allyl complexes,[3−5] however, have been prepared by anionic ligand displacement from parent π-allyl transition metals with Tp^-M^+ salts (M = Na, K, Tl).[4,5] We report herein that $Tp^{Me2}Rh(coe)$-(MeCN) (**1**)[6] (coe = cyclooctene) readily undergoes oxidative addition of allyl bromide to give **5** in high yield.

Results and Discussion

Oxidative Addition of Allyl Bromide. Three kinds of Tp^{Me2}−rhodium(I) complexes (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borato) (**1**−**3**, Chart 1)[6,7,9] were re-

Chart 1



(1) (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (b) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115.

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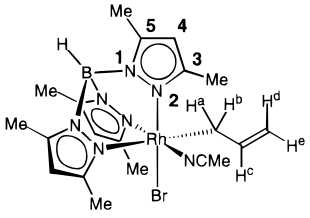
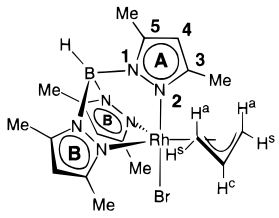
Table 1. NMR Data of 4 and 5[a]



4

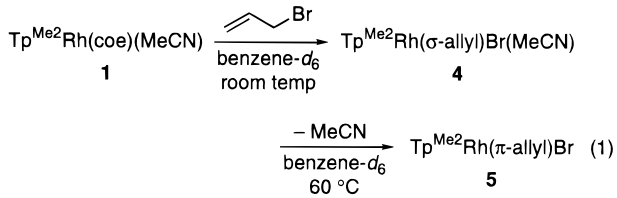


5

	^{1}H NMR		^{13}C{^{1}H} NMR		IR
complex	δ	assignment	δ	assignment	ν_{BH} (cm^{-1})
4	0.59 (s, 3H)	MeCN	4.3 (s)	MeCN	2532
	2.08 (s, 3H)	Me^{Pz}	12.4 (s)	Me^{Pz}	
	2.10 (s, 3H)	Me^{Pz}	13.1 (s)	Me^{Pz}	
	2.25 (s, 3H)	Me^{Pz}	13.4 (s)	Me^{Pz}	
	2.29 (s, 3H)	Me^{Pz}	14.4 (s)	Me^{Pz}	
	2.79 (s, 3H)	Me^{Pz}	14.7 (s)	Me^{Pz}	
	3.01 (s, 3H)	Me^{Pz}	16.1 (s)	Me^{Pz}	
	4.63 (m, 1H)[b]	allyl H^a	18.0 (d)[c]	allyl C^1	
	4.76 (m, 1H)[b]	allyl H^b	106.7 (s)	C^{Pz4}	
	5.12 (dd, 1H)	allyl H^e	108.1 (s)	C^{Pz4}	
	5.47 (s, 1H)	H^{Pz4}	109.0 (s)	C^{Pz4}	
	5.53 (ddt, 1H)	allyl H^d	109.5 (s)	allyl C^3	
	5.62 (s, 1H)	H^{Pz4}	121.8 (d)[d]	CH_3CN	
	5.79 (s, 1H)	H^{Pz4}	143.3 (s)	C^{Pz}	
	6.73 (dddd, 1H)	allyl H^c	144.3 (s)	C^{Pz}	
			144.4 (s)	C^{Pz}	
	$J_{H^a-H^b}$ = 8.8 Hz, $J_{H^a-H^d}$ = $J_{H^b-H^d}$ = 1.5 Hz		148.5 (s)	allyl C^2	
	$J_{H^a-H^c}$ = 6.8 Hz, $J_{H^b-H^c}$ = 8.8 Hz,		150.8 (s)	C^{Pz}	
	$J_{H^c-H^d}$ = 17.1 Hz, $J_{H^c-H^e}$ = 10.2 Hz		151.2 (s)	C^{Pz}	
	$J_{H^d-H^e}$ = 2.9 Hz		154.0 (s)	C^{Pz}	
5	1.39 (s, 3H)	Me^{PzA3}	12.4 (s)	Me^{PzB}	2529
	1.99 (s, 3H)	Me^{PzA5}	13.2 (s)	Me^{PzA}	
	2.18 (s, 6H)	Me^{PzB5}	13.8 (s)	Me^{PzA}	
	2.66 (s, 6H)	Me^{PzB3}	16.5 (s)	Me^{PzB}	
	3.79 (d, 2H)	allyl H^a	47.4 (d)[e]	allyl C^1, C^3	
	4.51 (d, 2H)	allyl H^s	107.8 (s)	C^{PzB4}	
	5.05 (s, 1H)	H^{PzA4}	110.2 (s)	C^{PzA4}	
	5.73 (s, 2H)	H^{PzB4}	110.2 (d)[f]	allyl C^2	
	6.07 (ttd, 1H)[b]	allyl H^c	143.7 (s)	C^{PzB}	
			144.0 (s)	C^{PzA}	
	$J_{H^a-H^c}$ = 13.2 Hz, $J_{H^s-H^c}$ = 8.3 Hz		151.0 (s)	C^{PzA}	
			154.0 (s)	C^{PzB}	

