Organometallics **1998,** *17,* 5397−5405

Reactions of (Trimethyltriazacyclononane)Rh(vinyl)$_3$, −Rh(*Z*-propenyl)$_3$, and −Rh(vinyl)$_2$Me with Protic Acids. The Relative Migratory Aptitude of Methyl and Vinyl Groups to an (Ethylidene)Rh Alkylidene Carbon

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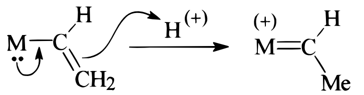
Received May 26, 1998

Preparations of CnRh(CH═CH$_2$)$_3$, CnRh(*Z*-CH═CHMe)$_3$, and CnRhMe(CH═CH$_2$)$_2$ (Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane) are reported. An X-ray crystal structure determination of CnRh(CH═CH$_2$)$_3$ revealed C_3 molecular symmetry with average lengths Rh−N, 2.25 Å; Rh−C, 2.00 Å; and C═C, 1.31 Å. Protonations of these compounds were carried out with HOTf (triflic acid, HOSO$_2$CF$_3$), [H(Et$_2$O)$_2$][BAr$_4$] (BAr$_4$ = $^{(-)}$B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$), and HCl in organic solvents as well as with methanol as solvent and acid. CnRh(CH═CH$_2$)$_3$ gave [CnRh(CH═CH$_2$)(η^3-*E*-CH$_2$CHCHMe)]X in isolated yields up to ca. 80%. Use of CD$_3$OD as acid/solvent led to formation of [CnRh(CH═CH$_2$)(η^3-CH$_2$CHCHCH$_2$D)]X (X = $^{(-)}$OCD$_3$ assumed) as the only isotopomeric product, suggesting [CnRh(═CHCH$_2$D)-(CH═CH$_2$)$_2$]$^+$ as a probable intermediate. No Rh(═CH−CH$_3$) functional group could be detected by NMR at −60 °C or above. Triflic acid protonation of CnRh(*Z*-CH═CHMe)$_3$ generated [CnRh(*Z*-CH═CHMe)(η^3-*E*,*E*-MeCHCHCHEt)], establishing that product formation is by alkenyl migration and not via an electrocyclic ring closure within the [Rh-(═CHEt)(CH═CHMe)]$^+$ moiety. Protonation of CnRhMe(CH═CH$_2$)$_2$ generated [CnRhMe-(η^3-CH$_2$CHCHMe)]$^+$ as the sole product (96% by NMR). Reaction of CnRh(CH═CH$_2$)$_2$Me in CD$_3$OD generated [CnRhMe(η^3-CH$_2$CHCHCH$_2$D)]$^+$ as the sole isotopomer. Thus, the migratory competition established between methyl and vinyl groups for migration to the carbene carbon in proposed intermediate [CnRh(═CHMe)(CH═CH$_2$)Me]$^+$ is dominated by the vinyl group.

Introduction

One of the established methods to generate electrophilic metal−alkylidene (metal−“carbene”) complexes is the protonation of vinyl−metal groups (eq 1).[1] Most



(1)

known examples involve CpFe (“Fp”)-coordinated vinyl groups, but examples involving (dmpe)$_2$Fe,[1b] Ru and Os,[1e,f] Re,[1m] and Pt[1c] are known. In most cases, the objective has been to transfer the metal-coordinated alkylidene to an alkene substrate to form a cyclopropane. However, potential also exists to use the electrophilic alkylidene fragment for intramolecular C−C bond formation in the coordination sphere of the metal. A few metal-to-alkylidene hydrocarbyl migratory insertions are known, although in those cases the alkylidene fragment has generally been generated by means other than vinyl protonation. Examples include transiently generated (inferred) carbenes [(Me$_3$P)$_3$Ir(═CH$_2$)-MeBr]$^+$,[2a] [Cp$_2$W(═CH$_2$)R]$^+$,[2b] [(η^6-C$_5$H$_4$CH$_2$CH$_2$)-(η^6-C$_5$H$_4$CH$_2$CH═)W]$^+$,[2c] and [(η^6-C$_6$H$_6$)Ru(═CH$_2$)Me]$^+$.[2d] Heating of Cp$_2$Ta(═CHMe)Me at 80 °C led to an apparent methyl migration to the alkylidene carbon.[3a] Heating (dmpe)W(CH$_2{}^t$Bu)(═CH^{t}Bu)(≡C^{t}Bu) in neat dmpe at 120 °C gave *trans*-(dmpe)$_2$W(H)(≡C^{t}Bu) and *E*-^{t}BuCH═CH^{t}Bu by a postulated migration of the neopentyl group to the neopentylidene.[3b] Jones et al.[3c] demonstrated a reversible migration of an alkyl group

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[1] (a) Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 9237. (b) Bellerby, J. M.; Mays, M. J. *J. Organomet. Chem.* **1976**, *117*, C21. (c) Bell, R. A.; Chisholm, M. H. *Inorg. Chem.* **1977**, *16*, 698. (d) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7763. (e) Bruce, M. I.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1471. (f) Bruce, M. I.; Swincer, A. G. *Aust. J. Chem.* **1980**, *33*, 1471. (g) Marten, D. F. *J. Org. Chem.* **1981**, *46*, 5422. (h) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31. (i) Selegue, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 119. (j) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761. (k) Kremer, K. A. M.; Kuo, G.-H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 6119. (m) Hatton, W. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6157. (n) Kuo, G.-H.; Helquist, P.; Kerber, R. C. *Organometallics* **1984**, *3*, 806. (o) Casey, C. P.; Miles, W. H.; Tukada, H. *J. Am. Chem. Soc.* **1985**, *107*, 2924.

[2] (a) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984. (b) Hays, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570. (c) Chong, K. S.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1982**, 991. (d) Roder, K.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 686.

[3] (a) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43. (b) Holmes, S. J.; Clark, D. N.; Turner, H. W., Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6322. (c) Stenstrum, Y.; Koziol, A. E.; Palenik, G. J.; Jones, W. M. *Organometallics* **1987**, *6*, 2079.

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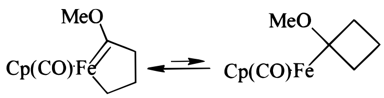
from the metal to a stabilized alkylidene center as shown in eq 2.



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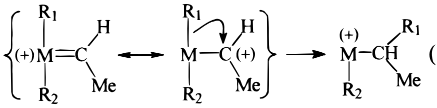
In the context of this approach to C−C bond formation, it could be useful to establish the relative aptitudes of various types of hydrocarbyl ligands for migration from the metal to the alkylidene moiety (eq 3). We report

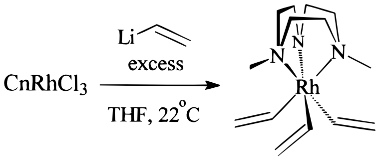


(3)

here the synthesis and protonation of $CnRh(CH{=}CH_2)_3$ (**1**), CnRh(*Z*-$CH{=}CHMe)_3$ (**2**), and $CnRhMe(CH{=}CH_2)_2$ (**3**) (Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane). Evidence is presented that protonation forms transient rhodium carbene complexes, and the preference for vinyl migration over methyl migration to the electrophilic ethylidene carbon is demonstrated. This system has the potential to allow competition experiments among a variety of migrating hydrocarbyl groups to a variety of alkylidene fragments, contingent on the synthesis of their precursors.

Results

Syntheses and Spectra. Wieghardt[4] has described the preparation of $CnRhCl_3$, which serves as the starting material for all of our CnRh complexes. Vinylation of $CnRhCl_3$ produces $CnRh(CH{=}CH_2)_3$, **1**, in 30 min with ca. 90% yield after workup (eq 4). Trivinyl **1** is a crystalline solid that is soluble in THF, CH_2Cl_2, and DMSO, but not in ether, benzene or alkanes.



