Reactions of $[Cp^*Ru(H_2O)(NBD)]^+$ with Dihydrogen, Silanes, Olefins, Alkynes, and Allenes

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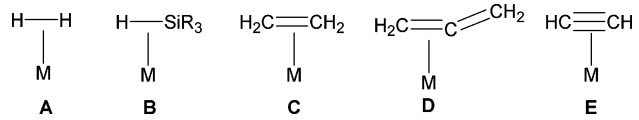
Formal [2+2+2] addition reactions of the NBD ligand in $[Cp^*Ru(H_2O)(NBD)]BF_4$ (NBD = norbornadiene) with H_2, Ph_3SiH, $ArCH{=}C{=}CH_2$, and $RC{\equiv}CPh$ were observed. In contrast, olefins such as styrene and NBD do not undergo similar [2+2+2] addition reactions with $[Cp^*Ru(H_2O)(NBD)]BF_4$. $[Cp^*Ru(H_2O)(NBD)]BF_4$ reacts with H_2 in benzene to give $[Cp^*Ru(\eta^6\text{-}C_6H_6)]BF_4$ and nortricyclene. Similarly, $[Cp^*Ru(H_2O)(NBD)]BF_4$ reacts with Ph_3SiH to give $[Cp^*Ru(\eta^6\text{-}C_6H_5SiPh_2OH)]BF_4$ and nortricyclene. Treatment of $[Cp^*Ru(H_2O)(NBD)]BF_4$ with styrene produces $[Cp^*Ru(\eta^6\text{-}C_6H_5\text{-}CH{=}CH\text{-}C_7H_9)]BF_4$, $[Cp^*Ru(\eta^6\text{-}C_6H_5\text{-}CH{=}CH_2)]BF_4$, $C_6H_5\text{-}CH{=}CH\text{-}C_7H_9$, and $Cp^*Ru(\eta^5\text{-}C_5H_4\text{-}C_9H_{11})$. The latter complex is also produced from the reaction of $[Cp^*Ru(H_2O)(NBD)]BF_4$ with NBD. Treatment of $[Cp^*Ru(H_2O)(NBD)]BF_4$ with $ArCH{=}C{=}CH_2$ produces $[Cp^*Ru(\eta^6\text{-}Ar\text{-}C_{10}H_{11})]BF_4$. Reactions of $[Cp^*Ru(H_2O)(NBD)]BF_4$ with $RC{\equiv}CC_6H_5$ (R = Ph, Me) give $[Cp^*Ru(\eta^6\text{-}C_6H_5\text{-}C_{10}H_8R)]BF_4$. The reaction pathways of the coupling reactions have been studied by computational chemistry.

Introduction

Dihydrogen, silanes, alkenes, allenes, and alkynes are important ligands in organometallic chemistry.[1] As illustrated below by structures **A**−**E**, they can form metal complexes through coordination of a single, double, or triple bond, respectively.



In terms of their bonding interactions with transition metal centers, these ligands are quite similar. Dihydrogen[2,3] and silanes[4,5] form metal−ligand σ-bonds by donating their σ-bonding electron pairs to an empty orbital of the metal and metal−ligand π-bonds by back-donation of metal dπ-electrons to the σ*-orbitals.[6] Alkenes, allenes, and alkynes form metal−ligand σ-bonds by donating their π-bonding electron pairs to an empty orbital of the metal and metal−ligand π-bonds by back-donation of metal dπ-electrons to the π*-orbitals. It is then of interest to see if these ligands could also undergo mechanistically related organometallic reactions. Such a comparative study may help to develop the chemistry or catalytic reactions of less-developed systems based on the knowledge of well-developed related systems.

In this work, we have studied the coupling reactions of H_2, Ph_3SiH, olefins, allenes, and $PhC{\equiv}CR$ with norbornadiene (NBD) mediated by $[Cp^*Ru]^+$. Cyclopentadienienyl-ruthenium fragments have been used widely in organometallic chemistry[7] and have found increasing applications in catalysis.[8,9] Experimentally, we found that formal [2+2+2] addition reactions occur between NBD and substrates such as H_2, Ph_3SiH, $ArCH{=}$

(1) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; John Wiley & Sons: New York, 2001.

(2) Reviews on dihydrogen complexes: (a) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (b) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913. (c) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (d) Esteruelas, M. A.; Oro, L. A. *Chem. Rev.* **1998**, *98*, 577. (e) Kubas, G. J. *Dihydrogen and σ-bond Complexes*, Kluwer Academic/Plenum Press: New York, 2001. (f) Peruzzini, M.; Poli, P. *Recent Advances in Hydride Chemistry*; Elsevier: Amsterdam, The Netherlands, 2001. (g) Kubas, G. J. *Adv. Organomet. Chem.* **2004**, *56*, 127.

(3) Examples of recent work: (a) Abbel, R.; Abdur-Rashid, K.; Faatz, M.; Hadzovic, A.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2005**, *127*, 1870. (b) Esteruelas, M. A.; Hernandez, Y. A.; Lopez, A. M.; Olivan, M.; Onate, E. *Organometallics* **2005**, *24*, 5989. (c) Kismartoni, L. C.; Weitz, E.; Cedeno, D. L. *Organometallics* **2005**, *24*, 4714. (d) Jimenez-Tenorio, M.; Palacios, M. D.; Puerta, M. C.; Valerga, P. *Organometallics* **2005**, *24*, 3088. (e) Kovacs, G.; Schubert, G.; Joo, F.; Papai, I. *Organometallics* **2005**, *24*, 3059. (f) Lachaize, S.; Essalah, K.; Montiel-Palma, V.; Vendier, L.; Chaudret, B.; Barthelat, J. C.; Sabo-Etienne, S. *Organometallics* **2005**, *24*, 2935. (g) Major, Q.; Lough, A. J.; Gusev, D. G. *Organometallics* **2005**, *24*, 2492. (h) Henry, R. M.; Shoemaker, R. K.; Newell, R. H.; Jacobsen, G. M.; DuBois, D. L.; DuBois, M. R. *Organometallics* **2005**, *24*, 2481. (i) Vogt, M.; Pons, V.; Heinekey, D. M. *Organometallics* **2005**, *24*, 1832. (j) Hamilton, R. J.; Leong, C. G.; Bigam, G.; Miskolzie, M.; Bergens, S. H. *J. Am. Chem. Soc.* **2005**, *127*, 4152.

(4) Reviews: (a) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151. (b) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175. (c) Lin, Z. *Chem. Soc. Rev.* **2002**, *31*, 239.

(5) Examples of recent work: (a) Osipov, A. L.; Gerdov, S. M.; Kuzmina, L. G.; Howard, J. A. K.; Nikonov, G. I. *Organometallics* **2005**, *24*, 587. (b) Bengali, A. A.; Fehnel, R. *Organometallics* **2005**, *24*, 1156. (c) Taw, F. L.; Bergman, R. G.; Brookhart, M. *Organometallics* **2004**, *23*, 886. (d) Vincent, J. L.; Luo, S.; Scott, B. L.; Butcher, R.; Unkefer, C. J.; Burns, C. J.; Kubas, G. J.; Lledos, A.; Maseras, F.; Tomas, J. *Organometallics* **2003**, *22*, 5307. (e) Sadow, A. D.; Tilley, T. D. *Organometallics* **2003**, *22*, 3577. (f) Ignatov, S. K.; Rees, N. H.; Tyrrell, B. R.; Dubbeley, S. R.; Mountford, P.; Nikonov, G. I. *Chem. Eur. J.* **2004**, *10*, 4991.

(6) Maseras, F.; Lledos, A.; Clot, E.; Eisenstein, O. *Chem. Rev.* **2000**, *100*, 601.

(7) For example: (a) Werner, H. *Organometallics* **2005**, *24*, 1036. (b) Davies, S. G.; McNally, J. P.; Smallridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 1. (c) Consiglio, G.; Morandini; F. *Chem. Rev.* **1987**, *87*, 761.

(8) Reviews: (a) Naota, T.; Takaya, H.; Murahashi, S. I. *Chem. Rev.* **1998**, *98*, 2599. (b) Trost, B. M.; Toste, F. D.; Pinkerton, A. B. *Chem. Rev.* **2001**, *101*, 2067. (c) Trost, B. M. *Acc. Chem. Res.* **2002**, *35*, 695. (d) Trost, B. M.; Frederiksen, M. U.; Rudd, M. T. *Angew. Chem., Int. Ed.* **2005**, *44*, 6630.

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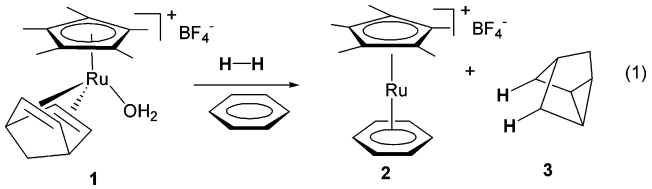
C═CH$_2$, and PhC≡CR, while a similar reaction is not observed for the reactions with olefins. To understand the origin of the similarity and difference in the reactivity, we have also carried out computational studies on the intramolecular coupling reactions of the model complex [CpRu(substrate)(NBD)]$^+$. The preliminary results have been communicated,[10] and we now report the details of this study.

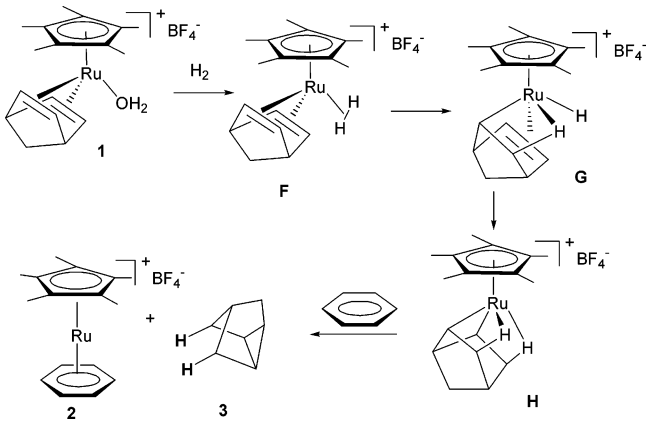
Results and Discussion

Reaction with Dihydrogen. Exposure of a solution of [Cp*Ru(H$_2$O)(NBD)]BF$_4$ (**1**)[11] to H$_2$ in the presence of benzene produced [Cp*Ru(η^6-C$_6$H$_6$)]BF$_4$ (**2**) and nortricyclene (**3**) (eq 1). In the reaction, benzene was purposely added to trap the [Cp*Ru]$^+$ fragment by forming complex **2**. In the absence of benzene, the reaction of **1** with H$_2$ in THF produced unidentified hydride species. Complex **2**[12] and nortricyclene (**3**)[13] could be readily identified by comparing their ^{1}H and ^{13}C NMR spectroscopic data with those reported.



Nortricyclene can be thought of as formed by a formal [2+2+2] addition reaction of H$_2$ with NBD. A plausible mechanism for the reaction is shown in Scheme 1. As complex [Cp*Ru(H$_2$)(COD)]$^+$ is known to contain a dihydrogen ligand,[14] it is reasonable to assume that reaction of [Cp*Ru(H$_2$O)(NBD)]$^+$ with H$_2$ initially gave the dihydrogen complex [Cp*Ru(H$_2$)(NBD)]$^+$ (**F**) (rather than the dihydride [Cp*RuH$_2$(NBD)]$^+$), which undergoes a hydrogen transfer reaction to give intermediate **G**. The intermediate **G** may then undergo an insertion reaction to give **H**. A reductive elimination reaction of **H** would give **3** and the [Cp*Ru]$^+$ fragment. Further reaction of the [Cp*Ru]$^+$ fragment with benzene would produce complex **2**. The related dihydrogen complexes *fac*-[M(H$_2$)(η^4-NBD)(CO)$_3$] (M = Cr, Mo, and W) have been characterized by IR spectroscopy and were proposed as the intermediates in photocatalytic hydrogenation of norbornadiene to nortricyclene.[15,16]

Scheme 1



The reaction pathway shown in Scheme 1 has been studied computationally with the model complex [CpRuH$_2$(NBD)]$^+$.[10] The calculations suggest that [CpRuH$_2$(NBD)]$^+$ is indeed a dihydrogen complex with a H−H distance of 0.857 Å and that the stepwise intramolecular hydrogen transfer reaction of the dihydrogen complex [CpRu(H$_2$)(NBD)]$^+$ can proceed readily with a very low reaction barrier (ca. 5.5 kcal/mol, see Figure 1a), confirming the proposed mechanism shown in Scheme 1.