[a] All NMR spectra were measured in C_6D_6 at room temperature except for the ^{13}C NMR spectrum of **4** ($CDCl_3$, −30 °C). [b] J_{RhH} = 1.5 Hz. [c] J_{RhC} = 18 Hz. [d] J_{RhC} = 7 Hz. [e] J_{RhC} = 10 Hz. [f] J_{RhC} = 5 Hz.

acted with allyl bromide (1.1 equiv) in benzene-d_6, with the reactions being followed by ^{1}H NMR spectroscopy. The reaction of **1** was complete within 1 h at room temperature to give the oxidative addition product Tp^{Me2}Rh(σ-allyl)Br(MeCN) (**4**) (eq 1). On prolonged reaction



time, complex **4** was further converted to the π-allyl complex Tp^{Me2}Rh(π-allyl)Br (**5**), with liberation of MeCN. The conversion of **4** to **5** proceeded slowly at room temperature but was complete within a few minutes at 60 °C. Complex **4** could not be isolated as an analytically pure compound because of the contamination by **5** during recrystallization, but its structure was unequivocally confirmed by NMR and IR spectroscopy. Complex **5** was isolated as red crystals in 76% yield and characterized by NMR and IR spectroscopy and elemental analysis.

The reaction of **2** with allyl bromide proceeded more slowly than that of **1**, taking about 2 days for completion at room temperature. The cod complex (**3**) did not react with allyl bromide even at 60 °C. When complex **1** was treated with other allylic substrates, such as crotyl, cinnamyl, and 2-methylallyl bromides and allyl acetate, the reactions were found to be significantly slower than that with allyl bromide; elevated temperatures led to uncharacterized mixtures of rhodium species.

Table 1 lists the NMR and IR data for **4** and **5**. The IR spectra exhibited a sharp absorption assignable to a ν_{BH} band at 2530 cm^{-1} for both complexes. The values correspond to κ^3 coordination of the Tp^{Me2} ligand.[6a]

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(8) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Yamamoto, A. *Organotransition Metal Chemistry, Fundamental Concepts and Applications*; Wiley-Interscience: New York, 1986.

(9) King, R. B.; Bond, A. *J. Organomet. Chem.* **1974**, *73*, 115.

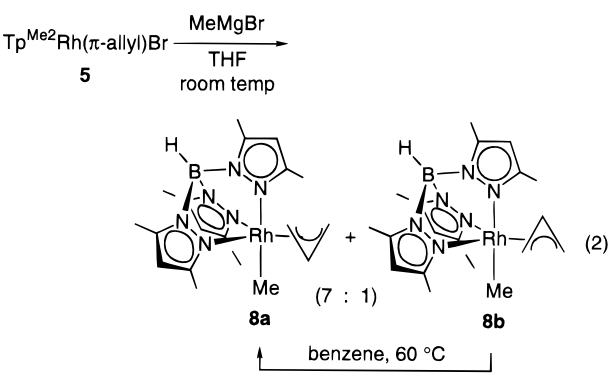
In the ^{1}H and ^{13}C NMR spectra of **4**, the three pyrazolyl groups exhibit three sets of signals, consistent with an octahedral structure having three different ligands at facial coordination sites. The five protons of the σ-allyl group were observed at δ 4.63, 4.76, 5.12, 5.53, and 6.73. The signals at δ 4.63 and 4.76, which are assignable to the two allylic protons (H^a and H^b) at diastereotopic positions, appeared as apparent triplets due to the geminal coupling to each other and to H^c. The ABX patterns observed for the three olefinic protons (H^c, H^d, and H^e) are typical of an uncoordinated vinyl group.

The ^{1}H and ^{13}C{^{1}H} NMR signals of the pyrazolyl groups in **5** were observed as two distinct sets of resonances in a 2:1 ratio, indicating C_s symmetry within the molecule. The π-allyl ligand also exhibited signals consistent with C_s symmetry. Thus, the two anti protons (H^a) and the two syn protons (H^s) were observed at δ 3.79 and 4.51, respectively. The two allylic carbons were observed to be equivalent. The signal of the proton (H^c) attached to the central carbon of the π-allyl ligand appeared at a significantly low magnetic field (δ 6.07), reflecting the highly electron-deficient nature of the cationic rhodium center. In a difference NOE experiment, the anti and syn proton signals were enhanced by 12% and 3%, respectively, by selective irradiation of the Me^{PzA3} protons. This confirms the endo orientation of the π-allyl ligand in **5**.