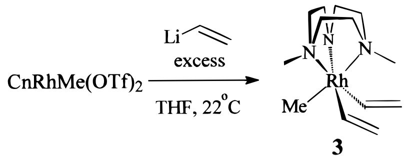
(4)

1

Slow evaporation of solvent from a methylene chloride solution of **1** afforded X-ray diffraction-quality crystals. The ^1H NMR spectrum in DMSO-d_6 is consistent with effective C_{3v} symmetry with a single *N*-methyl singlet and a single set of vinyl resonances, all three of which are rhodium coupled (J_{RhH}: cis = 1.9, trans = 3.8, gem = 3.0 Hz). The ^{13}C NMR spectrum is similarly simple, with the vinyl methylene (C_β) at δ 115.12 and the rhodium-vinyl carbon (C_α) doublet at δ 166.51 (J_{RhC} = 42 Hz). Spectral parameters appear to be typical. For example, the ^1H and ^{13}C parameters for the vinyl groups in **1** (and **3** below) are very similar to those in $Cp^*(CH_2{=}CH)Rh(\mu\text{-}CH_2)_2Rh(CH{=}CH_2)Cp^*$, including $^1J_{RhC}$ of 40−43 Hz for the vinyl α-carbons.[5]

Z-LiCH=CHMe and $CnRhCl_3$ react to form CnRh(*Z*-$CH{=}CHMe)_3$ (**2**), which was isolated in 9% yield. The ^1H and ^{13}C NMR spectra of **2** in acetone-d_6 are very similar to those of **1**, with the single NMe proton resonance at δ 2.53, indicating C_{3v} molecular symmetry. The geminal (δ 6.94) and trans (δ 5.90) protons with respect to Rh are Rh coupled with J = 4.0 and 3.4 Hz, respectively), but the propenyl Me (δ 1.70) is not. In the ^{13}C NMR spectrum, C_α of the propenyl group (δ 150.88) is Rh coupled with J = 42 Hz: C_β (δ 128.16) and Me (C_γ, δ 19.70) are not.

As shown in eq 5, $CnRhMe(OTf)_2$ (OTf = triflate or $^-OSO_2CF_3$) is also vinylated by vinyllithium. Benzene extraction of the residue after solvent removal affords ca. 70% yield of $CnRhMe(CH{=}CH_2)_2$, **3**. It is important not to use CH_2Cl_2 or $CHCl_3$ for workup of **3**, since this generates side products that are difficult to separate. It is interesting that **3** has less thermal stability than either **1** or $CnRhMe_3$. On standing at room temperature as a solid or in solution, Cn is liberated and metal precipitates. The approximate half-time for decomposition in benzene is 2 days, and as the solid ca. 1 week. For this reason, no combustion analysis was obtained and the crude material was used for the protonation experiments. The ^1H and ^{13}C NMR spectra in C_6D_6 are consistent with C_s molecular symmetry, but are otherwise very similar to the spectra of **1** and **2**. The Rh−methyl group appears at δ 0.57 (J_{RhH} = 2.5 Hz) in the proton spectrum and at δ 3.61 (J_{RhC} = 37 Hz) in the ^{13}C NMR. The spectra showed the crude material to be at least 95% free of organic impurities. Complex **3** is soluble in DMSO, CH_2Cl_2, and THF, moderately soluble in benzene, and insoluble in alkanes.



(5)

3

$CnRhMe(OTf)_2$, starting material for the synthesis of **3**, is generated by acid cleavage of $CnRhMe_3$,[6] so we wish to point out that we have found a much improved method for the preparation of the latter complex. The previously reported method which used MeLi required several days, and the yield and purity of the product were very dependent on the source of the MeLi.[6] More recently, we have found that $MgMe_2$ is a much better reagent for the methylation of $CnRhCl_3$ (see the Experimental Section).

Protonations of Rhodium Vinyls. For other synthetic purposes, it was intended to cleave one or two vinyl groups from **1** to prepare $CnRh(CH{=}CH_2)_2(OTf)$ and $CnRh(CH{=}CH_2)(OTf)_2$. In fact, when a CH_2Cl_2 solution of **1** at −78 °C was treated with 1 equiv of a titrated ether solution of triflic acid (CF_3SO_3H or HOTf) and allowed to warm to room temperature, the ^1H NMR spectrum was initially complex and uninterpretable. Over a period of 20−30 h, this mixture converted to a single material whose ^1H and ^{13}C NMR spectra are consistent only with the structure $[CnRh(CH{=}CH_2)(\eta^3\text{-}CH_2CHCHMe)]^+$ (**4**) (eq 6). The ^1H NMR spectrum

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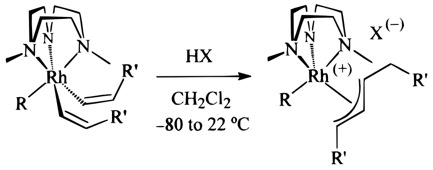
[4] (a) Wieghardt, K.; Chaudhuri, P.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1982**, *21*, 3086. (b) Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329.

[5] Martinez, J. M.; Gill, J. B.; Adams, H.; Bailey, N. A.; Saez, I. M.; Sunley, G. J.; Maitlis, P. M. *J. Organomet. Chem.* **1990**, *394*, 583.

[6] Wang, L.; Wang, C.; Bau, R.; Flood, T. C. *Organometallics* **1996**, *15*, 491.



(6)

1; R = CH=CH$_2$; R' = H **4**; R = CH=CH$_2$; R' = H
2; R = CH=CHMe; R' = Me **5**; R = CH=CHMe; R' = Me
3; R = Me; R' = H **6**; R = Me; R' = H

suggests nearly quantitative formation of **4**, but it was isolated in 79% yield. The presence of three distinct NMe groups in the ^{1}H NMR spectrum indicates that the metal center is chiral, in contrast to the C_s symmetry anticipated for CnRh(CH=CH$_2$)$_2$(OTf). In addition, the proton resonance intensities in **4** integrate as one vinyl group, not two. Proton resonances of the vinyl group in **4** are very similar to those in **1** and **3**, but the vinyl α-carbon of **4** exhibits a $^1J_{\mathrm{RhC}}$ of 26 Hz, in contrast to the values of 40−43 Hz for **1**−**3** and Cp*(CH$_2$=CH)Rh-(μ-CH$_2$)$_2$Rh(CH=CH$_2$)Cp*.[5] η^3-Butenyl proton resonances of **4** range from the RhMe doublet at δ 1.14 to the central allylic multiplet at 4.33 ppm and are very similar to those of a number of known η^3-allylic rhodium complexes.[5,7] The three π-allyl carbons of **4** have rhodium couplings in the carbon spectrum which are normal for allylic rhodium groups, but chemical shifts are slightly different from most CpRh or Cp*Rh allylic cationic or neutral complexes:[5,7a] labeled as C$_{(1)}$−C$_{(2)}$−C$_{(3)}$−Me; C$_{(1)}$ δ 46.64 (typical literature values δ 47−61), C$_{(2)}$ 109.28 (85−99), C$_{(3)}$ 60.17 (70−82). The geometry of the η^3-butenyl group was initially assigned by examination of the central allylic multiplet at δ 4.33 ppm, which appeared as a doublet of triplets with J_{anti}(triplet) = 11 Hz and J_{syn}(doublet) = 7.8 Hz. Hence, the methyl group must be syn to the central hydrogen. Attempted X-ray crystal structure determinations of **4** were plagued by disorder (see below), but the geometry assignment was corroborated by the spectra and X-ray structure of **6** (below).

Since it is believed that the protonation-induced rearrangements reported here proceed via rhodium alkylidene intermediates, an attempt was made to detect the [Rh=CHCH$_3$]$^+$ group by NMR spectroscopy at low temperature. An NMR sample of CnRh(CH=CH$_2$)$_3$ (**1**) and Brookhart's acid,[8] [H(Et$_2$O)$_2$][BAr$_4$] (BAr$_4$ = $^{(-)}$B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$) in CD$_2$Cl$_2$ was monitored at 210, 220, 240, and 300 K by NMR. ^{1}H spectra were acquired from δ 0 to 20 ppm and ^{13}C from δ 0 to 350 ppm.[9] At least 14 000 transients were acquired for the ^{13}C spectrum at each temperature. No trace of resonances attributable to the [Rh=CHCH$_3$]$^+$ group could be detected at any of these temperatures: that is, nothing was seen below δ 8 ppm in the ^{1}H spectrum and nothing below δ 170 ppm in the ^{13}C spectrum. Decreasing amounts of starting material were visible in the spectra from 210 to 240 K. The vinyl, ligand NCH$_3$, and butenyl ligand regions of the ^{1}H spectra at 210−240 K were very cluttered and changed continuously with temperature, so structural assignments could not be made. Resonances attributable to product **4** were increasingly evident at these temperatures, and after 2 days at room temperature only **4** was observed: no starting material or intermediates were present.

