Protonation Reactions of [MH(Cl)(PPh_3)$_2$(norbornadiene)] (M = Ru, Os)

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Protonation of [RuH(Cl)(PPh_3)$_2$(NBD)] (NBD = norbornadiene) in benzene with a limiting amount of HOTf gives [RuH(OTf)(PPh_3)$_2$(NBD)], norbornene, and [$RuCl_2(PPh_3)_2$]$_2$. In dichloromethane, [RuH(Cl)(PPh_3)$_2$(NBD)] reacts with a limiting amount of HOTf to give [RuH(OTf)(PPh_3)$_2$(NBD)], norbornene, and the trimetallic complex [$Ru_3Cl_5(PPh_3)_6$]OTf. In contrast, protonation of [OsH(Cl)(PPh_3)$_2$(NBD)] in benzene or dichloromethane with limiting HOTf only gives [OsH(OTf)(PPh_3)$_2$(NBD)]. In the protonation of [RuH(Cl)(PPh_3)$_2$(NBD)], the norbornene is likely produced through the intermediate [RuH(HCl)(PPh_3)$_2$(NBD)]OTf. The involvement of [RuH(HCl)(PPh_3)$_2$(NBD)]$^+$ in the formation of norbornene is supported by theoretical calculations based on the B3LYP density functional theory. The fact that norbornene is not produced in the protonation of [OsH(Cl)(PPh_3)$_2$(NBD)] can be attributed to the stronger osmium−olefin interaction.

Introduction

In the classic mechanisms of catalytic hydrogenation of olefins, insertion of an olefin to a metal−hydrogen bond followed by reductive elimination of hydride and alkyl ligands have been recognized as the key steps.[1] Recent studies on the chemistry of metal hydride complexes suggest that unsaturated substrates such as olefins, acetylenes, and ketones could also be hydrogenated through alternative pathways. For example, olefins could be hydrogenated through alkyl-dihydrogen complexes [M(R)(H_2)L_n]$^{2-6}$ or olefin-dihydrogen complexes [M(H_2)(olefin)L_n];[2,6−8] ketones could be hydrogenated through hydride complexes [MH(HB)L_n] where HB is potentially a proton donor (e.g., a coordinated RNH_2).[9−11] In reactions involving olefin-dihydrogen complexes [M(H_2)(olefin)L_n], the elementary steps include intramolecular hydrogen transfer from the dihydrogen ligand to the olefin ligand to give alkyl-hydride complexes [MH(alkyl)L_n] and reductive elimination of the hydride and alkyl ligands of [MH(alkyl)L_n]. In hydrogenation of ketones involving hydride complexes [MH(HB)L_n] where HB is potentially a proton donor, concerted hydrogen transfer from M−H and HB to ketones has been suggested.

When a halo hydride complex [MH(X)L_n] (X = halide) is treated with a protic acid, the proton could attack either the hydride or the halide (or the metal).[12] If the metal center is electron deficient, the protonation reaction could lead to the formation of either the dihydrogen complex [M(X)(H_2)L_n]$^+$ or the hydrohalide complex [MH(HX)L_n]$^+$. For example, protonation of [MH(X)L_4] (M = Ru, Os, L = phosphine, or pyridine) has been used conveniently to prepare dihydrogen complexes of the type [M(X)(H_2)L_4]$^+$.[13,14] Although possible, hydrohalide complexes of the type [MH(HX)L_4]$^+$ were usually not obtained from these protonation reactions, probably because the dihydrogen complexes [M(X)(H_2)L_4]$^+$ are thermodynamically more stable than the hydrohalide complexes [MH(HX)L_4]$^+$. However, selective protonation of halide ligands in [MH(X)L_n] has been observed in the protonation reactions of chloro hydride complexes such