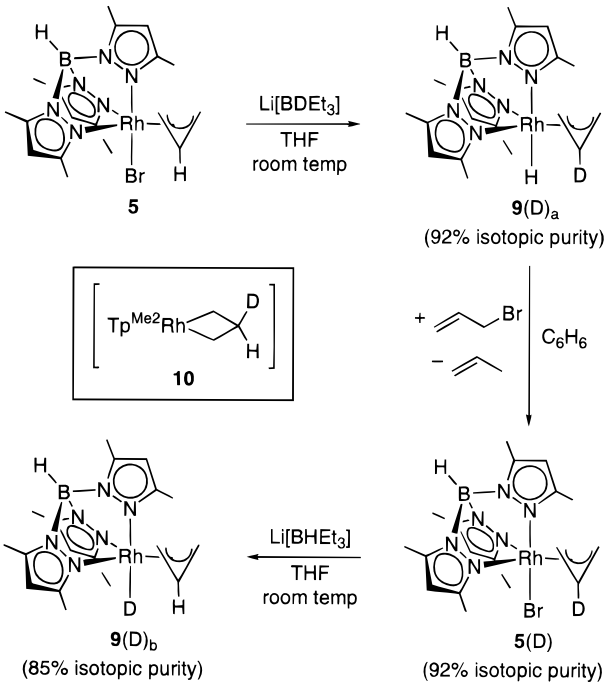
^{1}H NMR spectroscopy showed that complex **5** gradually converts to the σ-allyl complex **4** in neat CD_3CN at room temperature. This reaction was accompanied by partial decomposition. The reaction of **5** with PMe_2Ph (1 equiv) in benzene at room temperature over 2 days gave $Tp^{Me2}Rh(\sigma\text{-allyl})Br(PMe_2Ph)$ (**6**) in 61% isolated yield.

Reactions of 5 with Nucleophiles. Since the NMR chemical shifts suggested that the π-allyl moiety in **5** is highly electron deficient, the reactivity of **5** toward nucleophiles was examined. Complex **5** was found to be unreactive toward the soft carbanion generated from dimethyl malonate. The same soft carbanion also failed to react with a triflate derivative of **5**, $Tp^{Me2}Rh(\pi\text{-allyl})OTf$ (**7**), which was prepared by treatment of **5** with AgOTf (1 equiv) in benzene at 60 °C for 6 h. In contrast, complex **5** readily reacted with hard nucleophiles such as MeMgBr and Li[$BHEt_3$]. The reaction of MeMgBr took place at the rhodium center, whereas the hydride predominantly attacked the central carbon of the π-allyl ligand.

The reaction of **5** with MeMgBr (1.1 equiv) in THF at room temperature for 2 h gave a pair of structural isomers of $Tp^{Me2}Rh(\pi\text{-allyl})Me$ (**8a** and **8b**) in a 7:1 ratio



Scheme 1



(eq 2). ^{1}H NMR signals of the RhMe group appeared in C_6D_6 at δ 0.55 (d, $^3J_{RhH}$ = 1.8 Hz) for **8a** and at δ 0.88 (d, $^3J_{RhH}$ = 1.8 Hz) for **8b**. Upon heating at 60 °C for 1 h, the minor species **8b** was completely converted to **8a**, which was isolated in 63% yield based on **5**. Different NOE experiments indicated an endo orientation of π-allyl ligand in **8a**. Consequently, **8b** is assigned to the exo isomer.

Treatment of **5** with Li[$BHEt_3$] (1.1 equiv) in THF led to the selective formation of the hydride complex $Tp^{Me2}Rh(\pi\text{-allyl})H$ (**9**), which was isolated as a white solid in 63% yield. A similar reaction with Li[$BDEt_3$] afforded **9**$(D)_a$, in which the central carbon of the π-allyl ligand was deuterated in 92% selectivity (Scheme 1). Complex **9**$(D)_a$ was then converted to the bromide complex **5**(D) by the reaction with allyl bromide in benzene (vide infra), and the resulting **5**(D) was treated subsequently with Li[$BHEt_3$]. This sequence of reactions provided the deuteride complex **9**$(D)_b$ having a nondeuterated π-allyl ligand with 85% isotopic purity. These results suggest that the nucleophilic attack of H^- (or D^-) takes place at the central carbon of the π-allyl ligand and at the rhodium center in a 92:8 ratio. The major process provides a rhodacyclobutane intermediate (**10**), which successively undergoes β-hydrogen elimination to give **9**.[10,11]

Reactions of 9 with Organic Halides. (π-Allyl)rhodium hydride **9** cleanly reacted with a variety of organic bromides (RBr) in benzene-d_6 to give (π-allyl)rhodium bromide **5** and alkanes (RH). Table 2 summarizes the results. The reactivity of bromides decreased in the order benzyl bromide > allyl bromide >

(10) (a) Schwiebert, K. E.; Stryker, J. M. *Organometallics* **1993**, *12*, 600. (b) Tjaden, E. B.; Stryker, J. M. *Organometallics* **1992**, *11*, 16. (c) Wakefield, J. B.; Stryker, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 7057. (d) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346. (e) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7272.