A −78 °C solution of CnRh(CH=CH$_2$)$_3$ (**1**) in CH$_2$Cl$_2$ was treated with an ether solution of DOTf, and the product was worked up as usual after completion of the reaction. ^{1}H and ^{13}C NMR spectra of the product in DMSO-d_6 were identical to those of **4**, except that the butenyl Me proton resonance was substantially broadened (D coupling and shifting). Part of the butenyl methyl ^{13}C NMR singlet at δ 16.62 was split into a 1/1/1 triplet (J_{DC} = 19.7 Hz) and isotopically shifted to δ 16.54. Integration[10] showed about 30% **4**-d_1. Also, part of the intensity of the resonance for the adjacent allyl carbon at δ 60.19 (d, J_{RhC} = 10.9 Hz) was shifted upfield by 6 Hz (at 90 MHz). In a second experiment, 1 equiv of DOTf was added as neat acid to a solution of **1**. NMR spectra were identical to those just described except that the level of monodeuteration was now ca. 50%. In a final attempt to maximize the degree of monodeuteration in butenyl complex **4**, a small amount of **1** was suspended in CD$_3$OD, and progress of the reaction was monitored by ^{1}H and ^{13}C NMR spectroscopy. The solid dissolved slowly as the reaction progressed, and after ca. 3 days the sample was homogeneous. Both the proton and carbon resonances were shifted various small amounts in methanol-d_4, compared to DMSO-d_6, but were otherwise the same. The butenyl CH$_3$ resonance at δ 17.10 was very small, and the deuterium coupled CH$_2$D 1/1/1 triplet at δ 16.82 was dominant. The allyl carbon adjacent to CH$_3$ was not detectable in the baseline noise, while the carbon adjacent to CH$_2$D was now a clean doublet at δ 62.31 (J_{RhC} = 11 Hz). Integration[10] of the butenyl methyl resonances at δ 17.10/16.82 indicated that **4** was 92% monodeuterated under these conditions. No evidence of deuteration in any other position of **4** could be detected. The counterion could not be determined, and solvent removal led to decomposition.

Reaction of CnRh(Z-CH=CHMe)$_3$ (**2**) with [H(Et$_2$O)$_2$][BAr$_4$] in CH$_2$Cl$_2$ gave ca. 77% yield of [CnRh(CH=CHMe)(η^3-MeCHCHCHEt)]$^+$ (**5**), the structure of which, shown in eq 6, was unequivocal from its ^{1}H and ^{13}C NMR spectra. A clear triplet at δ 4.62 (J = 11 Hz) for the central allylic proton indicates that the methyl and ethyl groups of the η^3-MeCHCHCHEt ligand have the same geometry, and the coupling constant of 11 Hz is indicative of anti coupling in these molecules.

Protonation of CnRhMe(CH=CH$_2$)$_2$ (**3**) by [H(Et$_2$O)$_2$][BAr$_4$] gave an 84% isolated yield of [CnRh(η^3-CH$_2$CHCHMe)Me]$^+$ (**6**) (eq 6), which was recrystallized from ether/hexane and fully characterized, including an X-ray crystal structure (below). The ^{1}H and ^{13}C NMR spectra were very similar to those of **4** and **5** except for the absence of the vinyl group and the presence of a rhodium−methyl doublet at δ −0.14 (J_{RhH} = 1.8 Hz) in

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[7] (a) Powell, P.; Russell, L. J. *J. Organomet. Chem.* **1977**, *129*, 415. (b) Lee, H.-B.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1975**, 2316.

[8] Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.

[9] Proton chemical shifts for α-protons of alkylidene complexes are found from δ −2 to 20 ppm; at higher field (δ −2 to 12) for "Schrock"-type alkylidenes (Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98) and lower field (δ 10 to 20) for electrophilic alkylidene complexes (Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* **1980**, *102*, 1203). Carbon chemical shifts for electrophilic alkylidene complexes appear in the general range of δ 250 to 350 ppm (same references).

[10] No corrections for NOE and relaxation effects on the ^{13}C NMR integrals were made since the *exact* integral ratios are not significant.

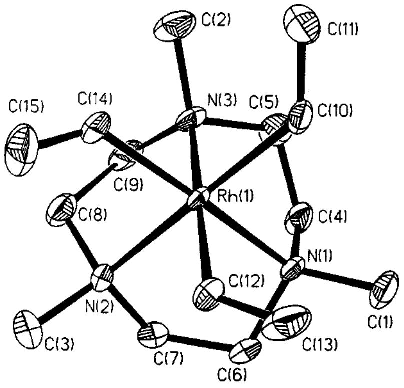

Figure 1. The molecular structure (50% probability ellipsoids) of the heavy atoms of $CnRh(CH{=}CH_2)_3$ (**1**).

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) of $CnRh(CH{=}CH_2)_3$ (1)

Rh−N(1)	2.253(4)	N(1)−Rh−N(2)	80.2(2)
Rh−N(2)	2.250(4)	N(2)−Rh−N(3)	80.0(3)
Rh−N(3)	2.254(5)	N(1)−Rh−N(3)	80.0(3)
Rh−C(10)	1.995(5)	C(1)−Rh−C(2)	87.6(3)
Rh−C(12)	2.001(5)	C(2)−Rh−C(3)	87.6(3)
Rh−C(14)	1.990(5)	C(3)−Rh−C(1)	87.2(5)
C(10)−C(11)	1.313(8)	Rh−C(10)−C(11)	132.9(4)
C(12)−C(13)	1.308(8)	Rh−C(12)−C(13)	133.4(4)
C(14)−C(15)	1.316(8)	Rh−C(14)−C(15)	133.9(5)

the proton spectrum and δ 3.85 (J_{RhC} = 25 Hz) in the carbon spectrum. The resonance at δ 3.68 of the central proton of the η^3-butenyl group appeared as a doublet of triplets (J_{anti}(triplet) = 11 Hz and J_{syn}(doublet) = 7.4 Hz) just as in **4**. In combination with the X-ray structure of **6**, these ^1H NMR data confirm the geometry assignments of **4**, **5**, and **6**. Protonation of an NMR sample was carried out in DMSO-d_6 with 1 equiv of a titrated solution of HCl in ether. Integration of the methyl proton resonances in starting **3** and product **6** with respect to internal $Ph_2Si(CH_3)_2$ indicated that **6** had formed in 96% yield. Suspension of $CnRhMe(CH{=}CH_2)_2$ (**3**) in CD_3OD in an NMR tube at 56 °C led to its gradual dissolution over 2 days and formation of $[CnRh(\eta^3\text{-}CH_2CHCH{-}CH_2D)Me]^+$ (**6**-d_1). The ^1H resonance of the butenyl $-CH_2D$ group at δ 1.28, a doublet for CH_3, was a broad multiplet, and the adjacent allylic CH group at δ 2.40, normally a doublet of quartets, was a doublet of triplets. No other changes were visible for any of the resonances, including that of the RhMe group.

Structure Determinations of $CnRh(CH{=}CH_2)_3$, 1, and $[CnRh(\eta^3\text{-}CH_2CHCH\text{-}Me)Me][BAr_4]$, 6($BAr_4$). Solution of the X-ray diffraction data proceeded very well for **1**. A drawing of its molecular structure is shown in Figure 1, and Table 1 contains selected bond lengths and bond angles. Average Rh−N and Rh−C bond lengths are 2.252 and 1.995 Å, respectively. Average angles of N−Rh−N, 80.1°, and C−Rh−C, 87.5°, clearly indicate that the Cn ligand is moved slightly away from the metal along the molecular 3-fold axis (not a crystallographic axis), and the Rh-vinyls are forced slightly toward one another, probably because of the steric congestion between the Rh-vinyls and the *N*-methyls. These angles and Rh−N lengths are all similar to those of $CnRhMe_3$ and [tris(N-neohexyl)Cn]$RhMe_3$ reported earlier.[6] The Rh−C lengths, though, are ca. 0.05 Å shorter than those of the previous two, as is reasonable for the change in hybridization from sp^3 to sp^2 in the present case. The average C=C length and average Rh−C=C angle of **1** are 1.312 Å and 133.4°. Solid-state structures of several vinyl or alkenyl rhodium complexes have been determined.[5,11] Of the examples cited, all contain Rh^{III} except one,[11c] but there are no statistically significant differences in their parameters on the average. The Rh−C lengths range from 2.00 to 2.12 Å, the C=C lengths from 1.25 to 1.36 Å (the shortest of which is surprisingly short[5]), and the Rh−C=C angles from 121° to 130°. This puts the Rh−C length of **1** on the short end of the range and the Rh−C=C angle at the high end of the range, but there is no obvious dependence of the metrics on the ligand array or oxidation state among these examples.