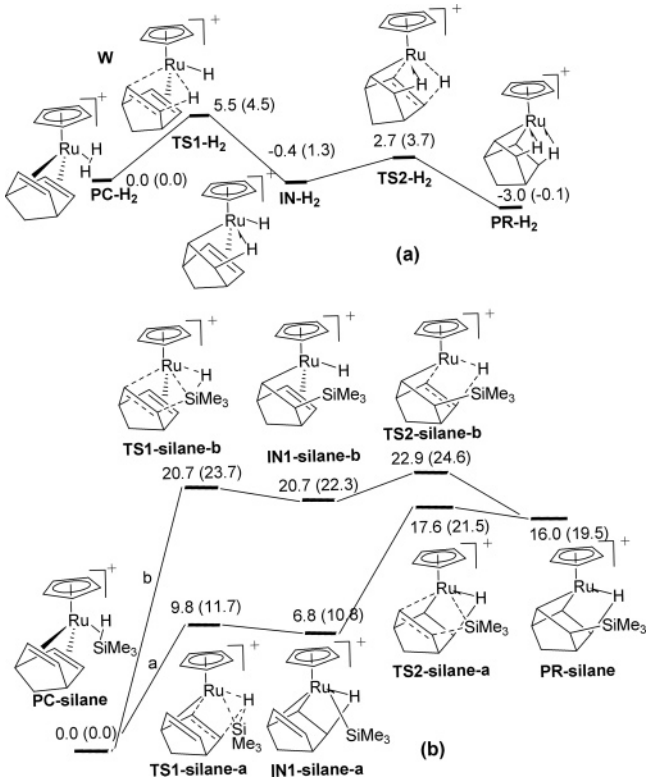


Figure 1. Schematic illustration of the stepwise reaction pathways for [CpRu(η^2-H$_2$)(NBD)]$^+$ (a) and [CpRu(η^2-Me$_3$SiH)(NBD)]$^+$ (b) together with calculated relative energies (kcal/mol) and free energies (kcal/mol, in parentheses) for species involved in the reactions.

Reaction with Ph$_3$SiH. Silanes R$_3$SiH are similar to dihydrogen in that both of them may form σ-complexes with the same metal fragment.[4] Thus, we expect that reaction of silanes

(9) Examples of recent work: (a) Onitsuka, K.; Matsushima, Y.; Takahashi, S. *Organometallics* **2005**, *24*, 6742. (b) Matsushima, Y.; Onitsuka, K.; Takahashi, S. *Organometallics* **2005**, *24*, 2747. (c) Yamamoto, Y.; Ishii, J. I.; Nishiyama, H.; Itoh, K. *J. Am. Chem. Soc.* **2005**, *127*, 9625. (d) Yamamoto, Y.; Kinpara, K.; Saigoku, T.; Takagishi, H.; Okuda, S.; Nishiyama, H.; Itoh, K. *J. Am. Chem. Soc.* **2005**, *127*, 605. (e) Trost, B. M.; Harrington, P. E.; Chisholm, J. D.; Wrobleski, S. T. *J. Am. Chem. Soc.* **2005**, *127*, 13589. (f) Trost, B. M.; Rudd, M. T. *J. Am. Chem. Soc.* **2005**, *127*, 4763. (g) Hedberg, C.; Kallstrom, K.; Arvidsson, P. I.; Brandt, P.; Andersson, P. G. *J. Am. Chem. Soc.* **2005**, 127, 15083. (h) Zhang, L.; Chen, X.; Xue, P.; Sun, H. H. Y.; Williams, I. D.; Sharpless, K. B.; Fokin, V. V.; Jia, G. *J. Am. Chem. Soc.* **2005**, 127, 15998. (i) Casey, C. P.; Bikzhanova, G. A.; Cui, Q.; Guzei, I. A. *J. Am. Chem. Soc.* **2005**, *127*, 14062. (j) Bustelo, E.; Guerot, C.; Hercouet, A.; Carboni, B.; Toupet, L.; Dixneuf, P. H. *J. Am. Chem. Soc.* **2005**, *127*, 11582. (k) Guan, H.; Iimura, M.; Magee, M. P.; Norton, J. R.; Zhu, G. *J. Am. Chem. Soc.* **2005**, *127*, 7805. (l) Hansen, E. C.; Lee, D. *J. Am. Chem. Soc.* **2005**, *127*, 3252.

(10) Liu, S. H.; Huang, X.; Ng, W. S.; Wen, T. B.; Lo, M. F.; Zhou, Z. Y.; Williams, I. D.; Lin, Z.; Jia, G. *Organometallics* **2003**, *22*, 904.

(11) Suzuki, H.; Kakigano, T.; Fukui, H.; Tanaka, M.; Moro-oka, Y. *J. Organomet. Chem.* **1994**, *473*, 295.

(12) (a) Stebler-Röthlisberger, M.; Salzer, A.; Bürgi, H. B.; Ludi, A. *Organometallics* **1986**, *5*, 298. (b) Chaudret, B.; Jalon, F. A. *J. Chem. Soc., Chem. Commun.* **1988**, 711. (c) Suzuki, H.; Omori, H.; Lee, D. H.; Yoshida, Y.; Moro-oka, Y. *Organometallics* **1988**, *7*, 2243.

(13) (a) Pretsch, E.; Buhlmann, P.; Affolter, C. In *Structure Determination of Organic Compounds: Tables of Spectral Data*, 3rd ed.; Springer-Verlag: Berlin, 2000; p 94. (b) Pouchert, C. J.; Behnke, J. In *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*, 1st ed.; Aldrich Chemical Co. Inc., 1993; Vol. 1, p 57.

(14) Jia, G.; Ng, W. S.; Lau, C. P. *Organometallics* **1998**, *17*, 4538.

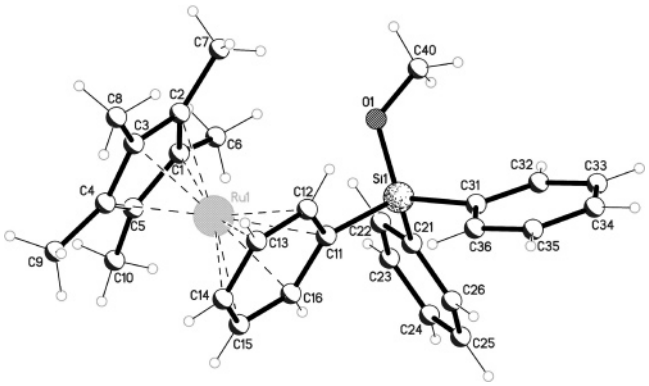
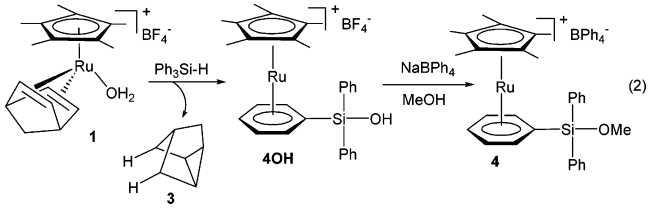


Figure 2. X-ray structure of the cation of [Cp*Ru(η^6-C_6H_5-$SiPh_2$-OCH_3)]BPh_4 (**4**). The counteranion is omitted for clarity.

with [Cp*Ru(H_2O)(NBD)]BF_4 would give [Cp*Ru(η^2-R_3SiH)(NBD)]BF_4, which may undergo a similar [2+2+2] addition reaction.

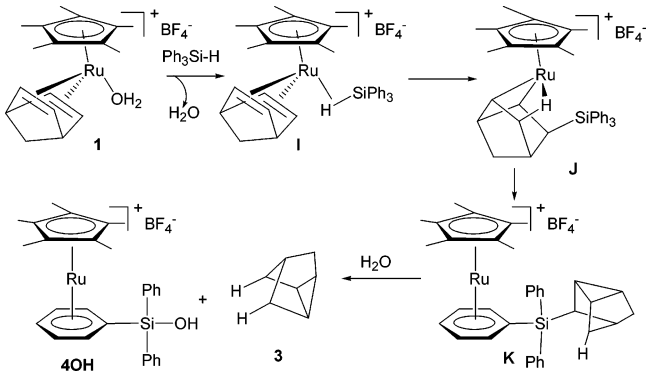
To test this hypothesis, we have studied the reaction of [Cp*Ru(H_2O)(NBD)]BF_4 with Ph_3SiH. Treatment of [Cp*Ru(H_2O)(NBD)]BF_4 (**1**) in dichloromethane or acetone with Ph_3SiH produced [Cp*Ru(η^6-$C_6H_5SiPh_2OH$)]BF_4 (**4OH**) and nortricyclene (**3**) (eq 2). We have tried to grow single crystals of **4OH** in order to confirm its structure by X-ray diffraction. However, all of our attempts to grow crystals of **4OH** from various solvent systems failed. The crystallization process often leads to the formation of an oily residue. With the hope of obtaining crystalline material, we have tried to exchange the counteranion BF_4^- in **4OH** with BPh_4^- by treatment with $NaBPh_4$. When the metathesis reaction was carried out in methanol, the OH group in **4OH** is changed to OMe, due to the reaction of the Si−OH functional group with MeOH (eq 2). Thus we have isolated compound **4** in good yield from the reaction of **4OH** with $NaBPh_4$ in methanol.



The structure of **4** has been determined by X-ray diffraction. A view of the cation of **4** is shown in Figure 2, and selected bond distances and angles are given in Table 1. The solid-state structure is consistent with the solution NMR data. In particular, the ^{1}H NMR spectrum in $CDCl_3$ showed the OMe signal at 3.67 ppm and the η^6-C_6H_5 signal at 4.91 (1H), 4.98 (2H), and 5.48 (2H) ppm.

Scheme 2 shows a plausible mechanism for the formation of complex **4OH**. Reaction of [Cp*Ru(H_2O)(NBD)]$^+$ with Ph_3SiH can initially give the σ-complex [Cp*Ru(η^2-Ph_3SiH)(NBD)]$^+$

Scheme 2



(**I**), which undergoes a stepwise hydrogen transfer reaction to give intermediate **J**. The stepwise hydrogen transfer reaction can occur by either first transferring an H followed by $SiPh_3$ or first transferring $SiPh_3$ followed by an H. A reductive elimination reaction of **J** followed by coordination of an aryl group to ruthenium would give **K**, which reacts with water to give nortricyclene **3** and complex **4OH**. Although we have failed to identify the η^2-silane intermediate, reported complexes closely related to the intermediate **I** including [Cp(PMe_3)$_2$Ru(η^2-$HSiCl_3$)]$^+$,[17a,b] Cp*RuCl(η^2-HSiClMe$_2$)(P^iPr_3),[17c] and [Cp(CO)(PEt_3)Fe(η^2-$HSiEt_3$)]$^+$ [17d] are known. We noted that hydrosilation of alkynes catalyzed by [CpRu(CH_3CN)$_3$]$^+$ has been reported recently. η^2-Silane intermediates were also suggested as the reaction intermediates in the hydrosilation reactions.[18]

To verify the proposed mechanism and to compare the reaction profile with that of the hydrogenation reaction, a computational study was carried out. The results confirm that the model complex [CpRu(H-$SiMe_3$)(NBD)]$^+$ (**PC-silane**) is a nonclassical silane complex with an Si−H bond distance of 1.717 Å.