(11) For related studies on the interconversion between π-allyl and metallacylobutane complexes, see: McNeill, K.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 11244.

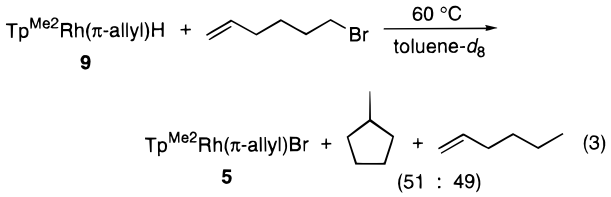
Table 2. Reactions of 9 with Alkyl Halides (RX)[a]

entry	R	X	temp (°C)	time (h)	conversion (%)
1	$PhCH_2$	Br	25	1	95
2	$CH_2{=}CHCH_2$	Br	25	3.5	96
3	$PhCH{=}CHCH_2$	Br	25	10	86
4	CH_3CH_2	Br	60	19	100
5	$CH_2{=}CHCH_2$	I	25	1	100
6	$CH_2{=}CHCH_2$	Cl	60	19	95
7	$CH_2{=}CHCH_2$	OAc	60	23	decomposition

[a] All reactions were run with 1.4 equiv of RX in benzene-d_6.

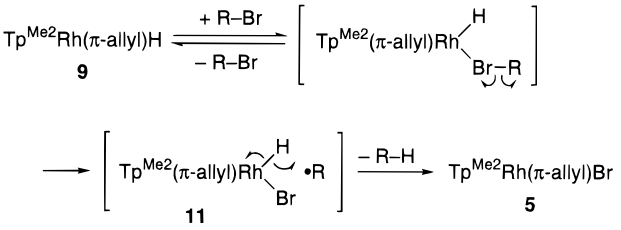
cinnamyl bromide ≫ ethyl bromide (entries 1−4). Allyl bromide was less reactive than allyl iodide but much more reactive than allyl chloride (entries 2, 5, and 6). The reaction of **9** with allyl acetate at 60 °C led to decomposition (entry 7).

The reactivity order observed is consistent with a pathway involving an alkyl radical, which was supported by the following experiment. Thus, the reaction of **9** with 6-bromo-1-hexene afforded methylcyclopentane in 51% selectivity, in addition to 1-hexene (eq 3).[12]



However, since the reactions in Table 2 did not provide homocoupling products (i.e., R−R) and the reaction of the deuteride complex **9**$(D)_b$ with benzyl bromide gave $PhCH_2D$ (see Experimental Section), the participation of a free alkyl radical can be excluded. Scheme 2 illustrates a possible mechanism. The first step is the coordination of alkyl bromide to rhodium via the Br atom. Electron transfer then takes place to generate an alkyl radical and the [$Tp^{Me2}Rh(\pi$-allyl)(Br)H] species (**11**). The alkyl radical subsequently abstracts the hydride ligand in **11** to give alkane and **5**.

Scheme 2



In summary, we have found routes to a variety of rhodium allyl complexes bearing a Tp^{Me2} ligand. Complex **1** has a coe ligand, which is easily dissociated to afford the coordinatively unsaturated species [Tp^{Me2}Rh(MeCN)], which undergoes oxidative addition of allyl bromide at room temperature to give the σ-allyl complex **4**. Dissociation of MeCN from **4** leads to the π-allyl complex **5**. Hard nucleophiles such as Me^- and H^- react with **5**. H^- adds regioselectively to the central carbon of the π-allyl ligand. The rhodacyclobutane complex thus produced is unstable and rapidly undergoes β-hydrogen elimination to give the π-allylhydrido complex (**9**), which can be reverted to **5** by reaction with alkyl bromides.

(12) Kramer, A. V.; Labinger, J. A.; Bradley, J. S.; Osborn, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 7145 and references therein.