X-ray diffraction data were acquired on single crystals of **4**(BAr_4) and **6**(BAr_4), but both structures were of poor quality despite low-temperature data collection on two or three different crystals of each of them. Unfortunately, neither **4**(X) nor **6**(X) (X = Cl or OTf) could be induced to give crystals suitable for X-ray diffraction. During the solution of both structures **4**(BAr_4) and **6**(BAr_4), the large BAr_4^- anion presented itself almost intact from the first E-map. Most of the CF_3 groups were disordered, but this was easily treated as described in the Experimental Section, and the anions of both **4** and **6** refined very well. The cations however, did not. Both cations showed signs of several types of disorder, which we suspect arise from the disparity in cation and anion sizes and from the approximately spherical shape of the cations. Bond lengths and angles of the ligands of cation **4** did not converge to reasonable values with any scheme devised to deal with its disorder. Accordingly, those data are not reported here even though the final *R* factor was below 6%. However, the quality of the solution was good enough to corroborate the structure assigned to the cation on the basis of spectroscopy. The methyl group of the butenyl ligand of cation **6** was disordered at the two ends of the allyl group. Refinement of both methyl sites led to C(5)/C(5A) populations of 0.56/0.44. With this minimal accommodation for disorder, the final parameters for the cation of **6** were ultimately good enough to establish its structure as shown in Figure 2. Table 2 contains selected bond lengths and bond angles. The structure is essentially octahedral at the metal with the butenyl ligand occupying two cis sites as expected. Rh−C distances of the butenyl group of **6** are typical in comparison with literature examples of π-allyl rhodium structures.[12]

Discussion

It has been reported that $[CnRhMe_2(\eta^2\text{-}CH_2{=}CH_2)]^+$ is observed by NMR at −40 °C and that above that

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(11) (a) Werner, H.; Wolf, J.; Schubert, U.; Ackermann, K. *J. Organomet. Chem.* **1986**, *317*, 327. (b) Marder, T. B.; Chan, D. M.-T.; Fultz, W. C.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1988**, 996. (c) Wiedemann, R.; Steinert, P.; Schafer, M.; Werner, H. *J. Am. Chem. Soc.* **1993**, *115*, 9864. (d) Dunaj-Jurco, M.; Kettmann, V.; Steinborn, D.; Ludwig, M. *Acta Crystallogr., Sect. C, Cryst. Struct. Commun.* **1994**, *50*, 1427.

(12) (a) Tanaka, I.; Jin-No, N.; Kushida, T.; Tsutsui, N.; Ashida, T.; Suzuki, H.; Sakurai, H.; Moro-Oka, Y.; Kawa, T. I. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 657. (b) Murray, B. D.; Power, P. P. *Organometallics* **1984**, *3*, 1199. (c) Batsanov, A. S.; Struchkov, Y. T. *J. Organomet. Chem.* **1984**, *265*, 305. (d) King, S. A.; Van Engen, D.; Fischer, H. E.; Schwartz, J. *Organometallics* **1991**, *10*, 1195. (e) Paiaro, G.; Pandolfo, L.; Ganis, P.; Valle, G.; Fioretto, S. D. *J. Organomet. Chem.* **1995**, *488*, 249.

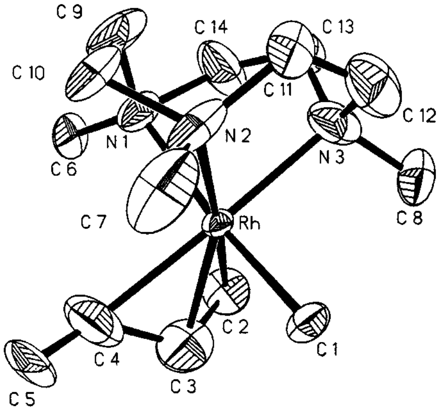
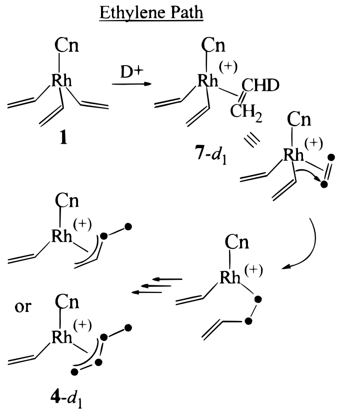


Figure 2. The molecular structure (30% probability ellipsoids) of the heavy atoms of [CnRhMe(η^3-CH$_2$CHCHMe)]$^+$ (**6**). The BAr$_4^-$ anion and the second site of the disordered methyl group, C(5A), bonded to C(2), have been omitted for clarity.

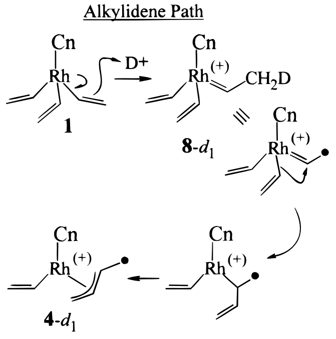
Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of [CnRhMe(η^3-CH$_2$CHCHMe)][BAr$_4$] (6)

Rh−N(1)	2.255(10)	N(1)−Rh−N(2)	81.3(4)
Rh−N(2)	2.177(11)	N(2)−Rh−N(3)	80.1(4)
Rh−N(3)	2.200(10)	N(1)−Rh−N(3)	81.2(4)
Rh−C(1)	2.025(11)	C(1)−Rh−C(2)	92.6(5)
Rh−C(2)	2.172(12)	C(1)−Rh−C(3)	77.0(3)
Rh−C(3)	2.078(15)	C(1)−Rh−C(4)	93.3(5)
Rh−C(4)	2.216(16)	N(1)−Rh−C(1)	171.7(4)
C(2)−C(3)	1.379(18)	N(2)−Rh−C(2)	174.7(4)
C(3)−C(4)	1.488(21)	N(3)−Rh−C(4)	170.8(5)
C(4)−C(5)	1.375(22)	C(2)−C(3)−C(4)	127.6(12)
C(2)−C(5A)	1.344(23)	C(3)−C(4)−C(5)	137.7(14)
		C(5A)−C(2)−C(3)	137.4(15)

Scheme 1



Scheme 2



temperature it undergoes insertion of the ethylene ligand into the Rh−Me bond, ultimately giving [CnRh(H)(η^3-CH$_2$CHCH$_2$)]$^+$.[13] In view of these facts, on finding that triflic acid cleavage of CnRh(CH═CH$_2$)$_3$ (**1**) does not yield CnRh(CH═CH$_2$)$_2$(OTf) but instead gives [CnRh(CH═CH$_2$)(η^3-CH$_2$CHCHMe)]$^+$ (**4**), one might propose the mechanism shown in Scheme 1, which shall be called the "ethylene path". In this sequence, the protic cleavage would generate ethylene, but rather than leave, the ethylene could remain π-coordinated to the metal as shown in intermediate **7**. Examples of protic cleavage of metal vinyl groups are known, although their mechanisms were not examined.[14] To continue, ethylene could undergo insertion into the Rh−vinyl bond, and hydride rearrangements would then give butenyl complex **4**. At least one apparent precedent exists for this rearrangement in iridium chemistry.[15]

On the other hand, as mentioned in the Introduction and illustrated in eq 1, protonation of vinyl−metal complexes is a known method of generating alkylidene complexes[1] and forms the basis of an alternative mechanism shown in Scheme 2, which shall be called the "alkylidene path". The divinyl(alkylidene)Rh cation **8** would undergo rearrangement with migration of a vinyl group to the alkylidene carbon. The resulting butenyl species need only coordinate the other two carbons to form **4**.

The ethylene and alkylidene paths can be easily distinguished in principle by the use of deuterated acid. Schemes 1 and 2 include the predicted labeling results assuming the system would be well behaved, that is, that it would not exhibit randomization of the label by irrelevant paths. Dark circles represent positions where part of the monodeuteration label would reside if **1** were cleanly monodeuterated. The ethylene path should generate ethylene-d_1 coordinated to rhodium regardless of whether the vinyl protonolysis would proceed by initial metal protonation or by direct attack on the Rh−C bond. Because of the symmetry of **7**-d_1, in effect it is labeled in two sites, and the subsequent ethylene insertion would lead to **4**-d_1, which would be labeled in at least two sites as shown. Depending on how the hydride shifting would occur, the label could be more widely dispersed, but *two* would be the *minimum* number of sites containing label. Now, considering the alkylidene path and assuming that the deuteration were irreversible, ethylidene cation **8**-d_1 would be labeled in the methyl group *only*, and the subsequent vinyl migration and η^3-coordination would leave the label unmoved.

Our attempts to deuterate trivinyl **1** with deuterated triflic acid were frustrated by the tendency of very small amounts of such a strong acid to undergo exchange with adventitious proton sources. The problem would undoubtedly be exacerbated by a large kinetic isotope effect favoring transfer of any H$^+$ over D$^+$. It was fortunate

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[13] (a) Wang, L.; Flood, T. C. *J. Am. Chem. Soc.* **1992**, *114*, 3169. (b) Wang, L.; Lu, R. S.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1993**, *115*, 6999.

[14] (a) Tripathy, P. B.; Renoe, B. W.; Adzamli, K.; Roundhill, D. M. *J. Am. Chem. Soc.* **1971**, *93*, 4406. (b) Mann, B. E.; Shaw, B. L.; Tucker, N. I. *J. Chem. Soc., A* **1971**, 2667. (c) Trocha-Grimshaw, J.; Henbest, H. B. *J. Chem. Soc., Chem. Commun.* **1968**, 757.