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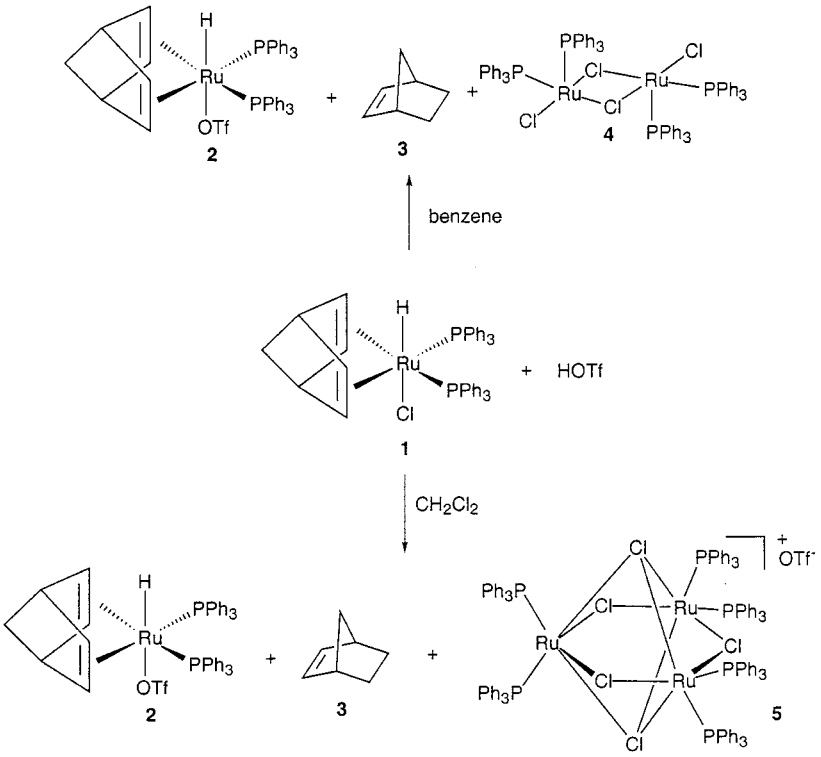
Scheme 1



as $[OsH_2Cl_2(P(i\text{-}Pr)_3)_2]$,[15a] $[PtHCl(P(t\text{-}Bu)_2Me)_2]$,[12] and $[OsH_2Cl(NO)(P(i\text{-}Pr)_3)_2]$.[15b] With this background in mind, we have investigated the protonation reactions of ruthenium and osmium complexes $[MH(X)(olefin)L_n]$, to see if complexes $[M(X)(H_2)(olefin)L_n]^+$ or $[MH(HX)(olefin)L_n]^+$ could be observed and if these complexes could be involved in the hydrogenation of the olefin ligands. In this paper, we wish to describe the protonation reactions of $[MH(Cl)(PPh_3)_2(NBD)]$ (M = Ru, Os) with HOTf.

Results and Discussion

Protonation of $[RuH(Cl)(PPh_3)_2(NBD)]$. The products of the protonation reaction are solvent dependent. $[RuH(Cl)(PPh_3)_2(NBD)]$ (**1**)[16] in C_6D_6 reacted with a limiting amount of HOTf to give $[RuH(OTf)(PPh_3)_2(NBD)]$ (**2**), norbornene (**3**), and $[RuCl_2(PPh_3)_2]_2$ (**4**) (Scheme 1). As indicated by an in situ NMR experiment, norbornene and $[RuH(OTf)(PPh_3)_2(NBD)]$ were produced in a ratio of ca. 1:2.1. If excess HOTf was used, complexes **2** and **4** could also be further protonated to give a mixture of complexes which proved to be difficult to characterize.

The products obtained from the protonation reaction can be easily identified by ^{31}P and ^1H NMR spectroscopy. The presence of the bimetallic complex **4** is indicated by the appearance of two broad singlet signals at 59.7 and 52.6 ppm in the in situ $^{31}P\{^1H\}$ NMR spectrum. The ^{31}P NMR property of complex **4** has been previously studied by K. G. Caulton's group[17] and T. A. Stephenson's group.[18] The presence of complex **2** is indicated by the appearance of a singlet signal at 41.5 ppm in the $^{31}P\{^1H\}$ NMR spectrum and a hydride signal at −13.47 ppm in the ^1H NMR spectrum. Complex **2** has been previously synthesized from the reaction of $[RuH(Cl)(PPh_3)_2(NBD)]$ with AgOTf.[19] The norbornene produced can be easily identified by the ^1H NMR.

In the protonation reaction, the hydride complex $[RuH(OTf)(PPh_3)_2(NBD)]$ is presumably formed by protonation of the Cl ligand. The bimetallic complex $[RuCl_2(PPh_3)_2]_2$ (**4**) is presumably formed from the reaction of $[RuCl(PPh_3)_2]^+$ (generated in the course of formation of norbornene) with HCl (generated by protolysis of the chloride ligand of **1** to give $[RuH(OTf)(PPh_3)_2(NBD)]$).