Experimental Section

General. All manipulations were carried out under a nitrogen atmosphere using conventional Schlenk techniques. Nitrogen gas was dried by passing through P_2O_5 (Merck, SICAPENT). The NMR spectra were recorded on a JEOL JNM-A400 spectrometer (^{1}H NMR, 399.65 MHz; ^{13}C NMR, 100.40 MHz; ^{31}P NMR, 161.70 MHz). Chemical shifts are reported in δ (ppm) and referenced to an internal $SiMe_4$ standard for ^{1}H and ^{13}C NMR and to an external 85% H_3PO_4 standard for ^{31}P NMR. Mass spectra were measured with a Shimadzu QP-5000 GC-mass spectrometer (EI, 70 eV, capillary column). GLC analysis was performed with a GL Sciences GC-353 instrument equipped with a FID detector and a capillary column (TC-1, 30 m). THF, Et_2O, benzene, and hexane were dried over sodium benzophenone ketyl and distilled just prior to use. CH_2Cl_2 was dried over CaH_2 and distilled just prior to use. Benzene-d_6 was dried over $LiAlH_4$ and vacuum transferred and stored under a nitrogen atmosphere. The complexes Tp^{Me2}Rh(MeCN)(coe) (**1**),[6] Tp^{Me2}Rh(MeCN)(ethylene) (**2**),[7] and Tp^{Me2}Rh(cod) (**3**)[9] were synthesized according to the literature. All other compounds were obtained from commercial sources and used without purification.

Preparation of $Tp^{Me2}Rh(\sigma$-allyl)Br(MeCN) (4). A yellow-orange solution of **1** (147 mg, 0.267 mmol) in benzene (9 mL) was placed in a Schlenk tube, and allyl bromide (25.4 μL, 0.293 mmol) was added at room temperature. When the solution was stirred for 1 h, the color turned to orange. The solution was concentrated to dryness to give an orange solid, which was washed with hexane (5 mL) and dried under vacuum (111 mg, 74%). The complex was spectroscopically pure (^{1}H NMR). Further purification by recrystallization led to contamination with **5** (ca. 5%). The NMR and IR data are listed in Table 1.

Preparation of $Tp^{Me2}Rh(\pi$-allyl)Br (5). A yellow-orange solution of **1** (254 mg, 0.461 mmol) in benzene (15 mL) was placed in a Schlenk tube, and allyl bromide (43.9 μL, 0.507 mmol) was added. The solution was stirred for 30 min at room temperature and then heated at 60 °C for 1 h. The color of the solution turned to reddish orange. The solution was concentrated to dryness to give an orange solid, which was washed with hexane (5 mL) and dried under vacuum. The orange solid was dissolved in CH_2Cl_2 at room temperature, diluted with Et_2O, and cooled to −70 °C to give red crystals of **5** (184 mg, 77%). Anal. Calcd for $C_{18}H_{27}N_6BBrRh$: C, 41.49; H, 5.22; N, 16.13. Found: C, 41.71; H, 5.38; N, 15.72. The NMR and IR data are listed in Table 1.

Preparation of $Tp^{Me2}Rh(\sigma$-allyl)Br(PMe_2Ph) (6). A reddish-orange solution of **5** (76.2 mg, 0.146 mmol) in benzene (5 mL) was placed in a Schlenk tube, and PMe_2Ph (20.8 μL, 0.146 mmol) was added at room temperature. On stirring the solution, the color gradually changed to yellow over 2 days. The solution was concentrated to dryness, and the yellow solid was washed with hexane (5 mL) and dried under vacuum. The yellow solid was dissolved in CH_2Cl_2 at room temperature, diluted with Et_2O, and cooled to −70 °C to give orange crystals of **6** (59.1 mg, 61%). ^{1}H NMR (C_6D_6, room temperature): δ 1.50 (d, J_{H-P} = 10.3 Hz, 3H, PMe), 1.62 (s, 3H, Me^{Pz}), 1.74 (d, J_{H-P} = 10.3 Hz, 3H, PMe), 2.10, 2.16, 2.34, 2.71, 2.96 (s, each 3H, Me^{Pz}), 3.53 (m, 1H, allyl H^a), 4.65 (d, $J_{H^e-H^c}$ = 10.3 Hz, 1H, allyl H^e), 5.07 (m, 1H, allyl H^b), 5.24 (d, $J_{H^d-H^c}$ = 17.6 Hz, 1H, allyl H^d), 5.31 (s, 1H, H^{Pz4}), 5.54 (s, 1H, H^{Pz4}), 5.55 (m, 1H, allyl H^c), 5.69 (s, 1H, H^{Pz4}), 6.82 (t, J_{H-H} = 8.8 Hz, 2H, *m*-Ph), 6.88 (t, J_{H-H} = 8.8 Hz, 1H, *p*-Ph), 6.99 (t, J_{H-H} = J_{P-H} = 8.8 Hz, 2H, *o*-Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, room temperature): δ 13.0, 13.1, 13.4 (s, Me^{Pz}), 14.6 (d, J_{P-C} = 35 Hz, PMe), 15.6, 15.8, 16.8 (s, Me^{Pz}), 18.7 (dd, J_{P-C} or J_{Rh-C} = 7 or 20 Hz, allyl C^1), 19.4 (d, J_{P-C} = 36 Hz, PMe), 107.8 (d, J_{P-C} = 5 Hz, C^{Pz4}), 108.2, 108.4 (s, C^{Pz4}), 109.9 (s, allyl C^3), 127.9 (d, J_{P-C} = 8 Hz, *m*-Ph), 129.3 (s, *p*-Ph), 130.2 (d, J_{P-C} = 8 Hz, *o*-Ph), 135.3