[15] (Tpb*)Ir(H)(CH═CH$_2$)(CH$_2$═CH$_2$) (tpb* = tris(3,5-dimethylpyrazolyl)borate anion) rearranges to (tpb*)Ir(H)(η^3-CH$_2$CHCHMe) via a postulated ethylene insertion into the Rh−vinyl bond: Boutry, O.; Gutierrez, E.; Monge, A.; Nicasio, M. C.; Perez, P. J.; Carmona, E. *J. Am. Chem. Soc.* **1992**, *114*, 7288.

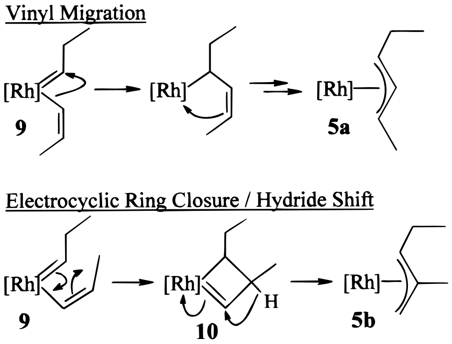
that the protonation could be effected by methanol-d_4 as solvent, since it gave clean monodeuteration. However, the counterion could not be determined in solution, and solvent removal gave only intractable materials. The obvious candidate for counterion is CD_3O^-, but it was surprising to us that such a strong nucleophile would not exhibit some kind of reactivity with the π-allyl cation. That the product in methanol clearly was the (π-butenyl)rhodium cation is in contrast to similar systems that undergo nucleophilic additions to either the central or terminal carbon of π-allyl cations of Rh, Ir, and Ru.[16]

The presence of only one deuterium in only the methyl group of the butenyl ligand gives a clear answer that the formation of **4** proceeds via an alkylidene path. Since no label was observed in remaining starting material late in the reaction (in the slow reaction in CD_3OD) or in the CH_2 of the vinyl group in **4**, it is also clear that protonation of the vinyl group is irreversible; that is, migration of the vinyl group to the alkylidene carbon in **8**-d_1 is much faster than deprotonation of **8**-d_1 back to **1**.

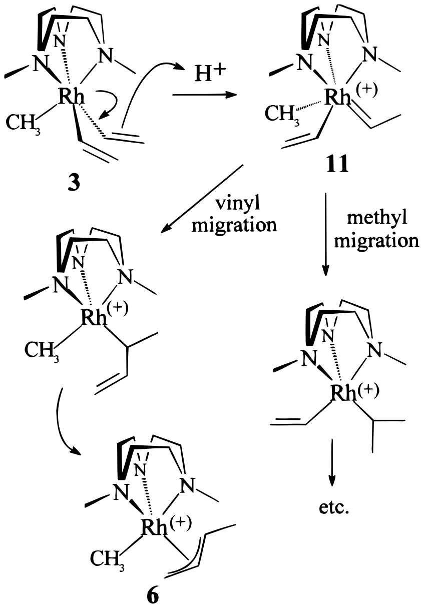
Attempts to observe any alkylidene-containing intermediates in the protonation of **1** at temperatures as low as 210 K by NMR spectroscopy revealed no signals between δ 8 and 20 ppm in the ^{1}H spectrum and no resonances between δ 170 and 350 ppm in the ^{13}C spectrum.[9] In addition, starting material was present in slowly diminishing quantity between 210 and 240 K. Thus, vinyl group migration to the alkylidene carbon is also faster than the initial alkylidene-forming protonation. To conclude that vinyl migration to the ethylidene carbon in **6** is faster than both protonation of **1** and deprotonation of **8** unfortunately is not very informative, since proton transfers to and from carbon when they involve rehybridization of the carbon center can be several orders of magnitude slower than the diffusion limit.[17] The same is true for proton transfers to and from metal centers.[18]

So far, rearrangement of ethylidene intermediate **8** to product **4** has been rationalized as migration of a vinyl group to the alkylidene carbon. Another possible mechanism for this rearrangement is an electrocyclic ring closure followed by rearrangement of the resulting metallacyclobutene to the π-allyl product. These two mechanisms can be differentiated by an appropriate labeling experiment. Scheme 3 shows the results predicted for each mechanism in the case where the label is a methyl group as in CnRh(*cis*-CH=CHMe)$_3$ (**2**). Protonation of **2** presumably generates the propylidene intermediate $[CnRh(=CHEt)(CH=CHMe)_2]^+$, represented in Scheme 3 by the partial structure **9**, and the vinyl migration path then is predicted to afford hexenyl product **5a**. Electrocyclic ring closure would generate metallacycle **10**, which, because hydrogen is well-known to migrate faster than methyl, would result in the 2-methylpentenyl product **5b**. The experimentally observed formation of only **5a** gives an unequivocal answer regarding this rearrangement. The geometry observed for the η^3-hexenyl ligand can be rationalized to result from a series of $\eta^3-\eta^1-\eta^3$ interconversions with C−C bond rotations in the η^1 intermediates.

Scheme 3



Scheme 4



The nature of the hydrocarbyl migration to the alkylidene ligand is of particular interest. Specifically, if a vinyl group could be protonated in the presence of two other hydrocarbyl ligands which were different from one another, then in principle a series of relative migratory aptitudes could be measured. This would depend, of course, on one's ability to synthesize the mixed-ligand starting materials, on selective protonation of the vinyl ligand, and on the ultimate products of the migrations being unique and characterizable. To determine the feasibility of such a competition, CnRhMe(CH=CH$_2$)$_2$, **3**, was prepared and its protonation examined. The predicted ethylidene intermediate, **11**, and subsequent migratory competition is depicted in Scheme 4. The fact that π-allyl complex **6** was formed in 96% yield by NMR and was the only product detectable indicates that the vinyl/methyl migratory rate ratio must be at least 24.

A referee suggested the possibility that the methyl migration might be faster than vinyl migration, but if it were reversible and only the vinyl migration product were stable, then the observed result could be misleading. Subsequent observation that dissolution of **3**

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(16) (a) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346. (b) Tjaden, E. B.; Stryker, J. M. *Organometallics* **1992**, *11*, 16. (c) McNeill, K.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 3625. (d) Curtis, D. M.; Eisenstein, O. *Organometallics* **1984**, *3*, 887.

(17) Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, 1969; pp 175−178.

(18) Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945.

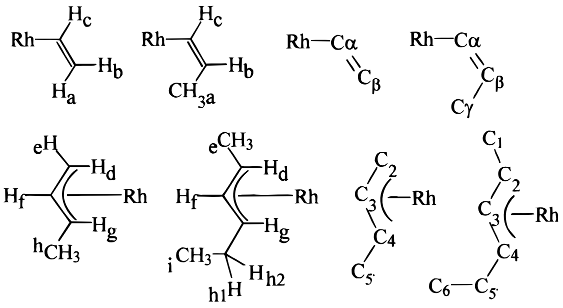
in CD_3OD yields only $[CnRh(\eta^3\text{-}CH_2CHCH{-}CH_2D)Me]^+$ (**6**-d_1) is inconsistent with this hypothesis. Thus, reversible formation of the intermediate $\{CnRh(CH{=}CH_2)[CH(CH_3)(CH_2D]\}^+$ would require the formation of some $[CnRh(\eta^3\text{-}CH_2CHCH\text{-}Me)(CH_2D)]^+$ product. No deuterium is observed in the RhMe group of **6**-d_1. Thus, it is confirmed that **6** is the kinetic product and vinyl group migration is faster than methyl group migration.

It is well-known in organic chemistry that sp^2 carbon centers migrate better than sp^3.[19] This is generally attributed to the greater steric accessibility of an sp^2 carbon at its π face. In addition, π participation during migration allows delocalization into the π system of any electron deficiency. Such delocalization can be so stabilizing that it leads to a discrete intermediate with σ bonding to both the departed and receiving atoms, as in the case of the well-known phenonium ion intermediates which intervene in phenyl migrations of carbocations. In the last mentioned systems, phenyl groups migrate much faster than either alkyl groups or hydrides.[19] Thus it is consistent with these precedents that sp^2 vinyl should migrate faster than sp^3 methyl to the electrophilic alkylidene group in intermediate **11**.

In summary, alkenyl rhodium groups in $CnRhR(CH{=}CHR')_2$ are efficiently and irreversibly protonated at the β position to form electrophilic rhodium alkylidene intermediates. These intermediates show a very high reactivity for intramolecular migration of a second vinyl group to the ethylidene carbon. In an intramolecular competition for migration of a methyl or vinyl group to the ethylidene carbon, vinyl migration is at least an order of magnitude faster.