In dichloromethane, $[RuH(Cl)(PPh_3)_2(NBD)]$ (**1**) reacted with a limiting amount of HOTf to give $[RuH(OTf)(PPh_3)_2(NBD)]$ (**2**), norbornene (**3**), and the unusual trimetallic complex $[Ru_3Cl_5(PPh_3)_6]OTf$ (**5**) (see Scheme 1). As indicated by an in situ NMR experiment, norbornene and $[RuH(OTf)(PPh_3)_2(NBD)]$ were produced in approximately 1:1.8 ratio. In the protonation reaction, the trimetallic complex $[Ru_3Cl_5(PPh_3)_6]OTf$ (**5**) is presumably formed from the reaction of $[RuCl(PPh_3)_2]^+$ (generated in the course of formation of norbornene) with HCl (generated by protolysis of the chloride ligand of **1** to give $[RuH(OTf)(PPh_3)_2(NBD)]$). Again, if excess HOTf was used, complexes **2** and **5** could also be further protonated to give a mixture of complexes which proved to be difficult to characterize.

Complex **5** can be isolated as a brown solid from the reaction of $[RuH(Cl)(PPh_3)_2(NBD)]$ (**1**) in dichloromethane with aqueous HOTf. In the $^{31}P\{^1H\}$ NMR spectrum in

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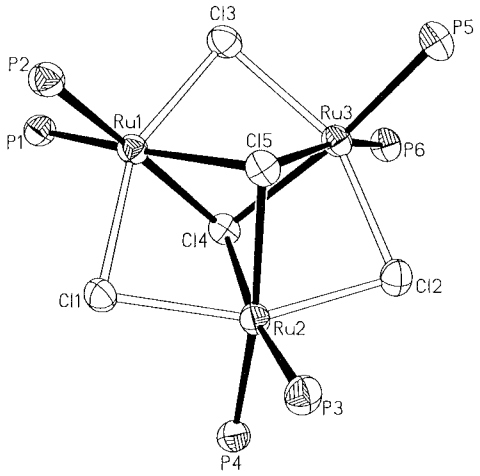


Figure 1. Molecular structure for the cation [Ru$_3$Cl$_5$(PPh$_3$)$_6$]$^+$ showing 50% probability of thermal ellipsoids. The phenyl rings of PPh$_3$ have been omitted for clarity.

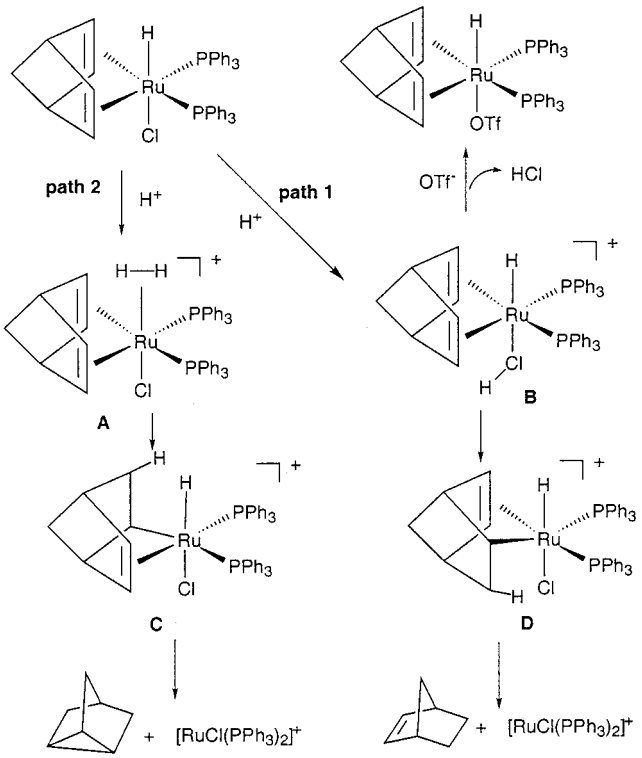
Table 1. Crystal Data and Refinement Details for [Ru$_3$Cl$_5$(PPh$_3$)$_6$]BPh$_4$·2.5CH$_2$Cl$_2$

formula	$C_{132}H_{110}BCl_5P_6Ru_3 \cdot 2.5CH_2Cl_2$
fw	2543.14
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	15.028(2)
b, Å	20.370(3)
c, Å	20.687(3)
α, deg	88.228(4)
β, deg	86.974(4)
γ, deg	87.961(3)
V, Å^3	6316.9
Z	2
d_{calc}, g cm^{-3}	1.337
abs coeff, mm^{-1}	0.668
radiation, Mo Kα, Å	0.71073
θ range, deg	0.99−27.61
no. of reflns collected	43 015
no. of ind reflns	25 880 (R_{int} = 3.58%)
no. of obsd reflns	14 720 ($I > 2\sigma(I)$)
no. of params refined	456
final R indices (obs. data)	R1 = 6.31%, wR2 = 16.36%
goodness of fit	0.925
largest diff peak, e Å^{-3}	1.48
largest diff hole, e Å^{-3}	−0.771