(d, J_{P-C}= 43 Hz, *ipso*-Ph), 143.0, 144.2, 144.3 (s, C^{Pz}), 147.2 (s, allyl C^2), 151.9 (s, C^{Pz}), 152.4 (d, J_{P-C} = 5 Hz, C^{Pz}), 153.3 (s, C^{Pz}). $^{31}P\{^1H\}$ NMR (C_6D_6, room temperature): δ 6.55 (d, J_{Rh-P} = 127 Hz, PMe_2Ph). IR (KBr): ν_{B-H} = 2535 cm^{-1}. Anal. Calcd for $C_{26}H_{38}N_6BBrPRh$: C, 47.37; H, 5.81; N, 12.75. Found: C, 47.49; H, 5.78; N, 12.66.

Preparation of $Tp^{Me2}Rh(\pi$-allyl)OTf (7). Complex **5** (179 mg, 0.344 mmol) was dissolved in benzene (10 mL), and AgOTf (89.0 mg, 0.346 mmol) was added. The mixture was stirred at 60 °C for 6 h to afford a yellow solution and brown precipitate. The mixture was filtered through a filter-paper-tipped cannula, and the filtrate was concentrated to dryness to give a yellow solid, which was washed with ether (5 mL) and dried under vacuum (164 mg, 81%). ^1H NMR (C_6D_6, room temperature): δ 1.11 (s, 3H, Me^{PzA3}), 1.85 (s, 3H, Me^{PzA5}), 2.08 (s, 6H, Me^{PzB5}), 2.61 (s, 6H, Me^{PzB3}), 3.86 (d, $J_{H^a-H^c}$ = 13.2 Hz, 2H, allyl H^a), 4.79 (s, 1H, H^{PzA4}), 5.26 (d, $J_{H^s-H^c}$ = 8.8 Hz, 2H, allyl H^s), 5.71(s, 2H, H^{PzB4}), 6.74 (tt, $J_{H^a-H^c}$ = 13.2 Hz, $J_{H^s-H^c}$ = 8.8 Hz, 1H, allyl H^c). $^{13}C\{^1H\}$ NMR (C_6D_6, room temperature): δ 12.2 (s, Me^{PzB}), 13.2 (s, Me^{PzA}), 14.1 (s, Me^{PzA}), 14.9 (s, Me^{PzB}), 51.2 (d, J_{Rh-C} = 8 Hz, allyl C^1, C^3), 108.0 (s, C^{PzB4}), 111.4 (s, C^{PzA4}), 113.0 (d, J_{Rh-C} = 5 Hz, allyl C^2), 144.6 (s, C^{PzB}), 145.3 (s, C^{PzA}), 152.4 (s, C^{PzA}), 153.5 (s, C^{PzB}). IR (KBr): ν_{B-H} = 2559 cm^{-1}. Anal. Calcd for $C_{19}H_{27}N_6BF_3O_3RhS$: C, 38.66; H, 4.61; N, 14.24. Found: C, 38.84; H, 4.54; N, 14.27.