Experimental Section

General. All reactions involving organometallic compounds, unless otherwise mentioned, were carried out under an atmosphere of N_2 or Ar purified over reduced Cu catalyst (BASF R3-11) and Aquasorb. Flamed-out glassware and standard vacuum line, Schlenk, and N_2-atmosphere box techniques were employed. Benzene, ether, hexanes, pentanes, and THF were distilled from purple solutions of sodium/benzophenone, and CH_2Cl_2 was distilled twice from CaH_2. Vinyllithium[20a] and *Z*-propenyllithium[20b] were prepared by standard procedures. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Hydrogen combustion analyses of CnRh and (tacn)Rh molecules generally are near or within convention tolerances, but there have been problems obtaining acceptable C analyses, particularly for neutral hydrocarbyls, which are usually 1–4% low. Rhodium compounds are prone to formation of nitrides and carbides that are stable at the combustion temperatures accessible with conventional instruments. The problem is highly dependent on the structure of the compound involved. In the present case, all three of the salts $[CnRh(hydrocarbyl)(allylic)][BAr_4]$ yielded acceptable results with the submission of a single sample. Neither $CnRh(vinyl)_3$ (**1**) nor $CnRh(propenyl)_3$ (**2**) yielded any carbon analysis closer than 2% (always low) after multiple sample submissions. Vigorous conditions and promoters were used, but with no improvement. We have therefore resorted to the alternative of high-resolution FAB MS, which were recorded at the Mass Spectrometry Facility of the University of California at Riverside. ^1H and ^{13}C NMR spectra of **1**, **2**, and **3** have been submitted with the Supporting Information as a demonstration of bulk purity. The hydrocarbyl ligand ^1H and ^{13}C NMR spectra given below for **1**–**6** are all labeled corresponding to the structures shown here, independent of X-ray structure labeling and independent of the actual combination of ligands in a given complex.



Improved Preparation of $CnRhMe_3$. A solution of 5 mmol of $MgMe_2$ (prepared by the standard dioxane method) in 30 mL of THF was added dropwise to a stirred suspension of $CnRhCl_3$ (0.9 g, 2.4 mmol)[4a] in 20 mL of THF, and the mixture was then heated at reflux for 12 h, during which the mixture turned to a clear yellow solution. Wet THF (THF/H_2O ca. 3:1 by volume) was added dropwise until gas evolution ceased. From this point, the mixture can be manipulated in air. The solvent was removed at reduced pressure, and the residue was extracted with 70 mL of CH_2Cl_2 by stirring for 0.5 h at 22 °C. The extract was filtered and the solvent removed at reduced pressure and then under vacuum to give the light yellow product in 92% yield. The ^1H NMR shows no $CnRhMeCl_2$ and only a trace of $CnRhMe_2Cl$, so the material is suitable for most purposes. If purer material is desired, it can be recrystallized from benzene, in which $CnRhMe_2Cl$ is much less soluble.

$CnRh(CH{=}CH_2)_3$ (1). A THF solution of vinyllithium (25 mL of a 0.26 M solution, 6.5 mmol) was added slowly at −78 °C to a stirred suspension of $CnRhCl_3$ (0.42 g, 1.3 mmol)[4a] in 45 mL of THF under an N_2 atmosphere. The mixture was allowed to warm to 22 °C, and the clear solution was stirred for an additional 25 min. Then CH_2Cl_2 was slowly added until gas evolution ceased. Volatiles were evaporated at reduced pressure, and the residue was extracted with 30 mL of CH_2Cl_2. The extract was filtered and the solvent was evaporated at reduced pressure to give a light brown solid (0.36 g, 93%). Slow evaporation of a CH_2Cl_2 solution of product gave off-white rectangular prisms, which were collected and washed with ether. ^1H NMR (DMSO-d_6, 360 MHz): δ 2.53 (s, NCH_3), 2.47–2.74 (m, NCH_2), 4.78 (ddd, $J_{ab} = 3.5$ Hz, $J_{ac} = 17$ Hz, $J_{RhH} = 1.9$ Hz, H_a), 5.20 (ddd, $J_{bc} = 10$ Hz, $J_{RhH} = 3.8$ Hz, H_b), 7.33 (ddd, $J_{RhH} = 3.0$ Hz, H_c). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 90 MHz): δ 47.73 (NCH_3), 56.83 (NCH_2), 115.12 (C_β), 166.51 (d, $J_{RhC} = 42$ Hz, C_α). Anal. Calcd for $C_{15}H_{30}N_3Rh$: C, 50.70; H, 8.51. Found: C, 48.88; H, 8.48. FAB mass spectrum: calcd for $[C_{15}H_{30}N_3Rh]H^+$ 356.1573; found 356.1566 (2 ppm); also $m/e = 328$ (20%) $[M^+ - (C_2H_3)]$.

$CnRh(Z\text{-}CH{=}CHMe)_3$ (2). A Schlenk flask charged with $CnRhCl_3$ (300 mg, 0.79 mmol) and *cis*-$CH_3CH{=}CHLi$ (260 mg, 5.4 mmol) was placed in an acetone/dry ice bath, and 60 mL of ether was added. This mixture was stirred for 30 min at −78 °C and 3 h at 0 °C, and the solvent was removed under vacuum. The residue was extracted with dry benzene (3 × 25 mL), and solvent was again removed, leaving a dark solid. The solid was washed with cold methanol and dried to afford 34 mg (9%) of crude product. Colorless crystals were obtained either by slow evaporation of an acetone solution or by slow diffusion of pentane into an ether solution. ^1H NMR (acetone-

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[19] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987. Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part A: Structure and Mechanism*, 3rd ed.;., Plenum Press: New York, 1984.

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d_6, 360 MHz): δ 1.70 (dd, $J_{ab} = 6.5$ Hz, $J_{ac} = 1.3$ Hz, $CH_{3(a)}$), 2.53 (s, NCH_3), 2.82 (s, NCH_2), 5.90 (ddq, $J_{bc} = 10$ Hz, $J_{RhHb} = 3.4$ Hz, H_b), 6.94 (ddq, $J_{RhHc} = 4.0$ Hz, H_c). ^{13}C{^{1}H} NMR (acetone-d_6, 90 MHz): δ 19.70 (C_γ), 48.81 (NCH$_3$), 57.87 (NCH$_2$), 128.16 (C_β), 150.88 (d, $J_{RhC} = 42$ Hz, C_α). The ^{1}H NMR revealed ca. 10% of resonances corresponding to CnRh(*Z*-CH=CHMe)$_2$(*E*-CH=CHMe). Anal. Calcd for $C_{18}H_{36}N_3Rh$: C, 54.40; H, 9.13. Found: C, 52.69; H, 9.18. FAB mass spectrum: calcd for $[C_{18}H_{36}N_3Rh]H^+$ 398.2043; found 398.2036 (2 ppm); also $m/e = 356$ (15%) $[M^+ - (C_3H_5)]$.

CnRh(CH=CH$_2$)$_2$Me (3). A THF solution of vinyllithium (20 mL of a 0.26 M solution, 5.2 mmol) was added slowly to a stirred suspension of CnRhMe(OTf)$_2$ (0.50 g, 0.85 mmol)[6] in 25 mL of THF at −78 °C under an N$_2$ atmosphere. The mixture was stirred for 5 min at −78 °C and then allowed to warm to 22 °C. The suspension quickly changed to a clear yellow solution. After stirring an additional 30 min, the volatiles were removed under vacuum and the resulting solid was extracted with 50 mL of benzene. Removal of the benzene gave 0.21 g (72%) of a yellow solid. This molecule slowly decomposes with liberation of Cn ligand at 22 °C in the solid state ($t_{1/2} \sim 1$ week) or in solution ($t_{1/2} \sim 2$ days), so further purification and combustion analysis were not attempted. ^{1}H NMR (C_6D_6, 250 MHz): δ 0.57 (d, $J_{RhH} = 2.5$ Hz, RhCH_3), 1.50−1.65 (m, 6H, NCH_2), 1.86−2.10 (m, 6H, NCH_2), 2.29 (s, 6H, NCH_3), 2.42 (s, 3H, NCH_3), 5.63 (ddd, 2H, $J_{ab} = 3.3$ Hz, $J_{ac} = 17$ Hz, $J_{RhH} = 2.0$ Hz, H_a), 6.18 (ddd, 2H, $J_{bc} = 10$ Hz, $J_{RhH} = 3.4$ Hz, H_b), 7.80 (ddd, 2H, $J_{RhH} = 3.1$ Hz, H_c). ^{13}C{^{1}H} NMR (C_6D_6, 90 MHz): δ 3.61 (d, $J_{RhC} = 37$ Hz, RhCH$_3$), 48.20 (2 NCH$_3$), 48.46 (1 NCH$_3$), 56.57, 56.83, 57.03 (each 2 NCH$_2$), 116.34 (C_β), 167.66 (d, $J_{RhC} = 42$ Hz, C_α). Integration of the ^{1}H and ^{13}C NMR spectra indicated that crude **3** was at least 95% pure. FAB mass spectrum: calcd for $[C_{14}H_{30}N_3Rh]H^+$ 344.1573; found 344.1571 (1 ppm); also $m/e = 328$ (20%) $[M^+ - (CH_3)]$.