We have examined the reaction profile of the formal [2+2+2] addition reaction of Me_3SiH with the NBD ligand in **PC-silane**. Figure 1b shows two possible pathways for the conversion of **PC-silane** to **PR-silane**, a model precursor complex to addition products. Path a starts with the hydride migration with the cleavage of the H−$SiMe_3$ bond to form the **IN1-silane-a** intermediate. Then the silyl migration gives the **PR-silane** intermediate. Path b starts with the silyl migration to form the **IN1-silane-b** intermediate. Then the hydride migration leads to the formation of **PR-silane**. One can see that not only is the barrier of the first step of path a lower than that of path b, but also the first intermediate (**IN1-silane-a**) is more stable than that of path b. It is understandable that a hydride migration is easier than a silyl transfer due to the bulky group of the latter. Moreover, the higher stability of **IN1-silane-a** versus **IN1-silane-b** is apparently related to the agostic bonding found in the former. Thus, path a was calculated to be more favorable. It is worth noting that at first glance the conversion of **PC-silane** to **PR-silane** seems thermodynamically unfavorable. A thermodynamic driving force for the experimental addition

(15) (a) Hodges, P. M.; Jackson, S. A.; Jacke, J.; Poliakoff, M.; Turner, J. J.; Grevels, F. W. *J. Am. Chem. Soc.* **1990**, *112*, 1234, and references therein. (b) Thomas, A. Haake, M.; Grevels, F. W.; Bargon, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 755. (c) Childs, G. I.; Cooper, A. I.; Nolan, T. F.; Carrott, M. J.; George, M. W.; Poliakoff, M. *J. Am. Chem. Soc.* **2001**, *123*, 6857.

(16) Other examples of hydrogen transfer involving olefin-dihydrogen complexes: (a) Jia, G.; Lin, Z.; Lau, C. P. *Eur. J. Inorg. Chem.* **2003**, 2551. (b) Liu, S. H.; Ng, S. M.; Wen, T. B.; Zhou, Z. Y.; Lin, Z.; Lau, C. P.; Jia, G. *Organometallics* **2002**, *21*, 4281. (c) Budzelaar, P. H. M.; Moonen, N. N. P.; de Gelder, R.; Smits, J. M. M.; Gal, A. W. *Eur. J. Inorg. Chem.* **2000**, 753. (d) Chan, W. C.; Lau, C. P.; Chen, Y. Z.; Fang, Y. Q.; Ng, S. M.; Jia, G. *Organometallics* **1997**, *16*, 34.

(17) (a) Freeman, S. T. N.; Lemke, F. R.; Brammer, L. *Organometallics* **2002**, *21*, 2030. (b) Lemke, F. R. *J. Am. Chem. Soc.* **1994**, *116*, 11183. (c) Osipov, A. L.; Vyboishchikov, S. F.; Dorogov, K. Y.; Kuzmina, L. G.; Howard, J. A. K.; Lemenovskii, D. A.; Nikonov, G. I. *Chem. Commun.* **2005**, 3349. (d) Scharrer, E.; Chang, S.; Brookhart, M. *Organometallics* **1995**, *14*, 5686.

(18) (a) Chung, L. W.; Wu, Y. D.; Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2003**, *125*, 11578−11582. (b) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2003**, *125*, 31. (c) Trost, B. M.; Ball, Z. T.; Joge, T. *J. Am. Chem. Soc.* **2002**, *124*, 7922. (d) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2001**, *123*, 12726.

Table 1. Crystal Data and Structure Refinement for [Cp*Ru(η^6-C$_6$H$_5$-SiPh$_2$OCH$_3$)]BPh$_4$ (4), [Cp*Ru(η^6-C$_6$H$_5$-C$_{10}$H$_{11}$)]BPh$_4$ (12BPh$_4$), and [Cp*Ru(η^6-*p*-CH$_3$C$_6$H$_4$-C$_{10}$H$_{11}$)]BPh$_4$ (12BPh$_4$)

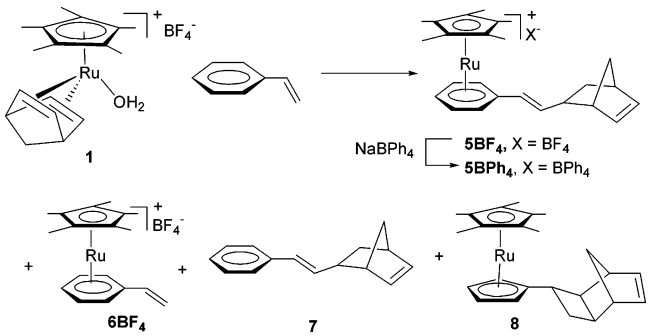
	4	**11BPh$_4$**	**12BPh$_4$**
empirical formula	$C_{53}H_{53}BORuSi$	$C_{50}H_{51}BRu$	$C_{51}H_{53}BRu\cdot0.25CH_3OH$
fw	845.92	763.79	785.82
wavelength, Å	0.71073	0.71073	0.71073
cryst syst	monoclinic	orthorhombic	triclinic
space group	$P2_1/c$	$P2_12_12_1$	$P\bar{1}$
a, Å	13.5964(10)	12.6430(9)	11.4214(8)
b, Å	15.9305(12)	16.8636(13)	12.2316(8)
c, Å	19.8104(15)	17.9064(13)	16.3587(11)
α, deg	90	90	99.6840(10)
β, deg	94.9360(10)	90	103.7620(10)
γ, deg	90	90	109.4750(10)
volume, Å^3	4275.0(6)	3817.8(5)	2014.8(2)
Z	4	4	2
density (calcd), g/cm^3	1.314	1.329	1.295
abs coeff, mm^{-1}	0.433	0.446	0.425
F(000)	1768	1600	825
cryst size, mm^3	0.40 × 0.25 × 0.15	0.35 × 0.15 × 0.10	0.40 × 0.15 × 0.10
θ range, deg	1.50 to 26.00	1.66 to 28.36	1.33 to 26.00
index ranges	$-15 \le h \le 16$, $-19 \le k \le 19$, $-23 \le l \le 24$	$-16 \le h \le 16$, $-22 \le k \le 19$, $-23 \le l \le 23$	$-12 \le h \le 14$, $-14 \le k \le 15$, $-20 \le l \le 20$
no. of rflns collected	28 177	26 318	12 961
no. of indep rflns	8339 [*R*(int) = 0.0350]	9107 [*R*(int) = 0.0439]	7732 [*R*(int) = 0.0174]
max./min. transmn	1.00/0.91	1.00/0.91	1.00/0.90
no. of data/restraints/params	8339/0/514	9107/0/471	7732/1/486
goodness-of-fit on F^2	1.021	1.002	1.073
final *R* indices [$I>2\sigma(I)$]	R1 = 0.0325, wR2 = 0.0781	R1 = 0.0355, wR2 = 0.0732	R1 = 0.0285, wR2 = 0.0707
largest diff peak and hole, e Å^{-3}	0.616 and −0.324	0.740 and −0.295	0.527 and −0.323

reaction is that the silyl-substituted nortricyclene ligand, resulting from the reductive elimination of **PR-silane**, is able to rearrange in such a way that the [Cp*Ru]$^+$ fragment coordinates with one of the phenyl rings (H-SiPh$_3$ was used in the experiments) in the silyl substituent, giving a much more stable η^6-aryl metal complex.

It is clear from Figure 1 that the hydrosilyation reaction is more difficult than the hydrogenation reaction, primarily due to the formation of the weaker Ru−Si and C−Si bonds in the hydrosilation reaction in comparison with the strong Ru−H and C−H bonds in the hydrogenation reaction and the inability of the formed C−Si bond to interact with Ru *β*-agostically in the hydrosilation reaction.

Reactions with Olefins. H$_2$ and Ph$_3$SiH undergo formal [2+2+2] addition reactions with the NBD ligand in [Cp*Ru(H$_2$O)(NBD)]BF$_4$. The reactivity is associated with the H−H or Si−H single bond. To see how a substrate with a C═C double bond may react with [Cp*Ru(H$_2$O)(NBD)]BF$_4$, we have studied the reaction of CH$_2$═CHPh with [Cp*Ru(H$_2$O)(NBD)]BF$_4$ (**1**). No appreciable reactions were observed when a mixture of **1** and styrene in dichloromethane was stored at room temperature for 3 h. When the reaction mixture was stored at room temperature for 2 days, a mixture of species was produced, from which complexes **5BPh$_4$** (after treatment with NaBPh$_4$), **6BF$_4$**, **7**, and **8** can be isolated (Scheme 3). Unlike the reaction of H$_2$ or Ph$_3$SiH, the product due to [2+2+2] addition of styrene to NBD was not detected in the styrene reaction. Formation of **5**−**8** is unusual because addition products are usually obtained in metal-promoted coupling reactions of norbornadiene with olefins.[19]

Scheme 3

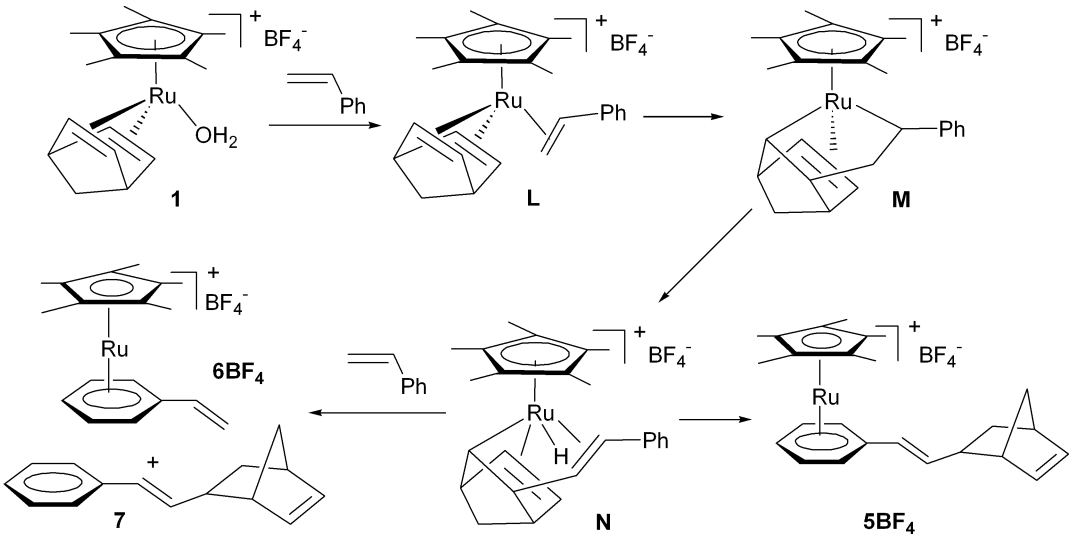


The new compounds **5BPh$_4$**, **6BF$_4$**, and **7** have been characterized by NMR spectroscopy and elemental analysis. The structure of **5BPh$_4$** has been confirmed by X-ray diffraction as mentioned in our preliminary report.[10] The complex cation [Cp*Ru(styrene)]$^+$ (**6**$^+$) was previously made from the reaction of [Cp*Ru(CH$_3$CN)$_3$]$^+$ with styrene.[20] Complex **8** is also a known complex and was previously obtained by Girolami et al. from the reaction of [Cp*RuCl$_2$]$_2$ with NBD in refluxing ethanol.[21] Our NMR data are fully consistent with those reported.

Compounds **5** and **7** can be thought of as being formally formed by addition of a C−H bond of styrene across one of the double bonds of NBD. Mechanistically, the production of compounds **5**−**7** can be rationalized by the sequence shown in Scheme 4. Reaction of [Cp*Ru(H$_2$O)(NBD)]$^+$ with PhCH═CH$_2$ initially could give the olefin complex [Cp*Ru(η^2-PhCH═CH$_2$)(NBD)]$^+$ (**L**), which undergoes an oxidative coupling reaction to give intermediate **M**. Oxidative coupling reactions of allenes with olefins on a [CpRu]$^+$ fragment to give metallacyclopentanes have been proposed previously for the coupling reactions of allenes with olefins mediated by CpRuCl(COD) (COD = 1,5-cyclooctadiene) or [CpRu(CH$_3$CN)$_3$]$^+$.[22] Closely related metallacycles, namely, ruthenacyclopentadienes with CpRu or Cp*Ru, have been isolated previously from the oxidative coupling of alkynes on a CpRu or Cp*Ru fragment.[23] Intermediate **M** can undergo a *β*-H elimination reaction to give the

(19) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49.
(20) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.
(21) Brumaghim, J. L.; Girolami, G. S. *J. Organomet. Chem.* **1999**, *586*, 258.
(22) (a) Trost, B. M.; Pinkerton, A. B. *J. Am. Chem. Soc.* **1999**, *121*, 4068. (b) Trost, B. M., Pinkerton, A. B.; Seidel, M. *J. Am. Chem. Soc.* **2001**, *123*, 12466.