Reaction of 5 with MeMgBr. Complex **5** (100 mg, 0.192 mmol) was placed in a Schlenk tube and dissolved in THF (5 mL) at room temperature. An Et_2O solution of MeMgBr (0.577 M, 0.370 mL, 0.213 mmol) was added, and the mixture was stirred for 2 h. The color of the solution turned from orange to yellow. The volatile materials were removed by pumping, and the residue was washed with cold hexane (2 mL) and extracted with benzene (6 mL). The extract was passed through a short Celite column. Evaporation of the filtrate gave a pale yellow solid (56 mg, 64%). The ^1H NMR spectrum indicated the presence of two isomers of $Tp^{Me2}Rh(\pi$-allyl)Me (**8a** and **8b**) in a 7:1 ratio. **8a**: ^1H NMR (C_6D_6, room temperature): δ 0.55 (d, J_{Rh-H} = 1.8 Hz, 3H, RhMe), 1.69 (s, 3H, Me^{PzA3}), 2.17 (s, 6H, Me^{PzB3}), 2.22 (s, 6H, Me^{PzA5}), 2.24 (s, 3H, Me^{PzB5}), 3.34 (d, $J_{H^a-H^c}$ = 12.2 Hz, 2H, allyl H^a), 3.52 (d, $J_{H^s-H^c}$ = 7.8 Hz, 2H, allyl H^s), 4.12 (ttd, $J_{H^a-H^c}$ = 12.2 Hz, $J_{H^s-H^c}$ = 7.8 Hz, J_{Rh-H} = 1.6 Hz, 1H, allyl H^c), 5.41 (s, 1H, H^{PzA4}), 5.70 (s, 2H, H^{PzB4}). **8b**: ^1H NMR (C_6D_6, room temperature) δ 0.88 (d, J_{Rh-H} = 1.8 Hz, 3H, RhMe), 1.82 (d, $J_{H^a-H^c}$ = 11.1 Hz, 2H, allyl H^a), 1.98 (s, 3H, Me^{PzA}), 2.13 (s, 3H, Me^{PzA}), 2.19 (s, 6H, Me^{PzB}), 2.34 (s, 6H, Me^{PzB}), 3.78 (d, $J_{H^s-H^c}$ = 7.8 Hz, 2H, allyl H^s), 5.39 (s, 1H, H^{PzA4}), 5.73 (s, 2H, H^{PzB4}), 5.88 (tt, $J_{H^a-H^c}$ = 11.1 Hz, $J_{H^s-H^c}$ = 7.8 Hz, 1H, allyl H^c).

The mixture of **8a** and **8b** (56 mg) was dissolved in benzene (3 mL) and heated at 60 °C for 1 h. The solution was cooled to room temperature and concentrated to dryness to give a pale yellow solid (55 mg, 98%). The ^1H NMR spectrum exhibited only the set of signals of **8a**. $^{13}C\{^1H\}$ NMR (C_6D_6, room temperature): δ −5.38 (d, J_{Rh-C} = 20 Hz, RhMe), 12.9 (s, Me^{PzB}), 13.0 (s, Me^{PzA}), 13.7 (s, Me^{PzA}), 14.9 (s, Me^{PzB}), 42.8 (d, J_{Rh-C} = 12 Hz, allyl C^1, C^3), 104.4 (d, J_{Rh-C} = 7 Hz, allyl C^2), 107.1 (s, C^{PzB4}), 107.9 (s, C^{PzA4}), 142.7 (s, C^{PzA}), 143.3 (s, C^{PzB}), 149.3 (s, C^{PzA}), 151.3 (s, C^{PzB}). IR (KBr): ν_{B-H} = 2525 cm^{-1}. Anal. Calcd for $C_{19}H_{30}N_6BRh$: C, 50.02; H, 6.63; N, 18.42. Found: C, 50.13; H, 6.56; N, 18.45.

Reaction of 5 with Li[$BHEt_3$]. A reddish-orange solution of **5** (435 mg, 0.835 mmol) in THF (20 mL) was placed in a Schlenk tube, and a THF solution of Li[$BHEt_3$] (1.0 M, 0.918 mL, 0.918 mmol) was added dropwise at −30 °C. The solution was stirred for 2 h at room temperature. The color turned to yellow. The mixture was concentrated to dryness and washed with cold Et_2O (5 mL). The solvent was removed by pumping, and the white solid was extracted with benzene (12 mL). The extract was concentrated to dryness to give a white solid of $Tp^{Me2}Rh(\pi$-allyl)H (**9**) (234 mg, 63%). ^1H NMR (C_6D_6, room temperature): δ −22.4 (d, J_{Rh-H} = 5.9 Hz, 1H, RhH), 1.78 (s, 3H, Me^{PzA3}), 2.08 (s, 6H, Me^{PzB3}), 2.24 (s, 6H, Me^{PzB5}), 2.30 (s, 3H, Me^{PzA5}), 2.92 (d, $J_{H^a-H^c}$ = 11.7 Hz, 2H, allyl H^a), 3.30 (d, $J_{H^s-H^c}$ = 7.3 Hz, 2H, allyl H^s), 5.32 (tt, $J_{H^a-H^c}$ = 11.7 Hz, $J_{H^s-H^c}$ = 7.3 Hz, 1H, allyl H^c), 5.52 (s, 1H, H^{PzA4}), 5.65 (s, 2H, H^{PzB4}). $^{13}C\{^1H\}$ NMR (C_6D_6, room temperature): δ 12.7 (s, Me^{PzB}), 13.0 (s, Me^{PzA}), 14.1 (s, Me^{PzA}), 15.8 (s, Me^{PzB}), 39.0 (d, J_{Rh-C} = 12 Hz, allyl C^1, C^3), 91.0 (d, J_{Rh-C} = 5 Hz, allyl C^2), 105.7 (s, C^{PzB4}), 107.8 (s, C^{PzA4}), 143.1 (s, C^{PzA}), 143.5 (s, C^{PzB}), 150.3 (s, C^{PzA}), 150.8 (s, C^{PzB}). IR (KBr): ν_{Rh-H} = 2076 cm^{-1}, ν_{B-H} = 2513 cm^{-1}. Anal. Calcd for $C_{18}H_{28}N_6BRh$: C, 48.89; H, 6.38; N, 19.01. Found: C, 48.84; H, 6.38; N, 18.42.