Protonation Experiments. [CnRh(CH=CH$_2$)(η^3-CH$_2$CHCHMe)][BAr$_4$], 4(BAr$_4$). A 15 mL portion of CH$_2$Cl$_2$ was added to a mixture of CnRh(CH=CH$_2$)$_3$ (**1**, 0.12 g, 0.33 mmol) and HBAr$_4$·(Et$_2$O)$_2$ (0.32 g, 0.32 mmol)[8] under N$_2$ in a Schlenk flask in a −78 °C bath. The mixture was stirred for 5 min and then allowed to warm to 22 °C. The resulting bright yellow solution was stirred overnight. Volatiles were removed in vacuuo to afford 0.30 g (79% yield) of a slightly yellow solid. Use of HCl or HOTf in ether solution to react with **1** also yielded **4**(Cl) or **4**(OTf). Diffusion of hexane vapor into a CH$_2$Cl$_2$ solution of **4** afforded off-white crystals. Cation resonances: ^{1}H NMR (DMSO-d_6, 250 MHz) δ 1.16 (d, $J_{gh} = 6.0$ Hz, butenyl $CH_{3(h)}$), 1.74 (d, $J_{df} = 11$ Hz, H_d), 2.06, 2.77, 2.86 (3s, NCH_3), 2.5−3.5 (m, NCH_2), 2.39 (dq, $J_{fg} = 11$ Hz, H_g), 3.00 (d, $J_{ef} = 7.8$ Hz, H_e), 4.33 (ddd, $J_{df} = J_{fg} = 11$ Hz, $J_{ef} = 7.8$ Hz, H_f), 4.74 (d, $J_{ac} = 16$ Hz, H_a), 5.13 (d, $J_{bc} = 8.5$ Hz, H_b), 6.51 (ddd, $J_{RhH} = 4.6$ Hz, H_c). ^{13}C{^{1}H} NMR (DMSO-d_6, 90 MHz) δ 16.51 (C_5), 46.64 (d, $J_{RhC} = 14$ Hz, C_2), 47.49, 50.13, 52.97 (3 NCH$_3$), 55.66, 57.38, 57.73, 58.76, 59.32, 61.18 (6 NCH$_2$), 60.17 (d, $J_{RhC} = 11$ Hz, C_4), 109.28 (d, $J_{RhC} = 4.9$ Hz, C_3), 119.32 (C_β), 156.44 (d, $J_{RhC} = 26$ Hz, C_α). Anion resonances: ^{1}H NMR (DMSO-d_6) δ 7.60 (br s, 8H, H_{ortho}), 7.66 (br s, 4H, H_{para}); ^{13}C{^{1}H} NMR (DMSO-d_6) δ 117.64 (C_{para}), 123.98 (q, $J_{FC} = 273$ Hz, CF$_3$), 128.46 (q, $J_{FC} = 33$ Hz, C_{meta}), 134.00 (C_{ortho}), 160.92 (1:1:1:1 q, $J_{BC} = 50$ Hz, C_{ipso}). Anal. Calcd for $C_{47}H_{43}N_3F_{24}BRh$: C, 46.29; H, 3.55. Found: C, 45.95; H, 3.65.

NMR Search for [Rh=CHCH$_3$]$^+$. CnRh(CH=CH$_2$)$_3$, **1** (10 mg), and solid HBAr$_4$·(Et$_2$O)$_2$ (28 mg) were combined in an NMR tube, 0.5 mL of CD$_2$Cl$_2$ was added by vacuum transfer, and the tube was sealed. The cold sample was transferred to an NMR probe, which was precooled at 210 K. ^{1}H and ^{13}C NMR spectra were recorded at 210, 220, 240, and 300 K. See the Results section for details.

[CnRh(CH=CHMe)(η^3-MeCHCHCHEt][BAr$_4$], 5(BAr$_4$). A 10 mL portion of CH$_2$Cl$_2$ was added to a mixture of CnRh(CH=CHMe)$_3$ (**2**, 18 mg, 0.045 mmol) and HBAr$_4$·(Et$_2$O)$_2$ (45 mg, 0.044 mmol) under N$_2$ in a Schlenk flask in a −78 °C bath. The mixture was stirred at room temperature for 2 days. Volatiles were removed in vacuo to afford 43 mg (77% yield) of a light yellow solid. The crude was extracted with 25 mL of Et$_2$O, the solvent was evaporated, and the residue was washed with pentane. The solid was dissolved in Et$_2$O, and diffusion of pentane into the solution gave colorless rectangular crystals. Cation resonances: ^{1}H NMR (acetone-d_6, 360 MHz) δ 1.18 (t, $J_{ih1} = J_{ih2} = 7.4$ Hz, $CH_{3(i)}$), 1.75 (ddq, $J_{gh1} = 3.8$ Hz, $J_{h1h2} = 13$ Hz, H_{h1}), 1.98 (ddq, $J_{gh2} = 3.8$ Hz, H_{h2}), 1.42 (d, $J_{de} = 6.8$ Hz, $CH_{3(e)}$), 1.70 (dd, $J_{ab} = 6.8$ Hz, $J_{ac} = 1.4$ Hz, $CH_{3(a)}$), 2.67, 3.03, 3.17 (3s, NCH_3), 2.4 (m, H_d and H_g), 2.65−3.70 (m, NCH_2), 4.62 (t, $J_{df} = J_{fg} = 11$ Hz, H_f), 5.37 (ddq, $J_{bc} = 9.4$ Hz, $J_{RhH} = 3.2$ Hz, H_b), 6.34 (ddq, $J_{RhH} = 5.2$ Hz, H_c); ^{13}C{^{1}H} NMR (acetone-d_6, 90 MHz) δ 16.08 (C_6), 17.38 (C_5), 18.64 (C_γ), 26.59 (C_1), 53.12, 53.52, 54.77 (3 NCH$_3$), 58.01, 58.14, 58.76, 59.56, 60.85 64.10 (6 NCH$_2$), 66.72 (d, $J_{RhC} = 13$ Hz, C_2), 61.28 (d, $J_{RhC} = 7.9$ Hz, C_4), 108.83 (d, $J_{RhC} = 6.6$ Hz, C_3), 127.95 (C_β), 145.28 (d, $J_{RhC} = 30$ Hz, C_α). Anion resonances: ^{1}H NMR (acetone-d_6) δ 7.67 (br s, 4H, H_{para}), 7.79 (br s, 8H, H_{ortho}); ^{13}C{^{1}H} NMR (acetone-d_6) δ 118.42 (C_{para}), 125.40 (q, $J_{FC} = 273$ Hz, CF$_3$), 130.06 (q, $J_{FC} = 33$ Hz, C_{meta}), 135.54 (C_{ortho}), 162.60 (1:1:1:1 q, $J_{BC} = 50$ Hz, C_{ipso}). Anal. Calcd for $C_{50}H_{49}N_3F_{24}BRh$: C, 47.60; H, 3.91. Found: C, 47.32; H, 4.25. FAB mass spectrum: calcd for $[C_{18}H_{37}N_3Rh]^+$ 398.2043; found 398.2053 (3 ppm).

[CnRhMe(η^3-CH$_2$CHCHMe][BAr$_4$], 6(BAr$_4$). A 40 mL portion of CH$_2$Cl$_2$ at −78 °C was transferred by cannula to a mixture of CnRh(CH=CH$_2$)$_2$Me (**3**, 0.17 g, 0.50 mmol) and HBAr$_4$·(Et$_2$O)$_2$ (0.47 g, 0.47 mmol) under N$_2$ in a Schlenk flask in a −78 °C bath. The mixture was stirred for 5 min and then allowed to warm to 22 °C. The resulting bright yellow solution was stirred overnight. Volatiles were removed in vacuo, and the resulting yellow solid was extracted with 25 mL of Et$_2$O to afford 0.47 g (84% yield) of a pale yellow solid. Diffusion of hexane vapor into a CH$_2$Cl$_2$ solution of **6** afforded off-white crystals. ^{1}H NMR (DMSO-d_6, 250 MHz): δ −0.14 (d, $J_{RhH} = 1.8$ Hz, RhCH_3), 1.14 (d, $J_{gh} = 6.0$ Hz, H_h), 1.58 (d, $J_{df} = 11$ Hz, H_d), 2.03, 2.59, 2.73 (3s, NCH_3), 2.40 (dq, $J_{fg} = 11$ Hz, H_g), 2.5−3.4 (m, NCH_2), 2.63 (d, $J_{ef} = 7.4$ Hz, H_e), 3.68 (dt, $J_{ef} = 7.4$ Hz, $J_{df} = J_{fg} = 11$ Hz, H_f). ^{13}C{^{1}H} NMR (DMSO-d_6, 90 MHz): δ 3.85 (d, $J_{RhC} = 25$ Hz, RhCH$_3$), 15.62 (C_5), 44.84 (d, $J_{RhC} = 14$ Hz, C_2), 47.22, 50.81 53.51 (3 NCH$_3$), 56.21, 56.69, 58.03, 58.55 60.76, 61.13 (6 NCH$_2$), 58.50 (d, $J_{RhC} = 11$ Hz, C_4), 107.01 (d, $J_{RhC} = 6.5$ Hz, C_3). BAr$_4$ anion resonances as above for **4**. Anal. Calcd for $C_{46}H_{43}N_3F_{24}BRh$: C, 45.75; H, 3.59. Found: C, 45.64; H, 3.29.