Scheme 4

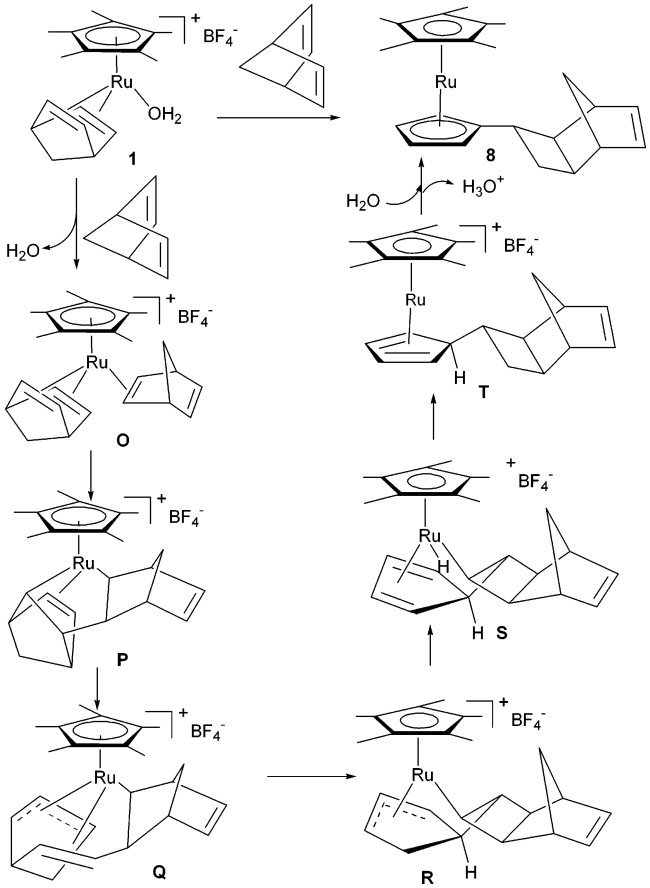


key intermediate **N**. A recent study shows that a β-H elimination reaction involving five-membered ruthenacyclopentanes can occur easily.[24] A reductive elimination reaction of **N** followed by coordination of the Ph group of the coupled organic ligand to $[Cp^*Ru]^+$ would give **$5BF_4$**, and by coordination of the Ph group of styrene present in solution to $[Cp^*Ru]^+$ would give **$6BF_4$**.

It is interesting to note that a small amount of complex **8** was also produced in the reaction of $[Cp^*Ru(H_2O)(NBD)]BF_4$ with styrene. Apparently, complex **8** is formed from the reaction of $[Cp^*Ru(H_2O)(NBD)]BF_4$ with NBD, which may be released from substitution reaction of $[Cp^*Ru(H_2O)(NBD)]BF_4$ with styrene. In fact, it can be demonstrated that complex **8** was produced cleanly when a mixture of $[Cp^*Ru(H_2O)(NBD)]BF_4$ and NBD was stood at room temperature overnight.

Scheme 5 shows a plausible mechanism for the formation of **8** in the reaction of $[Cp^*Ru(H_2O)(NBD)]BF_4$ with NBD. Reaction of $[Cp^*Ru(H_2O)(NBD)]^+$ with NBD initially could give the olefin complex $[Cp^*Ru(\eta^2\text{-NBD})(\eta^4\text{-NBD})]^+$ (**O**), which undergoes an oxidative coupling reaction to give intermediate **P**. Although we have not being able to identify **P** in our case, a few complexes related to intermediate **P**, i.e., formed from oxidative coupling of two NBD ligands, have been previously isolated and well characterized.[25] Intermediate **P** can undergo a C−C bond cleavage reaction to give the allyl complex **Q**. The allyl complex **Q** could undergo olefin insertion to give another allyl complex **R**, which can undergo a β-H elimination reaction to give the cyclopentadiene complex **S**. A reductive

Scheme 5



elimination reaction of **S** would give **T**, which can be deprotonated by water to give **8**. Although rare, other examples of skeletal rearrangements of NBD or norbornenyl ligands on coordinated unsaturated metal centers to form organic ligands with a five-membered ring are known, for example, in the reaction of Cp*RuCl(NBD) with $AgBF_4$ to give $[Cp^*Ru(\eta^6\text{-}C_5H_4{=}CHCH_3)]BF_4$[11] and in the reaction of CpCo(NBD) with HBF_4 to form $[CpCo(C_5H_6CH{=}CH_2)]BF_4$.[26]

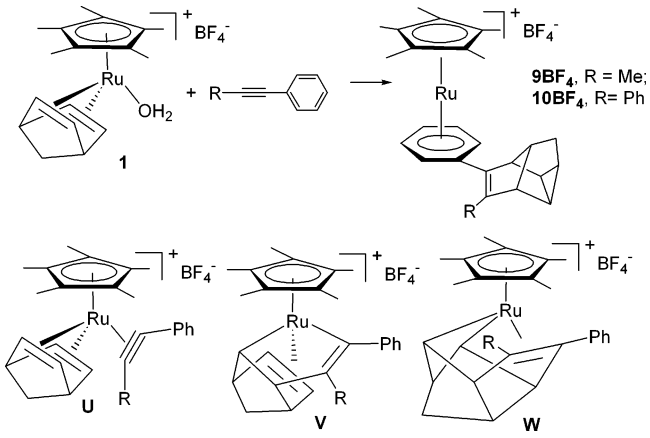
(23) (a) Yamamoto, Y.; Arakawa, T.; Itoh, K. *Organometallics* **2004**, *23*, 3610. (b) Yamamoto, Y.; Arakawa, T.; Ogawa, R.; Itoh, K. *J. Am. Chem. Soc.* **2003**, *125*, 12143. (c) Kirchner, K.; Calhorda, M. J.; Schmid, R.; Veiros, L. F. *J. Am. Chem. Soc.* **2003**, *125*, 11721. (d) Yamada, Y.; Mizutani, J. Kurihara, M.; Nishiyama, H. *J. Organomet. Chem.* **2001**, *637*−*639*, 80. (e) Ernst, C.; Walter, O.; Dinjus, E. *J. Organomet. Chem.* **2001**, *627*, 249. (f) Ernst, C.; Walter, O.; Dinjus, E.; Arzberger, S.; Gorls, H. *J. Prakt. Chem.* **1999**, *341*, 801. (g) Gemel, C.; Lapensee, A.; Mauthner, K.; Mereiter, K.; Schmid, R.; Kirchner, K. *Monatsch. Chem.* **1997**, *128*, 1189. (h) Albers, M. O.; de Waal, D. J. A.; Liles, D. C.; Robinson, D. J.; Singleton, E.; Wiege, M. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1680. (i) Yi, C. S.; Torres-Lubian, J. R.; Liu, N. *Organometallics* **1998**, *17*, 1257.

(24) Huang, X.; Zhu, J.; Lin, Z. *Organometallics* **2004**, *23*, 4154.

(25) See for example: (a) Itoh, K.; Oshima, N.; Jameson, G. B.; Lewis, H. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 3014. (b) Itoh, K.; Oshima, N. *Chem. Lett.* **1980**, 1219. (c) Bezman, S. A.; Bird, P. H.; Fraser, A. R.; Osborn, J. A. *Inorg. Chem.* **1980**, *19*, 3755. (d) Brumaghim, J. L.; Feldhoff, U.; Grevels, F. W.; Grubbs, R. H.; Miyashita, A. *J. Organomet. Chem.* **1979**, *173*, 253.

(26) (a) Bennett, M. A.; Nicholis, J. C.; Rahman, A. K. F.; Redhouse, A. D.; Spencer, J. L.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1328. (b) Nicholis, J. C.; Redhouse, A. D.; Spencer, J. L. *Organometallics* **1994**, *13*, 1781.

Scheme 6



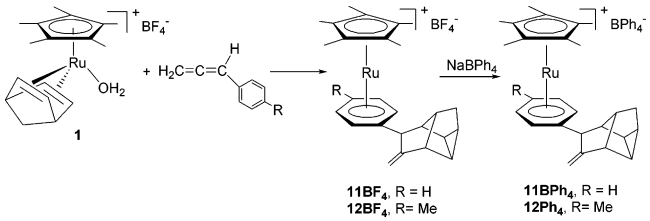
Reactions with Alkynes. Both alkynes and olefins are unsaturated organic substrates. However, alkynes are slightly different from olefins in that olefins have only one π-bond but alkynes have one extra π-bond. It is therefore interesting in knowing whether alkynes will have similar or different reactivity toward [Cp*Ru(H$_2$O)(NBD)]BF$_4$ compared with olefins. It was found that alkynes are more reactive toward **1** than styrene or NBD. [Cp*Ru(H$_2$O)(NBD)]BF$_4$ in dichloromethane rapidly reacted with MeC≡CPh to give **9BF$_4$** (Scheme 6), which has been characterized by NMR as well as X-ray diffraction, as reported in our preliminary report.[10] Similarly, reaction with PhC≡CPh also gave the analogous complex **10BF$_4$**, the structure of which can be readily assigned on the basis of its NMR spectroscopy.

Overall, the reaction between RC≡CPh and **1** is similar to that between hydrogen or Ph$_3$SiH and **1** in that a formal [2+2+2] addition of RC≡CPh to NBD also occurred. It is assumed that complexes **9** and **10** are formed through the alkyne complexes **U**, which evolve to the isolated products through intermediates **V** and **W** by oxidative coupling of alkyne and NBD, followed by olefin insertion, reductive elimination, and coordination of an aryl group. The reaction pathway is supported by theoretical calculations (see discussion below). Ruthenacyclopentene complexes have been proposed as the key intermediates in alkyne−alkene coupling reactions catalyzed by ruthenium complexes such as CpRuCl(COD) and [CpRu(CH$_3$CN)$_3$]PF$_6$.[8]

Formation of complexes **9** and **10** is probably not surprising, as catalytic [2+2+2] homo-Diels−Alder cycloadditions of RC≡CR′ to NBD have been achieved with complexes such as [Co(acac)$_3$]/PR$_3$/Et$_2$AlCl.[19] Homo-Diels−Alder cycloadditions of RC≡CR′ to COD could also be effected by ruthenium complexes such as (η^5-C$_9$H$_7$)RuCl(COD) and CpRuCl(COD).[27] Interestingly, Cp*RuCl(COD) catalyzed [2+2] cycloadditions of alkynes to NBD.[28]

Reactions with Arylallenes. Allenes RCH═C═CH$_2$ have two adjacent double bonds. Allenes are structurally similar to olefins in that they all have a C═C double bond. Allenes RCH═C═CH$_2$ can also be related to alkynes RC≡CR′ in that they have two π-bonds. One may wonder whether the reactivity of allenes toward [Cp*Ru(H$_2$O)(NBD)]BF$_4$ is similar to that of olefins or alkynes. To address this question, the reactions of

Scheme 7



[Cp*Ru(H$_2$O)(NBD)]BF$_4$ with ArCH═C═CH$_2$ were carried out. Reactions of [Cp*Ru(H$_2$O)(NBD)]BF$_4$ with phenylallenes PhCH═C═CH$_2$ produced a mixture of species, from which complex **11BF$_4$** can be isolated. Complex **11BF$_4$** can be converted to **11BPh$_4$** on treatment with NaBPh$_4$. Similarly, reactions of *p*-tolylCH═C═CH$_2$ produced **12BF$_4$**, which can be converted to **12BPh$_4$** on treatment with NaBPh$_4$ (Scheme 7).