The reaction of **5** with Li[$BDEt_3$] was similarly conducted. ^1H and ^2D NMR analyses revealed that the product contains $Tp^{Me2}Rh(\pi$-allyl-d_1)H (**9**$(D)_a$) and $Tp^{Me2}Rh(\pi$-allyl)D (**9**$(D)_b$), and the π-allyl-d_1 ligand in **9**$(D)_a$ is deuterated at the central carbon in 92% selectivity, the value was determined based on the relative peak integration of the central proton (H^c) at δ 5.32 and the anti (H^a) and syn (H^s) protons at δ 2.92 and 3.30, respectively, in the ^1H NMR spectrum.

Reaction of 9$(D)_a$ with Allyl Bromide. The complex $Tp^{Me2}Rh(\pi$-allyl-d_1)H (**9**$(D)_a$) obtained in the above experiment (92% isotopic purity at the central carbon of the π-allyl ligand) (190 mg, 0.429 mmol) was dissolved in benzene (10 mL), and allyl bromide (200 μL, 2.31 mmol) was added at room temperature. The mixture was heated at 60 °C for 1 h and then concentrated to dryness. The residue was washed with hexane (5 mL) and dried under vacuum (187 mg, 84%). ^1H and ^2D NMR analyses revealed that the product contains $Tp^{Me2}Rh(\pi$-allyl-d_1)Br (**5**(D)) and $Tp^{Me2}Rh(\pi$-allyl)Br (**5**) in a 92:8 ratio.

Reaction of 5(D) with Li[$BHEt_3$]. The complex $Tp^{Me2}Rh(\pi$-allyl-d_1)Br (**5**(D)) with 92% isotopic purity (60.0 mg, 0.115 mmol) was dissolved in THF (6 mL), and a THF solution of Li[$BHEt_3$] (1.0 M, 130 μL, 0.130 mmol) was added at −30 °C. The mixture was stirred for 2 h at room temperature and concentrated to dryness. The resulting solid was washed with cold Et_2O (1 mL) and extracted with benzene (5 mL). The benzene extract was concentrated to dryness by pumping to give a white solid of $Tp^{Me2}Rh(\pi$-allyl)D (**9**$(D)_b$) with 85% isotopic purity, as confirmed by ^1H NMR spectroscopy (34.8 mg, 68%).

Reaction of 9$(D)_b$ with Benzyl Bromide. Complex **9**$(D)_b$ (85% isotopic purity, 4.1 mg, 9.3 μmol) was placed in an NMR sample tube equipped with a rubber septum cap and dissolved in benzene-d_6 (0.6 mL) at room temperature. Benzyl bromide (1.2 μL, 10 μmol) was added, and the sample was allowed to stand at room temperature for 12 h. The ^1H NMR spectrum exhibited the signals of $PhCH_2D$ [δ 2.09 (t, $^2J_{H-D}$ = 2.2 Hz)] and $PhCH_3$ [δ 2.11 (s)] in a 85:15 ratio.

Reaction of 9 with Organic Halides. A typical procedure (Table 2, entry 1) is as follows. Hydrido complex **9** (12.2 mg, 28 μmol) was placed in a Schlenk tube and dissolved in benzene-d_6 (1 mL). Benzyl bromide (4.6 μL, 39 μmol) was added, and a part of the solution was transferred into an NMR sample tube equipped with a rubber septum cap and examined at intervals by ^1H NMR spectroscopy at room temperature. The signals of **9** disappeared after 1 h, and the signals of **5** and toluene appeared. The formation of toluene was also confirmed by GC-MS spectrometry.

Reaction of 9 with 6-Bromo-1-hexene. Complex **9** (17.1 mg, 39 μmol) was dissolved in toluene-d_8 (2 mL) in a Schlenk tube. 6-Bromo-1-hexene (6.0 μL, 45 μmol) was added, and the mixture was heated at 60 °C for 24 h. GLC and ^1H NMR analyses of the solution revealed the formation of methylcyclopentane and 1-hexene in a 51:49 ratio.

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