Protonations with Deuterated Acids. [CnRh(CH=CH$_2$)(η^3-CH$_2$CHCH−CH$_2$D)]$^+$ (4-*d*). (a) Deuterated Triflic Acid. DOTf was purchased from Aldrich and used as received. A −78 °C solution of 50 mg of CnRh(CH=CH$_2$)$_3$ (**1**) in 10 mL of CH$_2$Cl$_2$ was treated with 0.84 mL of a 0.1703 N solution of DOTf in ether. The solution was allowed to warm to 22 °C and was stirred for an additional hour. Solvent removal under vacuum gave an off-white solid, which was examined by ^{1}H and ^{13}C NMR in DMSO-d_6. Over a period of hours, the initial complex spectrum simplified to that of a single material. Overall, the spectra were identical to those given above for **4**, except that the butenyl Me group was partially deuterated. See the Results section for details. In a second experiment, a −78 °C solution of 50 mg of CnRh(CH=CH$_2$)$_3$ (**1**) in 8 mL of CH$_2$Cl$_2$ was treated directly with 12 μL of neat DOTf. The solution was allowed to warm to 22 °C and was stirred for an additional hour. Solvent removal under vacuum gave an off-white solid for which the ^{1}H and ^{13}C NMR (DMSO-d_6) spectra were identical to those just described except that the level of monodeuteration was now ca. 50%.

(b) Reaction of 1 in Methanol-d_4. About 10 mg of **1** was suspended in CD$_3$OD in an NMR tube. ^{1}H and ^{13}C NMR spectra were acquired periodically. The solid dissolved slowly as the reaction progressed, and after ca. 3 days the solid was gone and NMR showed the reaction to be complete and clean. $^{13}C\{^1H\}$ NMR, hydrocarbyl ligand resonances (methanol-d_4, 90 MHz): δ 16.82 (1:1:1 t, $J_{CD} = 20$ Hz, butenyl CH_2D (C_5)), 17.10 (s, butenyl CH_3 (C_5), $\Delta\delta$ CH_2D vs $CH_3 = 0.28$ ppm), 47.82 (d, $J_{RhC} = 15$ Hz, C_2), 62.31 (d, $J_{RhC} = 11$ Hz, C_4), 111.43 (d, $J_{RhC} = 5.1$ Hz, C_3), 120.61 (C_β), 156.62 (d, $J_{RhC} = 28$ Hz, C_α). The counterion could not be determined, and solvent removal led to decomposition.

(c) Exchange Control of Butenyl Complex 6 in Methanol-d_4. About 10 mg of the butenyl complex **6**(BAr$_4$) was dissolved in CD_3OD in an NMR tube and was let stand for several days at room temperature. The ^1H NMR revealed slight changes in the chemical shifts from the same material in DMSO-d_6, but no changes in intensity or coupling pattern were observed, indicating no H/D exchange with the solvent. ^1H NMR (methanol-d_4, 360 MHz): δ 0.03 (d, $J_{RhH} = 1.8$ Hz, $RhCH_3$), 1.28 (d, $J_{gh} = 6.0$ Hz, H_h), 1.72 (d, $J_{df} = 11$ Hz, H_d), 2.13, 2.73, 2.85 (3s, NCH_3), 2.40 (dq, $J_{fg} = 11$ Hz, H_g), 2.7−3.4 (m, NCH_2), H_e obscured by NCH_2 resonances, 3.86 (dt, $J_{ef} = 7.4$ Hz, $J_{df} = J_{fg} = 11$ Hz, H_f).

(d) Reaction of 3 in Methanol-d_4. About 10 mg of **3** was suspended in CD_3OD in an NMR tube. ^1H and ^{13}C NMR spectra were acquired periodically. The solid dissolved slowly as the reaction progressed, and after ca. 2 days the solid was gone and NMR showed the reaction to be essentially complete. ^1H NMR (methanol-d_4, 360 MHz): only resonances at δ 1.28 (H_h normally a doublet, now a multiplet) and δ 2.40 (H_g normally a dq, now a dt from H_f and CH_2D (H_h)) show changes from those of control experiment (c) above: in particular, no changes were detectable in H_d or H_f. Although H_e was obscured by NCH_2, the observation of no change in the H_d and H_f resonances rules out label incorporation into the H_e site. Observation of no change in the H_f resonance rules out any deuteration in the H_g site. There was no deuterium incorporation into the $RhCH_3$ group.

X-ray Single-Crystal Analysis of 1. X-ray diffraction data were acquired at −90 °C on a single crystal of **1**, and solution of the data proceeded uneventfully via standard heavy-atom techniques. The structure was refined anisotropically to final agreement factors of $R = 3.30\%$ and $R_w = 3.71\%$. A structural drawing of **1** is shown in Figure 1; selected bond lengths and angles of **1** are given in Table 1; Table 3 lists selected crystallographic information about the structure determination. Complete crystallographic data for the molecule appear in the Supporting Information.

X-ray Single-Crystal Analysis of 6(BAr$_4$). X-ray diffraction data were acquired at −110 °C on single crystals of **6**(BAr$_4$). Solution of the data gave poor-quality structures despite low-temperature data collection on two or three different crystals. During solution of the structure, the large BAr_4^- anion presented itself almost intact from the first E-map phased by a direct methods calculation. Most of the CF_3 groups were disordered. Each disordered CF_3 was refined with two independent sets of partially populated F_3 groups. All F−F distances (within F_3 groups) and all C−F distances in the structure were constrained to refine to single values, but the F−F distances between F_3 sets on a given CF_3 carbon were not constrained. In this way, the anion refined very well. The cation, however, did not refine as well. It showed signs of several types of disorder, especially the methyl group of the butenyl ligand, which was disordered at the two ends of the allyl group. Refinement of both methyl sites led to C(5)/C(5A) populations of 0.56/0.44. There was also some evidence for additional orientations of the allyl group and certain carbons of the Cn ligand, but these did not refine properly and so were finally ignored.

Table 3. Selected Crystallographic Information for Structures of CnRh(CH═CH$_2$)$_3$ (1) and [CnRhMe(η^3-CH$_2$CHCHMe)][BAr$_4$] (6)

	(**1**)	(**6**)
empirical formula	$C_{15}H_{30}N_3Rh$	$C_{46}H_{43}N_3F_{24}BRh$
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$ (No. 14)	$Pbca$ (No. 61)
a (Å)	7.679(2)	17.755(2)
b (Å)	15.828(2)	19.718(3)
c (Å)	13.505(2)	28.136(3)
β (deg)	92.59(2)	
volume (Å^3)	1639.8(5)	9850(2)
Z	4	8
fw	355.3	1207.6
calcd density (g/cm^3)	1.439	1.629
temp (K) of collection	183	163
reflns collcd	2455	6173
obs reflns [$F > 4\sigma(F)$]	1708	3560
no. of params refined	172	884
final R indices (obs data)	$R = 0.0330$ $R_w = 0.0371$	$R = 0.0623$ $R_w = 0.0880$

With the minimal accommodation for butenyl methyl disorder, the final parameters for the cation of **6** were ultimately good enough to warrant reporting. A structural drawing of **6** is shown in Figure 2; selected bond lengths and angles of **6** are given in Table 2; Table 3 lists selected crystallographic information about the structure determination. Complete crystallographic data for **6** appear in the Supporting Information.

Acknowledgment. This work was supported by the National Science Foundation. We thank Prof. Robert Bau for helpful discussions.

Supporting Information Available: Complete crystallographic data on **1** and **6** and ^1H and ^{13}C NMR spectra of **1**, **2**, and **3** (21 pages). Ordering information is given on any current masthead page.

OM980423Y