The structures of complexes **11BPh$_4$** and **12BPh$_4$** have been determined by X-ray diffraction studies. The structures of the cations of these two complexes are shown in Figures 3 and 4, respectively. Selected bond distances and angles are given in Table 2. The X-ray structures clearly reveal that an allene molecule is cycloadded to the NBD ligand through the aryl-substituted C═C bond of allenes. The solution ^{1}H NMR data are consistent with the solid structures. It is interesting to note that the aryl-substituted C═C bond rather than the nonsubstituted C═C bond is coupled with NBD. The higher reactivity of the aryl-substituted C═C bond versus the nonsubstituted C═C bond

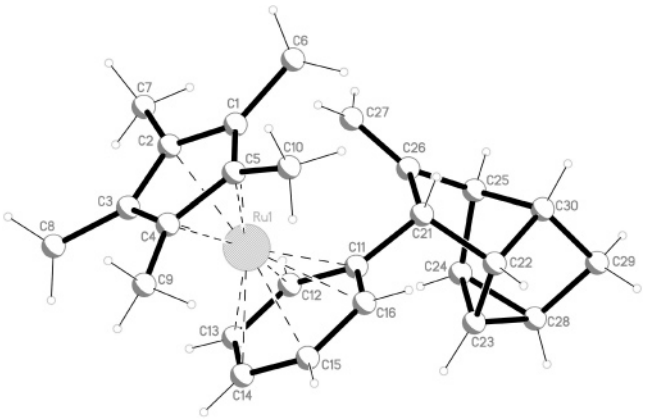


Figure 3. X-ray structure of the cation of [Cp*Ru(η^6-C$_6$H$_5$-C$_{10}$H$_{11}$)]-BPh$_4$ (**11BPh$_4$**). The counteranion is omitted for clarity.

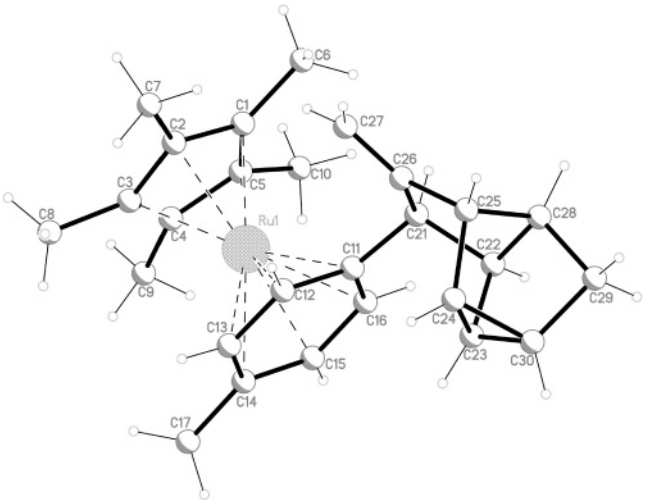


Figure 4. X-ray structure of the cation of [Cp*Ru(η^6-*p*-CH$_3$C$_6$H$_4$-C$_{10}$H$_{11}$)]BPh$_4$ (**12BPh$_4$**). The counteranion is omitted for clarity.

(27) (a) Trost, B. M.; Imi, K.; Indolese, A. F. *J. Am. Chem. Soc.* **1993**, *115*, 8831. (b) Butenschon, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 636. (c) Alvarez, P.; Gimeno, J.; Lastra, E.; García-Granda, S.; Van der Maelen, J. F. Bassetti, M. *Organometallics* **2001**, *20*, 3762. (d) Huang, X.; Lin, Z. *Organometallics* **2003**, *22*, 5478.

(28) Mitsudo, T.; Naruse, H.; Kondo, T.; Ozaki, Y.; Watanabe, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 580.

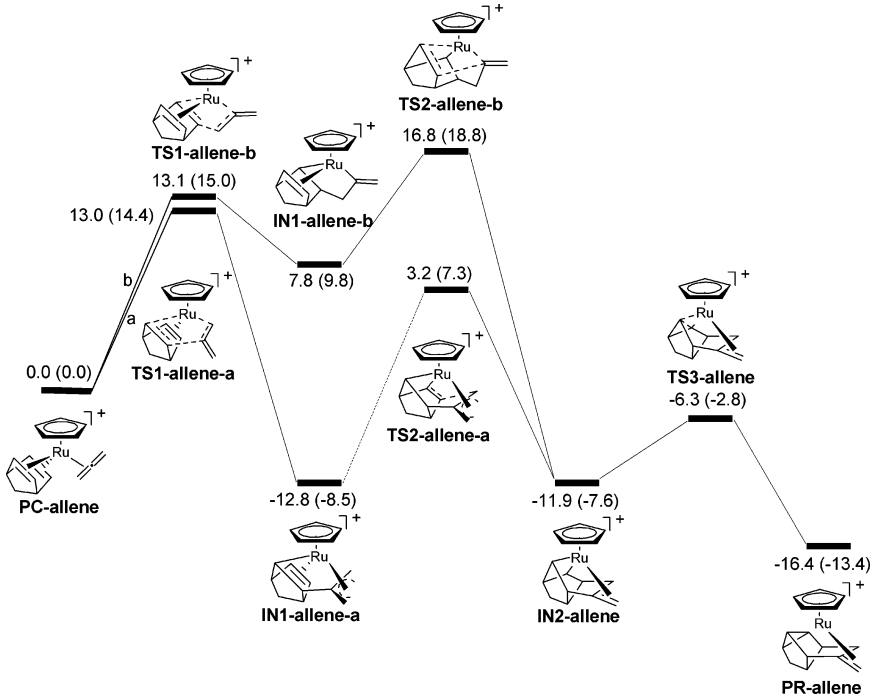
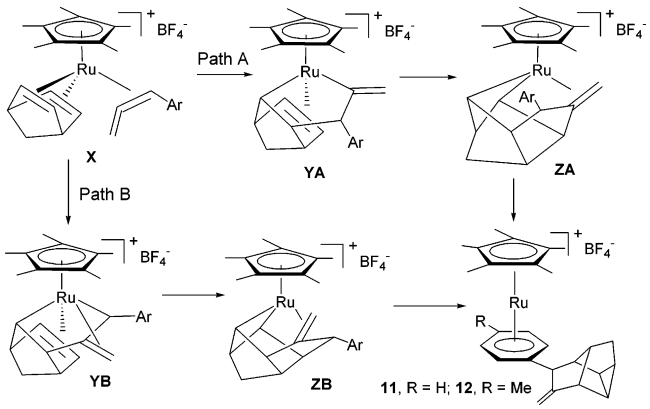


Figure 5. Energy profiles for the [2+2+2] addition between NBD and allene in the ruthenium cationic complex $[CpRu(NBD)(allene)]^+$. The relative energies and free energies (in parentheses) are given in kcal/mol.

Table 2. Selected Bond Lengths [Å] for $[Cp^*Ru(\eta^6\text{-}C_6H_5\text{-}SiPh_2OCH_3)]BPh_4$ (4), $[Cp^*Ru(\eta^6\text{-}C_6H_5\text{-}C_{10}H_{11})]BPh_4$ (11BPh$_4$), and $[Cp^*Ru(\eta^6\text{-}p\text{-}CH_3C_6H_4\text{-}C_{10}H_{11})]BPh_4$ (12BPh$_4$)

	4	11BPh$_4$	12BPh$_4$
Ru(1)−C(1)	2.194(2)	2.185(3)	2.1831(18)
Ru(1)−C(2)	2.189(2)	2.186(3)	2.1771(18)
Ru(1)−C(3)	2.173(2)	2.173(2)	2.1838(18)
Ru(1)−C(4)	2.166(2)	2.177(3)	2.1811(18)
Ru(1)−C(5)	2.183(2)	2.176(3)	2.1736(18)
Ru(1)−C(11)	2.253(2)	2.271(3)	2.2449(18)
Ru(1)−C(12)	2.200(2)	2.233(3)	2.2195(18)
Ru(1)−C(13)	2.204(2)	2.195(3)	2.2013(19)
Ru(1)−C(14)	2.214(2)	2.197(3)	2.2361(19)
Ru(1)−C(15)	2.202(2)	2.200(3)	2.2081(18)
Ru(1)−C(16)	2.223(2)	2.214(3)	2.1994(18)

Scheme 8



is likely related to the electron-withdrawing property of the aryl substituent. The addition reaction presumably starts with an oxidative coupling step (see the discussion below). It is expected that electron-deficient C═C bonds undergo oxidative coupling reactions more easily.

Mechanistically, complexes **11** and **12** could be formed through a reaction sequence similar to those of the alkyne reactions, as illustrated in Scheme 8, starting from allene complexes **X**. There are two possible pathways for the coupling reactions to proceed. The NBD ligand could initially link to the central carbon of the allene or to one of the terminal carbons. Unfortunately, we have not been able to identify the intermediates. Thus the two pathways cannot be differentiated experimentally.

To gain more insight into the reaction mechanism, the two reaction pathways relevant to the [2+2+2] addition of allene with the NBD ligand of $[Cp^*Ru(H_2O)(NBD)]^+$ (**1**) have been examined by density functional theory calculations at the Becke3LYP level using model complex $[CpRu(NBD)(allene)]^+$. The energy profiles for the reactions are illustrated in Figure 5.

As shown in Figure 5, path a starts with the middle carbon and then one of the terminal carbons of the allene ligand in the first and second C−C couplings, giving intermediates **IN1-allene-a** and **IN2-allene**, respectively. In path b, one of the terminal carbons and the middle carbon of the allene take turns to have the first and second carbon−carbon coupling steps, giving intermediates **IN1-allene-b** and **IN2-allene**, respectively. Finally, a reductive elimination from **IN2-allene** leads to the formation of **PR-allene**. It is interesting to note that although the energy difference (0.6 kcal/mol) between **TS1-allene-a** and **TS1-allene-b** for the two reaction pathways is small, the energy difference (18.3 kcal/cal) between **IN1-allene-a** and **IN1-allene-b** is large. The higher stability of **IN1-allene-a** is apparently related to the Ru−η^3-allyl interaction, while in **IN1-allene-b**, no Ru−η^3-allyl interaction is possible. The results shown in Figure 5 clearly indicate that path a is kinetically more favorable than path b.

Comments on the Reactivity of H_2, Ph_3SiH, Olefins, RC≡CPh, and ArCH═C═CH_2. It is noted that H_2, Ph_3SiH, RC≡CPh, and ArCH═C═CH_2 readily undergo formal [2+2+2] addition reactions with the NBD ligand of **1**. However olefins such as styrene and NBD are much less reactive toward **1** and do not react in a similar manner to give the [2+2+2] addition products. The differences can be understood by careful examination of the energy profiles of the relevant addition reactions.

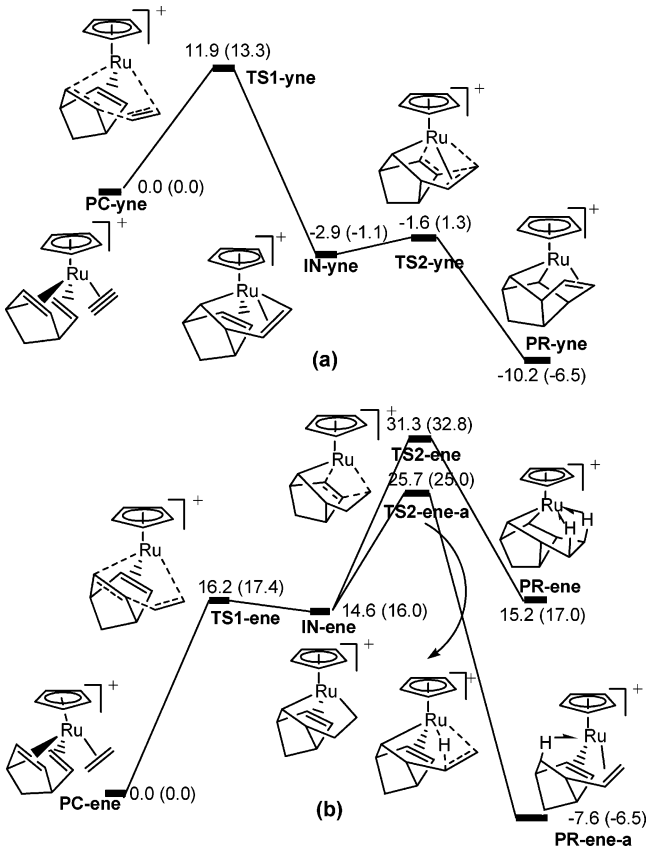


Figure 6. Energy profiles for the [2+2+2] addition reactions of the ruthenium cationic complexes [CpRu(NBD)(HC≡CH)]$^+$ (a) and [CpRu(NBD)(CH_2=CH_2)]$^+$ (b). The relative energies and free energies (in parentheses) are given in kcal/mol.