CDCl$_3$, compound **5** displayed a singlet ^{31}P signal at 40.2 ppm. The ^{1}H NMR in CD$_2$Cl$_2$ showed broad signals in the region 6.34−7.69 ppm. It is difficult to assign the structure on the basis of the spectroscopic data. Thus a single-crystal X-ray diffraction study on **5** was attempted. Although a crystalline solid of **5** can be easily obtained by slow diffusion of hexane to a CH$_2$Cl$_2$ solution of **5**, it is difficult to solve the structure because of the poor quality of the crystal and the disorder of the triflate anion. Thus [Ru$_3$Cl$_5$(PPh$_3$)$_6$]OTf was converted to [Ru$_3$Cl$_5$(PPh$_3$)$_6$]BPh$_4$ by treatment with NaBPh$_4$. The X-ray diffraction study was then carried out with a crystal of [Ru$_3$Cl$_5$(PPh$_3$)$_6$]BPh$_4$.

Figure 1 shows the molecular structure of the cation [Ru$_3$Cl$_5$(PPh$_3$)$_6$]$^+$. Crystallographic details and selected bond lengths and angles are given in Tables 1 and 2, respectively. The three ruthenium atoms are in an triangular arrangement and are linked by three μ_2-bridging chlorides and two face-caped chlorides. The geometry around each ruthenium atom can be described as a distorted octahedron with four chlorine atoms and two cis PPh$_3$ ligands. Similar complexes have been reported for [Ru$_3$Cl$_5$(PP)$_3$]$^+$ (PP = BINAP and (Ph$_2$P)$_2$C$_6$H$_4$).[20] [Ru$_3$Cl$_5$(PPh$_3$)$_6$]$^+$ appears to be the first structurally characterized complexes of the type [Ru$_3$Cl$_5$(P)$_6$]$^+$ with monodentate phosphine ligands.

Scheme 2



We have tried to detect the reaction intermediates by performing the protonation reaction in CD$_2$Cl$_2$ at low temperature. Unfortunately, no intermediate could be observed. To gain some insight into the protonation reaction, we have also performed the protonation reaction with DOTf. The ^{2}D NMR spectrum of norbornene isolated from the protonation reactions carried out in benzene or dichloromethane showed a ^{2}D signal at 0.9 ppm, indicating that the deuterium is incorporated at the endo position.[21] The experimental result indicates that the deuterium is transferred to the olefin from the same side of the ruthenium.

Comments on the Possible Route to the Formation of Norbornene. There are many sites in [RuH(Cl)(PPh$_3$)$_2$(NBD)] that can be initially attacked by a proton. For example, the proton could attack the hydride or the chloride to give the dihydrogen complex [RuCl(H$_2$)(NBD)(PPh$_3$)$_2$]$^+$ (**A**) or the hydrochloride complex [RuH(HCl)(NBD)(PPh$_3$)$_2$]$^+$ (**B**), respectively (see Scheme 2). The proton could also attack the olefin ligand or the metal center.

Protonation of ruthenium complexes [RuH(X)L$_4$] (L$_4$ = (dppe)$_2$, X = Cl, Br;[13a,b] L$_4$ = (dppp)$_2$, X = Cl;[13c] L$_4$ = (dcpe)$_2$, X = Cl;[13d] L$_4$ = (PPh$_3$)(2,6-(Ph$_2$PCH$_2$)$_2$C$_5$H$_3$N), X = Cl[14]) are known to give dihydrogen complexes of the type [M(X)(H$_2$)L$_4$]$^+$. Thus one might expect that protonation of [RuH(Cl)(PPh$_3$)$_2$(NBD)] could also produce the dihydrogen complex [Ru(Cl)(H$_2$)(PPh$_3$)$_2$(NBD)]$^+$