The energy profiles for [2+2+2] addition reactions of [CpRu(L)(NBD)]$^+$ (L = H_2, Me_3SiH, CH_2=C=CH_2) are shown in Figures 1 and 5. The energy profiles of the corresponding addition reactions of [CpRu(L)(NBD)]$^+$ (L = CH_2=CH_2, HC≡CH) have been briefly described in our preliminary report. To aid the following discussion, these profiles are reproduced in Figure 6.

In the reaction of H_2, the first hydrogen transfer leads to the formation of a hydride intermediate (**IN-H$_2$**) containing an agostic interaction (Figure 1a). In the reaction of Me_3SiH, the first hydrogen transfer leads to the formation of a silyl intermediate (**IN1-silane-a**) also containing an agostic interaction (Figure 1b). In the reaction of CH_2=C=CH_2, the intermediate formed after the first C−C bond formation corresponds to an η^3-allyl structure (**IN1-allene-a**) (Figure 5). In the reaction of HC≡CH, the intermediate formed after the first C−C bond formation corresponds to an η^2-alkenyl structure (**IN-yne**) (Figure 6a). The intermediates **IN−H$_2$**, **IN1-allene-a**, and **IN-yne** are more stable than the corresponding parent model complexes. However, the corresponding intermediates **IN-ene** formed from the reaction of H_2C=CH_2 and **IN1-silane-a** formed from the reaction of $HSiMe_3$ are found to be significantly unstable. The stabilities of **IN-H$_2$**, **IN1-allene-a**, and **IN-yne** are apparently related to the additional C−H agostic bond and metal−π interaction in the Ru-η^3-allyl and Ru-η^2-alkenyl units, respectively. The presence of these interactions makes these intermediates formally 18*e* complexes. **IN1-silane-a** is also an 18*e* species. Its instability is likely related to the weaker Ru−Si bond. It is understandable that **IN-ene** is less stable, because it is formally a 16*e* species. Although there are β-H's in **IN-ene**, no agostic interaction is possible because of the five-membered ring structural arrangement. In addition, **IN-ene** shows greater H- - -H repulsions because two hydrogens originally from H_2C=CH_2 orient in such a way that creates significant repulsion with the hydrogens on the Cp ring.

The barriers for the oxidative coupling reactions (the first step in the coupling reactions) are in the order H_2 (5.5 kcal/mol) < Me_3SiH (9.8 kcal/mol) < HC≡CH (11.9 kcal/mol) < CH_2=C=CH_2 (13.0 kcal/mol) < CH_2=CH_2 (16.2 kcal/mol). The low barriers for **TS1-H$_2$** and **TS1-silane-a** can be related to the spherical property of hydrogen's 1s orbital. The spherical property of hydrogen's 1s orbital increases the tendency of its orbital to overlap with the receiving carbon.[29] The lower barrier of **TS1-yne** can be related to the extra $\pi_\perp$-bonding orbital of alkyne. The extra $\pi_\perp$-bonding orbital of alkyne is oriented in such a way that it is ready to interact with the orbitals from the receiving carbon. The barriers of the reactions involving CH_2=C=CH_2 (14.4 kcal/mol) and CH_2=CH_2 (16.2 kcal/mol) are higher than those involving H_2, Me_3SiH, and HC≡CH.

The barriers for the second step of the coupling reactions are in the order of HC≡CH (1.3 kcal/mol) < H_2 (3.1 kcal/mol) < Me_3SiH (10.8 kcal/mol) < CH_2=C=CH_2 (16.0 kcal/mol) < CH_2=CH_2 (16.7 kcal/mol). When **TS2** is considered, very small barriers are calculated for the reactions of the H_2 and HC≡CH cases. For the H_2 case, the easy C−H bond formation is again due to hydrogen's spherical σ-type orbital. The calculated structure of **IN-yne** shows that the α-carbon of the η^2-alkenyl unit has a pyramidal geometry. The orientation of the hydrogen associated with the α-carbon indicates that the Ru−C σ-bond bends toward the adjacent olefinic carbon. Apparently, the bending of the Ru−C σ-bond facilitates orbital overlap between the α-carbon and the adjacent olefinic carbon, and thus favors the C−C formation and lowers the reaction barrier from **IN-yne** to **PR-yne**. The slightly higher barrier for **TS2-silane-a** can be related to the weaker C−Si bond. The barriers of **TS2-allene-a** (16.0 kcal/mol) and **TS2-ene** (16.7 kcal/mol) are significantly higher than those of **TS2-H2**, **TS2-silane-a**, and **TS2-yne**, but are similar to those of the first step.

Overall, the reaction barriers for the conversion of [CpRu(L)(NBD)]$^+$ to the complexes that are precursors to the [2+2+2] addition products are relatively small (5−15 kcal/mol) for L = H_2, HC≡CH, and CH_2=C=CH_2, or moderate (22 kcal/mol) for L = Me_3SiH, and significantly high for CH_2=CH_2 (ca. 30 kcal/mol). Thus we see that H_2, Ph_3SiH, RC≡CPh, and RCH=C=CH_2 readily undergo formal [2+2+2] addition reactions with the NBD ligand of **1**, but olefins such as styrene and NBD are much less reactive toward **1** and do not react in a manner similar to give the [2+2+2] addition products. It is interesting to note that the barriers for the two separated steps in the coupling reactions of CH_2=C=CH_2 and CH_2=CH_2 are similar, but the overall barriers are significantly different in these two cases. Apparently, the high stability of **IN1-allene-a** helps to lower the overall barrier for the addition reaction of allene with NBD.

Due to the higher overall barrier and unfavorable thermodynamics for the formation of the precursor to the addition product, the reactions of [Cp*Ru(H$_2$O)(NBD)]$^+$ with olefins do not lead to [2+2+2] addition products, but to other compounds. The barrier of the first step of the reaction of [Cp*Ru(H$_2$O)(NBD)]$^+$ with CH_2=CH_2 is not that unusually high (Figure 6b), but is close to that of allene. Thus it is still possible for the reaction of [Cp*Ru(H$_2$O)(NBD)]$^+$ with olefin to proceed through metallacyclopentane by oxidative coupling. Once formed, metallacyclopentane can undergo other side reactions. In the reaction

(29) Ziegler, T.; Folga, E.; Berces, A. *J. Am. Chem. Soc.* **1993**, *115*, 636, and references therein.

of styrene, the intermediate undergoes β-H elimination followed by reductive elimination to give complex **5** (Scheme 4). The proposition is supported by calculations. As shown in Figure 6b, the barrier for the formation of the model complex **PR-ene-a** via **TS2-ene-a** is indeed quite low compared to the second step of the addition reaction via **TS2-ene**. In the case of reaction of NBD, the intermediate can undergo C−C bond cleavage reaction to give an allyl intermediate, which further evolves to complex **8**. β-H elimination does not occur in this case because the β-H's are oriented away from the ruthenium center.

Summary. We have demonstrated that reactions of [Cp*Ru(H$_2$O)(NBD)]$^+$ with H$_2$ Ph$_3$SiH, MeC≡CPh, and ArCH=C=CH$_2$ lead to formal [2+2+2] addition between the substrates and the coordinated NBD, while similar reactions are not observed for the reactions with styrene or NBD. Theoretical calculations suggest that [Cp*Ru(substrate)(NBD)]$^+$ is the active species in the observed reactions. The facile reactions of H$_2$ and Ph$_3$SiH can be attributed to the sperical nature of the H 1s orbital, which can lower the reaction barriers and the ability of the formed C−H bond to interact with the metal center agostically, which can stabilize the intermediate. The easy reactions of alkynes can be attributed to the extra $\pi_\perp$-bond of alkynes. The extra $\pi_\perp$-bond has been found to play a key role in stabilizing the relevant reaction intermediate by forming 18*e* η^2-vinyl species, as well as lowering the reaction barriers. The easy reactions of allenes can also be attributed to the extra π-bond of allenes. The extra π-bond helps to stabilize the relevant reaction intermediate by forming 18*e* η^3-allyl species and lower the overall reaction barrier. The olefin reaction has a very high overall reaction barrier for the [2+2+2] addition reaction. Thus the metallacyclopane intermediate formed after oxidative coupling evolves to other products through C−H or C−C bond cleavage reactions.

Experimental Section

All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium-benzophenone (hexane, diethyl ether, THF, benzene) or calcium hydride (dichloromethane, CHCl$_3$). The starting materials [Cp*Ru(H$_2$O)(NBD)]BF$_4$,[11] phenylallene, and *p*-tolylallene[30] were prepared following the procedures described in the literature. Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were collected on a Bruker ARX-300 spectrometer (300 MHz). ^{1}H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H$_3$PO$_4$. Mass spectra were obtained on a Finnigan LCQ MAT mass spectrometer.

Reaction of [Cp*Ru(H$_2$O)(NBD)]BF$_4$ with H$_2$; Identification of Nortricyclene (3) and [Cp*Ru(η^6-C$_6$H$_6$)]BF$_4$ (2). To an NMR tube charged with [Cp*Ru(H$_2$O)(NBD)]BF$_4$ (40 mg, 0.092 mmol) were added CD$_3$COCD$_3$ (1.0 mL) and C$_6$D$_6$ (0.2 mL). The reaction mixture was allowed to stand for 15 h under H$_2$. The volatile portion of the reaction mixture was then collected by vacuum transfer. The ^{1}H NMR spectrum shows that the vacuum-transferred portion contains nortricyclene.[13] ^{1}H NMR (300 MHz, acetone-d_6, 298 K): δ 1.09 (br s, 3 H, CH), 1.27 (br s, 6H, CH$_2$), 2.00 (m, 1 H, CH). ^{13}C NMR (CD$_2$Cl$_2$, 75.5 MHz): δ 9.4 (s), 29.2 (s), 32.6 (s). To identify [Cp*Ru(η^6-C$_6$H$_6$)]BF$_4$ (**2**), the reaction was carried out with C$_6$H$_6$ instead of C$_6$D$_6$. After the volatile portion of the reaction mixture was removed under vacuum, the NMR data showed that the residue contains [Cp*Ru(η^6-C$_6$H$_6$)]BF$_4$.[20] ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 298 K): δ 2.08 (s, 15 H, Cp*), 5.78 (s, 6 H, C$_6$*H*$_6$). ^{13}C{^{1}H} NMR (75.48 MHz, CD$_2$Cl$_2$, 298 K): δ 12.8 (s, Cp*), 89.2 (s, *C*$_6$H$_6$), 99.1 (s, Cp*).

Reaction of [Cp*Ru(H$_2$O)(NBD)]BF$_4$ with Ph$_3$SiH; Preparation of [Cp*Ru(η^6-C$_6$H$_5$-SiPh$_2$OH)]BF$_4$ (4OH). To a stirred solution of [Cp*Ru(H$_2$O)(NBD)]BF$_4$ (**1**) (168 mg, 0.388 mmol) in acetone (8 mL) was added dropwise a solution of Ph$_3$SiH (106 mg, 0.407 mmol) in acetone (18 mL). After the addition was completed, the mixture was stirred for a further 2 h, and then it was filtered. The volume of the filtrate was reduced to ca. 3 mL, and then hexane (3 mL) was added along the flask wall to give a two-layer mixture. A brown oil was formed at the bottom of the flask after standing for 2 h. This oily material was separated, and the solution was concentrated to dryness. The residue was washed with hexane (5 mL), diethyl ether (4 mL × 3), and a mixture of CH$_2$Cl$_2$/hexane (1 mL/5 mL) to give an oil, which changed to a yellow solid when completely dried under vacuum. The ^{1}H NMR spectrum showed that the solid is mainly **4OH**. Yield: 187 mg, 86%. ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ 1.82 (s, 15 H, Cp*), 5.68−5.82 (m, 4 H, SiO*H* and η^6-Ph), 5.97 (d, *J*(HH) = 5.4 Hz, 2 H, η^6-Ph), 7.34−7.46 (m, 6 H, Ph), 7.63 (d, *J*(HH) = 6.5 Hz, 4 H, Ph). MS (FAB, *m*/*z*): 527.1 (M − BF$_4$).

Preparation of [Cp*Ru(η^6-C$_6$H$_5$-SiPh$_2$OCH$_3$)]BPh$_4$ (4). A solution of NaBPh$_4$ (450 mg, 1.31 mmol) in MeOH (1 mL) was added dropwise to a stirred solution of [Cp*Ru(η^6-C$_6$H$_5$-SiPh$_2$OH)]BF$_4$ (**4OH**) (200 mg, 0.357 mmol) in MeOH (5 mL) to give an off-white precipitate. The mixture was stirred for a further 1 h. The precipitate was collected by filtration, washed with MeOH (1 mL) and diethyl ether (2 mL), and dried under vacuum. The product is further purified by column chromatography on silica (deactivated by 5% H$_2$O, v/v) with CH$_2$Cl$_2$ as the eluent to afford **4** as a white solid. Yield: 196 mg, 65%. MS (TOF, *m*/*z*): 527.1135 (M − BPh$_4$). Anal. Calcd for C$_{53}$H$_{53}$BORuSi: C, 75.25; H, 6.31. Found: C, 75.10; H, 6.53. ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ 1.67 (s, 15 H, Cp*), 3.67 (s, 3 H, OCH$_3$), 4.91 (t, *J*(HH) = 5.7 Hz, 1 H, η^6-Ph), 4.98 (t, *J*(HH) = 5.7 Hz, 2 H, η^6-Ph), 5.48 (d, *J*(HH) = 5.7 Hz, 2 H, Ph), 6.89 (t, *J*(HH) = 7.1 Hz, 4 H, Ph), 7.03 (t, *J*(HH) = 7.3 Hz, 8 H, Ph), 7.38−7.58 (m, 18 H, Ph). Single crystals of **4** were grown by layering diethyl ether on top of a solution of **4** in CDCl$_3$.

Identification of Nortricyclene (3) in the Reaction of [Cp*Ru(H$_2$O)(NBD)]BF$_4$ with Ph$_3$SiH. A mixture of [Cp*Ru(H$_2$O)(NBD)]BF$_4$ (37 mg, 0.085 mmol) and Ph$_3$SiH (24 mg, 0.092 mmol) in CD$_2$Cl$_2$ (1 mL, freshly distilled by vacuum-transfer) was stirred for 1 h. The volatile portion was then collected by vacuum transfer. The ^{1}H NMR spectrum shows that the vacuum-transferred portion contains nortricyclene. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 298 K): δ 0.92 (br s, 3 H, CH), 1.11 (br d, *J*(HH) = 1.2 Hz, 6H, CH$_2$), 1.83−1.86 (m, 1 H, CH).

Reaction of [Cp*Ru(H$_2$O)(NBD)]BF$_4$ with Styrene. Isolation of [Cp*Ru(η^6-C$_6$H$_5$-CH=CH−C$_7$H$_9$)]BPh$_4$ (5BPh$_4$), [Cp*Ru(η^6-C$_6$H$_5$-CH=CH$_2$)]BF$_4$ (6BF$_4$), C$_6$H$_5$-CH=CH−C$_7$H$_9$ (7), and Cp*Ru(η^5-C$_5$H$_4$-C$_9$H$_{11}$) (8). A mixture of [Cp*Ru(H$_2$O)(NBD)]BF$_4$ (1.30 g, 3.00 mmol) and styrene (1.00 mL, 10.6 mmol) in acetone (25 mL) was stirred at RT for 2 days. Hexane (20 mL) was added, and the mixture was stirred for 10 min to give a pale yellow solid. The solid was collected by filtration, washed with hexane, and dried under vacuum. ^{1}H, ^{13}C, COSY, HC-COSY NMR and MS data indicate that the solid is **6BF$_4$**, which was obtained previously from the reaction of [Cp*Ru(CH$_3$CN)$_3$]$^+$ with styrene. Yield: 0.40 g, 31%. The solvents of the filtrate were removed completely under vacuum to give a brown oil. The brown oil was extracted with hexane (30 mL). The residue was redissolved in methanol (30 mL), and then NaBPh$_4$ (1.30 g, 3.80 mmol) was added. The mixture was stirred for 1 h to give a pale yellow solid, which was collected by filtration, washed with methanol and diethyl ether in turn, and dried under vacuum overnight to give **5BPh$_4$**.

(30) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: Amsterdam, 1981.

Yield: 0.86 g, 38%. The volume of hexane extraction obtained above was reduced to ca. 2 mL. The residue was subjected to column chromatography (silica gel) and eluted by hexane to give **7** (yield: 0.053 g, 9%) and the known compound **8**[21] (yield: 0.14 g, 11%). The colorless single crystals of **5BPh$_4$** were grown by layering hexane on top of a CH_2Cl_2 solution of **5BPh$_4$**. Characterization data for **5BPh$_4$**: Anal. Calcd for $C_{49}H_{51}BRu\cdot H_2O$: C, 76.45; H, 6.94. Found: C, 76.88; H, 6.63. ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 1.00 (m, 1 H, CH_2), 1.48 (d, 1 H, J(HH) = 8.3 Hz, CH_2), 1.61 (d, br, 1 H, J(HH) = 6.7 Hz, CH_2), 1.93 (s, 15 H, Cp*), 2.19 (m, 1 H, CH_2), 3.03 (br, 3 H, CH), 5.44 (m, 5 H, Ph), 5.89 (d, 1 H, J(HH) = 15.8 Hz, =CH), 6.10 (m, 2 H, =CH), 6.41 (dd, 1 H, J(HH) = 5.8, 3.1 Hz, =CH), 7.00−7.44 (m, 20 H, BPh_4). ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2): δ 10.21 (s, Cp*), 32.74 (s, CH_2), 42.69 (s, CH), 42.93 (s, CH), 48.28 (s, CH), 49.70 (s, CH2), 83.84 (s, η^6-Ph), 86.27 (s, η^6-Ph), 86.62 (s, η^6-Ph), 96.02 (s, Cp*), 98.61 (s, η^6-Ph), 121.7 (s, =CH), 121.8 (s, BPh_4), 125.6 (s, BPh_4), 132.1 (s, =CH), 135.9 (s, BPh_4), 138.3 (s, BPh_4), 144.2 (s, =CH), 163.9 (q, BPh_4). Characterization data for **7**: ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 0.93 (m, 1 H, CH_2), 1.30 (m, 1 H, CH_2), 1.48 (m, 1 H, CH_2), 2.26 (m, 1 H, CH_2), 2.90 (br, 3 H, CH), 5.88 (dd, 1 H, J(HH) = 15.8, 8.6 Hz, =CH), 6.05 (dd, 1 H, J(HH) = 5.8, 2.5 Hz, =CH), 6.24 (dd, 1 H, J(HH) = 5.8, 3.0 Hz, =CH), 6.40 (d, 1 H, J(HH) = 15.7 Hz, =CH), 7.27−7.36 (m, 5 H, Ph). MS(FAB, m/z): 197 [M + 1]$^+$.

Reaction of [Cp*Ru(H$_2$O)(NBD)]BF$_4$ with NBD; Preparation of Cp*Ru(η^5-C$_5$H$_4$-C$_9$H$_{11}$) (8). A mixture of [Cp*Ru(H$_2$O)(NBD)]-BF_4 (11.7 mg, 0.027 mmol) and NBD (0.0100 mL, 0.0927 mmol) in acetone-d_6 (0.35 mL) was allowed to stand overnight at room temperature. The ^{1}H NMR spectrum showed that compound **8**[20] is formed as the sole product. Column chromatography on silica gel with hexane as the eluent gave a colorless solid of **8** after removal of the solvent. Yield: 6 mg, 53%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.24−1.34 (m, 1 H, CH), 1.59 (s, 2 H, CH_2-bridge), 1.62−1.68 (m, 1 H, CH), 1.70−1.88 (m, 2 H, CH_2), 1.92 (s, 15 H, CH_3, Cp*), 2.16−2.24 (m, 1 H, CH), 2.63 (br s, 1 H, CH-bridgehead), 2.69 (br s, 1 H, CH-bridgehead), 4.04−4.12 (m, 4 H, C_5H_4), 5.92−5.99 (m, 2 H, CH=).

Reaction of [Cp*Ru(H$_2$O)(NBD)]BF$_4$ with MeC≡CPh; Preparation of [Cp*Ru(η^6-PhCH$_3$C$_2$(C$_7$H$_8$))]BF$_4$ (9BF$_4$). A mixture of [Cp*Ru(H$_2$O)(NBD)]BF_4 (0.50 g, 1.15 mmol) and methylphenylacetylene (0.14 g, 1.20 mmol) in acetone (40 mL) was stirred for 20 min. The volume of the reaction mixture was reduced to 5 mL under vacuum, and diethyl ether was added to give an off-white solid. The solid was collected by filtration, washed with diethyl ether, and dried under vacuum overnight. Yield: 0.53 g, 87%. Anal. Calcd for $C_{26}H_{31}BF_4Ru$: C, 58.77; H, 5.88. Found: C, 58.67; H, 6.18. ^{1}H NMR (300.13 MHz, CD_3COCD_3): δ 1.6−1.9 (m, 4 H, CH), 2.09 (s, 15 H, Cp*), 2.16 (s, 3 H, CH_3), 2.19 (m, 2 H, CH), 2.80 (m, 1 H, CH), 2.94 (m, 1 H, CH), 6.00−6.21 (m, 5 H, Ph). ^{13}C{^{1}H} NMR (75.48 MHz, CD_3COCD_3): δ 10.83 (s, Cp*), 16.00 (s, CH_3), 24.07 (s, CH), 24.20 (s, CH), 25.96 (s, CH), 33.04 (s, CH_2), 52.93 (s, CH), 55.11 (s, CH), 57.60 (s, CH), 85.10−88.21 (m, η^6-Ph), 97.11 (s, Cp*), 105.2 (s, Ph), 132.9(s, C=C), 149.8 (s, C=C).

[Cp*Ru(η^6-PhCH$_3$C$_2$(C$_7$H$_8$))]BPh$_4$ (9BPh$_4$). A mixture of [Cp*Ru(η^6-PhCH$_3$C$_2$(C$_7$H$_8$))]BF_4 (0.53 g, 1 mmol) and $NaBPh_4$ (0.51 g, 1.5 mmol) in methanol (30 mL) was stirred for 30 min to give a white solid. The solid was collected by filtration, washed with methanol and diethyl ether in turn, and dried under vacuum overnight. Yield: 0.70 g, 82%. Anal. Calcd for $C_{50}H_{51}BRu$: C, 78.62; H, 6.73. Found: C, 78.79; H, 6.85. ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 1.50 (br, 2 H, CH), 1.61 (br, 2 H, CH), 1.94 (s, 3 H, CH_3), 1.97 (s, 15 H, Cp*), 2.14 (br, 2 H, CH), 2.73 (br, 1 H, CH), 2.83 (br, 1 H, CH), 5.36−5.67 (m, 5 H, η^6-Ph), 7.02 (t, 4 H, J(HH) = 7.1 Hz, BPh_4), 7.16 (t, 8 H, J(HH) = 7.2 Hz, BPh_4), 7.46 (br, 8 H, BPh_4).