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Table 2. Selected Bond Distances and Angles for $[Ru_3Cl_5(PPh_3)_6]BPh_4 \cdot 2.5CH_2Cl_2$

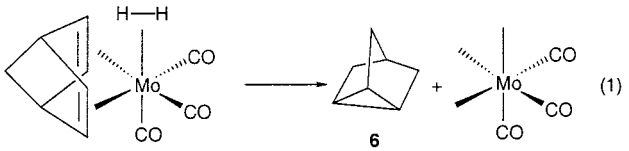
Bond Distances (Å)

Ru(1)−P(1)	2.33214(16)	Ru(1)−P(2)	2.3247(16)	Ru(1)−Cl(1)	2.4369(14)
Ru(1)−Cl(3)	2.4610(14)	Ru(1)−Cl(4)	2.4799(14)	Ru(1)−Cl(5)	2.4775(15)
Ru(2)−P(3)	2.3286(16)	Ru(2)−P(4)	2.3232(16)	Ru(2)−Cl(1)	2.4297(15)
Ru(2)−Cl(2)	2.4410(15)	Ru(2)−Cl(4)	2.5073(14)	Ru(2)−Cl(5)	2.4691(14)
Ru(3)−P(5)	2.3299(16)	Ru(3)−P(6)	2.3229(15)	Ru(3)−Cl(2)	2.4344(16)
Ru(3)−Cl(3)	2.4591(16)	Ru(3)−Cl(4)	2.4782(14)	Ru(3)−Cl(5)	2.4773(14)
Ru(1)−Ru(2)	3.3177(8)	Ru(1)−Ru(3)	3.3640(7)	Ru(2)−Ru(3)	3.3346(7)

Bond Angles (deg)

Ru(2)···Ru(1)···Ru(3)	59.87(1)	Ru(1)···Ru(2)···Ru(3)	60.75(1)
Ru(1)···Ru(3)···Ru(2)	59.37(2)	P(1)−Ru(1)−P(2)	95.37(6)
P(1)−Ru(1)−Cl(1)	104.29(5)	P(2)−Ru(1)−Cl(1)	92.03(5)
P(1)−Ru(1)−Cl(3)	93.81(5)	P(2)−Ru(1)−Cl(3)	105.39(5)
P(1)−Ru(1)−Cl(4)	94.88(5)	P(2)−Ru(1)−Cl(4)	168.52(5)
P(1)−Ru(1)−Cl(5)	170.82(5)	P(2)−Ru(1)−Cl(5)	92.15(5)
Cl(1)−Ru(1)−Cl(3)	153.63(5)	Cl(1)−Ru(1)−Cl(4)	80.44(5)
Cl(1)−Ru(1)−Cl(5)	80.66(5)	Cl(3)−Ru(1)−Cl(4)	79.04(5)
Cl(3)−Ru(1)−Cl(5)	79.08(5)	Cl(5)−Ru(1)−Cl(4)	78.16(5)
P(4)−Ru(2)−P(3)	96.56(6)	Cl(1)−Ru(2)−Cl(2)	154.58(5)
P(3)−Ru(2)−Cl(1)	103.21(5)	P(4)−Ru(2)−Cl(1)	93.71(5)
P(3)−Ru(2)−Cl(2)	94.94(5)	P(4)−Ru(2)−Cl(2)	101.82(6)
P(3)−Ru(2)−Cl(4)	170.21(5)	P(4)−Ru(2)−Cl(4)	92.41(5)
P(3)−Ru(2)−Cl(5)	93.48(5)	P(4)−Ru(2)−Cl(5)	169.50(5)
Cl(1)−Ru(2)−Cl(4)	80.03(5)	Cl(1)−Ru(2)−Cl(5)	80.97(5)
Cl(2)−Ru(2)−Cl(4)	79.34(5)	Cl(2)−Ru(2)−Cl(5)	80.30(5)
Cl(5)−Ru(2)−Cl(4)	77.80(4)	P(5)−Ru(3)−P(6)	95.72(6)
P(5)−Ru(3)−Cl(2)	104.82(6)	P(6)−Ru(3)−Cl(2)	92.27(6)
P(5)−Ru(3)−Cl(3)	94.06(6)	P(6)−Ru(3)−Cl(3)	104.80(6)
P(5)−Ru(3)−Cl(5)	95.44(5)	P(6)−Ru(3)−Cl(5)	167.87(5)
P(5)−Ru(3)−Cl(4)	171.37(6)	P(6)−Ru(3)−Cl(4)	91.16(5)
Cl(2)−Ru(3)−Cl(3)	153.18(5)	Cl(2)−Ru(3)−Cl(4)	80.04(5)
Cl(2)−Ru(3)−Cl(5)	80.26(5)	Cl(3)−Ru(3)−Cl(4)	79.11(5)
Cl(3)−Ru(3)−Cl(5)	79.13(5)	Cl(5)−Ru(3)−Cl(4)	78.19(4)
Ru(2)−Cl(1)−Ru(1)	85.96(5)	Ru(3)−Cl(2)−Ru(2)	86.31(5)
Ru(3)−Cl(3)−Ru(1)	86.27(5)	Ru(3)−Cl(4)−Ru(1)	85.45(4)
Ru(3)−Cl(4)−Ru(2)	83.96(4)	Ru(1)−Cl(4)−Ru(2)	83.40(4)
Ru(2)−Cl(5)−Ru(3)	84.78(4)	Ru(2)−Cl(5)−Ru(1)	84.24(4)
Ru(3)−Cl(5)−Ru(1)	85.52(4)		