Reaction of [Cp*Ru(H$_2$O)(NBD)]BF$_4$ with PhC≡CPh; Preparation of [Cp*Ru(η^6-Ph$_2$C$_2$(C$_7$H$_8$))]BF$_4$ (10BF$_4$). A mixture of [Cp*Ru(H$_2$O)(NBD)]BF_4 (0.35 g, 0.80 mmol) and diphenylacetylene (0.15 g, 0.84 mmol) in acetone (20 mL) was stirred for 20 min. The volume of the reaction mixture was reduced under vacuum, and diethyl ether was added to give an off-white solid. The solid was collected by filtration, washed with diethyl ether, and dried under vacuum overnight. Yield: 0.42 g, 82%. Anal. Calcd for $C_{31}H_{33}BF_4Ru$: C, 62.74; H, 5.60. Found: C, 62.63; H, 5.56. MS(FAB, m/z): 593 [M − BPh_4]. ^{1}H NMR (300.13 MHz, CD_3COCD_3): δ 1.64 (m, 1 H, CH), 1.7−1.9 (m, 3 H, CH), 1.95 (m, 1 H, CH), 2.10 (s, 15 H, Cp*), 2.48 (m, 1 H, CH), 3.11 (m, 1 H, CH), 3.17 (m, 1H, CH), 5.64 (d, J(HH) = 6.0 Hz, 1 H, =CH), 5.88 (t, J(HH) = 6.0 Hz, 1 H, =CH), 6.03 (t, J(HH) = 6.0 Hz, 1 H, =CH), 6.17 (t, J(HH) = 6.0 Hz, 1 H, =CH), 6.27 (d, J(HH) = 6.0 Hz, 1 H, =CH), 7.30−7.50 (m, 5 H, Ph). ^{13}C{H} NMR (75.48 MHz, CD_3COCD_3): δ 11.05 (s, Cp*), 23.94 (s, CH), 26.52 (s, CH), 33.36 (s, CH_2), 53.98 (s, CH), 56.07 (s, CH), 57.81 (s, CH), 85.7−87.5 (m, *o*,*p*,*m*-η^6-Ph), 88.58 (s, *ipso*-η^6-Ph), 97.55 (s, Cp*), 102.6−131.0 (m, *o*,*m*,*p*-Ph), 136.83 (s, C=C), 137.97 (s, C=C), 152.89 (s, *ipso*-Ph).

Preparation of [Cp*Ru(η^6-Ph$_2$C$_2$(C$_7$H$_8$))]BPh$_4$ (10BPh$_4$). A mixture of [Cp*Ru(η^6-Ph$_2$C$_2$(C$_7$H$_8$))]BF_4 (0.59 g, 1.0 mmol) and $NaBPh_4$ (0.51 g, 1.5 mmol) in methanol (30 mL) was stirred for 30 min to give a white solid. The solid was collected by filtration, washed with methanol and diethyl ether, and dried under vacuum overnight. Yield: 0.76 g, 92%. Anal. Calcd for $C_{55}H_{53}BRu$: C, 79.99, H, 6.47. Found: C, 80.16, H, 6.52. The NMR data are essentially the same as those of [Cp*Ru(η^6-Ph$_2$C$_2$(C$_7$H$_8$))]BF_4, except the additional ^{1}H and ^{13}C signals of BPh_4^-.

Reaction of [Cp*Ru(H$_2$O)(NBD)]BF$_4$ with PhCH=C=CH$_2$; Preparation of [Cp*Ru(η^6-C$_6$H$_5$-C$_{10}$H$_{11}$)]BF$_4$ (11BF$_4$) and [Cp*Ru(η^6-C$_6$H$_5$-C$_{10}$H$_{11}$)] BPh$_4$ (11BPh$_4$). To a solution of [Cp*Ru(H$_2$O)(NBD)]BF_4 (436 mg, 1.01 mmol) in acetone (10 mL) was slowly added (in 1 h) a solution of phenylallene (367 mg, 3.16 mmol) in pentane (1 mL). The resulting solution was stirred for a further 0.5 h. The mixture was then concentrated to dryness. The residue was purified by column chromatography on silica gel (deactivated by 5% H_2O, v/v), by first eluting with CH_2Cl_2 to remove a mixture of some unidentified organic products, and then with a mixture of Me_2CO/CH_2Cl_2 (4−8:100, v/v) to give an orange-red band, from which compound **11BF$_4$** was isolated (with a small amount of unknown species as indicated by ^{1}H NMR) as a brownish-yellow solid. Yield: 169 mg, 31%. Characterization data of **11BF$_4$**: ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 0.49 (br t, J(HH) = 4.8 Hz, 1 H, CH, Δ-C_3H_3), 1.10 (br t, J(HH) = 4.5 Hz, 1 H, CH, Δ-C_3H_3), 1.21 (br t, J(HH) = 4.3 Hz, 1 H, CH, Δ-C_3H_3), 1.54−1.58 (br m, 1 H, CH), 1.97 (s, 15 H, CH_3, Cp*), 2.00−2.04 (br s, 2 H, CH_2), 2.39 (br s, 1 H, CH), 2.57 (br t, 1 H, CH), 3.57 (br s, 1 H, CH), 4.79 (br s, 1 H, =CH_2), 5.26 (br s, 1 H, CH_2=), 5.74−5.82 (m, 2 H, η^6-Ph), 5.86 (t, J(HH) = 5.7 Hz, 1 H, η^6-Ph), 5.94 (t, J(HH) = 5.9 Hz, 1 H, η^6-Ph), 6.00 (d, J(HH) = 5.9 Hz, 1 H, η^6-Ph). To further purify the compound, the BF_4^- counteranion was changed to BPh_4^- to give **11BPh$_4$**. A solution of $NaBPh_4$ (71.9 mg, 0.210 mmol) in MeOH (0.8 mL) was added to a stirred solution of **11BF$_4$** (92 mg, 0.173 mmol) in MeOH (1.5 mL) to give a pale yellow precipitate. The mixture was stirred for 0.5 h. The precipitate formed was collected by filtration, washed with MeOH (0.8 mL) and diethyl ether (2 mL), and dried under vacuum. Yield: 73 mg, 54%. Single crystals of **11BPh$_4$** were grown by layering MeOH on the top of a solution of **11BPh$_4$** in CH_2Cl_2, followed by layering of hexane on top of MeOH. Characterization data of **11BPh$_4$**: Anal. Calcd for $C_{50}H_{51}BRu$: C, 78.62; H, 6.73. Found: C, 78.69; H, 6.96. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 0.42 (br t, J(HH) = 5.7 Hz, 1 H, CH, Δ-C_3H_3), 0.99 (br t, J(HH) = 6.0 Hz, 1 H, CH, Δ-C_3H_3), 1.22 (br t, J(HH) = 6.0 Hz, 1 H, CH, Δ-C_3H_3), 1.48−1.72 (m, 2 H, CH_2), 1.76 (s, 15 H, CH_3, Cp*), 1.98 (br s, 1 H,

CH), 2.17 (br s, 1 H, CH), 2.57 (br t, 1 H, CH), 3.33 (br s, 1 H, CH), 4.69 (br s, 1 H, CH═), 4.78−4.90 (m, 2 H, η^6-Ph), 5.00 (t, J(HH) = 5.4 Hz, 1 H, η^6-Ph), 5.07 (d, J(HH) = 5.2 Hz, 1 H, η^6-Ph), 5.25 (br s, 1 H, CH═), 5.69 (d, J(HH) = 6.0 Hz, 1 H, η^6-Ph), 6.92 (t, J(HH) = 7.2 Hz, 4 H, Ph), 7.05 (t, J(HH) = 7.2 Hz, 8 H, Ph), 7.38−7.62 (m, 8 H, Ph).

Reaction of [Cp*Ru(H$_2$O)(NBD)]BF$_4$ with *p*-CH$_3$C$_6$H$_4$CH═C═CH$_2$; Preparation of [Cp*Ru(η^6-*p*-CH$_3$C$_6$H$_4$-C$_{10}$H$_{11}$)]BF$_4$ (12BF$_4$) and [Cp*Ru(η^6-*p*-CH$_3$C$_6$H$_4$-C$_{10}$H$_{11}$)]BPh$_4$ (12BPh$_4$). These complexes were prepared following the same procedures as for **11BF$_4$** and **11BPh$_4$**, respectively. From the reaction of [Cp*Ru(H$_2$O)(NBD)]BF$_4$ (593 mg, 1.37 mmol) with *p*-tolylallene (525 mg, 4.05 mmol) in acetone (15 mL), **12BF$_4$** was isolated as a brownish-yellow solid after purification by column chromatography. Yield: 247 mg, 33%. Counterion transformation of **12BF$_4$** (178 mg, 0.327 mmol) with NaBPh$_4$ (135 mg, 0.393 mmol) gave compound **12BPh$_4$** as a pale yellow solid. Single crystals of **12BPh$_4$** were grown from a three-layer solvent system similar to that for **11BPh$_4$**. Yield: 112 mg, 44%. Found: C, 78.90; H, 7.00. Anal. Calcd for $C_{51}H_{53}BRu$: C, 78.75; H, 6.87. Found: C, 78.90; H, 7.00. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 0.50 (br t, J(HH) = 4.7 Hz, 1 H, CH, Δ-C_3H_3), 1.01 (br t, J(HH) = 3.4 Hz, 1 H, CH, Δ-C_3H_3), 1.29 (br t, 1 H, CH, Δ-C_3H_3), 1.54−1.68 (m, 2 H), 1.83 (s, 15 H, CH_3, Cp*), 1.95 (s, 3 H, CH_3, tolyl), 2.04 (br s, 1 H, CH), 2.44 (br s, 1 H, CH), 2.62 (br s, 1 H, CH), 3.41 (br s, 1 H, CH), 4.76 (br s, 1 H, CH═), 5.14 (d, J(HH) = 6.0 Hz, 1 H, η^6-C_6H_4), 5.22 (d, J(HH) = 6.0 Hz, 1 H, η^6-C_6H_4), 5.30 (d + s, 2 H, CH═, η^6-C_6H_4), 5.80 (d, J(HH) = 6.0 Hz, 1 H, C_6H_4), 6.99 (t, J(HH) = 7.2 Hz, 4 H, Ph), 7.12 (t, J(HH) = 7.2 Hz, 8 H, Ph), 7.46−7.62 (m, 8 H, Ph).

Crystallographic Analysis. Selected yellow crystals of **4**, **11BPh$_4$**, and **12BPh$_4$**, with crystal sizes of 0.40 × 0.25 × 0.15, 0.35 × 0.15 × 0.10, and 0.40 × 0.15 × 0.10 mm^3, respectively, were mounted on top of glass fiber and transferred into the cold stream of nitrogen. Data collections were performed on a Bruker Apex CCD area detector, by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 100(2) K. Multiscan absorption corrections (SADABS) were applied. All structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full matrix least-squares on F^2 using the Bruker SHELXTL (Version 6.10) program package. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were positioned geometrically and refined using a riding model. Further details on crystal data, data collection, and refinements are summarized in Table 1.

Computational Study. All structures were optimized at the B3LYP level of density functional theory.[31] Frequency calculations were also performed to confirm the characteristics of the calculated structures as minima or transition states. In the B3LYP calculations, the effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (LanL2DZ)[32] were used to describe Ru and Si atoms, while the standard 6-31g basis set was used for C and H. Polarization functions[33] were added for the η^2-H$_2$ ligand (ζ(p) = 1.1), Si (ζ(d) = 0.262), and the carbon atoms (ζ(d) = 0.6) of the HSiMe$_3$, H$_2$C═CH$_2$, CH$_2$═C═CH$_2$, and HC≡CH substrates. Calculations of intrinsic reaction coordinates (IRC)[34] were also performed on transition states to confirm that such structures are indeed connecting two minima. All the calculations were performed with the Gaussian 03 software package.[35]

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Supporting Information Available: Crystallographic data for **4**, **11BPh$_4$**, and **12BPh$_4$** in CIF format. Cartesian coordinates for all the calculated structures and references for citations with more than 10 authors. The materials are available free of charge via the Internet at http://pubs.acs.org.

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(31) (a) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett*. **1989**, *157*, 200. (c) Lee, C.; Yang, W.; Parr, G. *Phys. Rev. B* **1988**, *37*, 785.

(32) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299

(33) Huzinaga, S. *Gaussian Basis Sets for Molecular Calculations*; Elsevier Science Pub. Co.: Amsterdam, 1984.

(34) (a) Fukui, K.; *J. Phys. Chem.* **1970**, *74*, 4161. (b) Fukui, K. *Acc. Chem. Res*. **1981**, *14*, 363.

(35) Frisch, M. J.; et al. *Gaussian 03*, revision B05; Gaussian, Inc.: Pittsburgh, PA, 2003.