(**A**). It has been previously reported that the dihydrogen complex $[Mo(H_2)(CO)_3(\eta^4\text{-NBD})]$ would undergo a hydrogen transfer reaction to give nortricyclene (**6**) (eq 1).[7a] Thus, hydrogenation through intermediate **A** would



(1)

more likely produce nortricyclene (**6**) (or a mixture of nortricyclene and norbornene) through intermediate **C** rather than norbornene (see Scheme 2). In reality, no nortricyclene (**6**) was detected by NMR spectroscopy in our experiment. We also found no experimental evidence for the formation of the dihydrogen intermediate **A**. Thus, formation of norbornene in the protonation reaction of $[RuH(Cl)(PPh_3)_2(NBD)]$ is unlikely related to the dihydrogen complex $[Ru(Cl)(H_2)(PPh_3)_2(NBD)]^+$, although such a possibility cannot be confidently eliminated.

There is a possibility that formation of norbornene in the protonation reaction is related to the protonation of the chloride ligand (path 1 of Scheme 2). Protonation of the chloride would give the hydrochloride complex $[RuH(HCl)(NBD)(PPh_3)_2]^+$ (**B**) which can then undergo a hydrogen transfer reaction to give intermediate **D**. Intermediate **D** can undergo reductive elimination to produce norbornene. Formation of $[RuH(OTf)(PPh_3)_2(NBD)]$ from the protonation reaction strongly suggests that protonation of chloride indeed occurred in the reaction. Involvement of hydrochloride complex **B** in the formation of norbornene is also consistent with the deuterium labeling experiment where protonation of $[RuH(Cl)(PPh_3)_2(NBD)]$ with DOTf produced deuterated norbornene in which the deuterium is at the endo position. Protonation of halide ligands has been observed in the protonation reactions of chloro hydride complexes such as $[OsH_2Cl_2(P(i\text{-}Pr)_3)_2]$,[15a] $[PtHCl(P(t\text{-}Bu)_2Me)_2]$,[12] and $[OsH_2Cl(NO)(P(i\text{-}Pr)_3)_2]$.[15b] Although well-characterized hydrohalide complexes are still rare,[22] well-characterized alkylhalide complexes $[M(XR)L_n]$[23] and halide complexes with intra- or intermolecular MX···H interaction[24] are numerous.

To prove that protonation of the chloride is likely one of the initial events in the protonation reaction, we have

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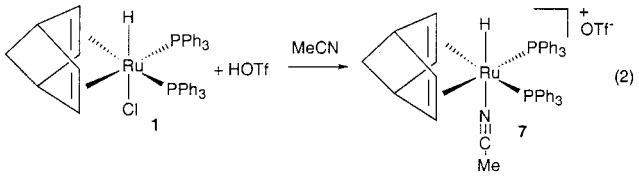
(24) See for example: (a) Roe, D. C.; Marshall, W. J.; Davidson, F.; Soper, P. D.; Grushin, V. V. *Organometallics* **2000**, *19*, 4575, and references therein. (b) Jasim, N. A.; Perutz, R. N. *J. Am. Chem. Soc.* **2000**, *122*, 8685. (c) Lee, D. H.; Kwon, H. J.; Patel. B. P.; Liable-Sands, L. M.; Rheingold, A. L.; Crabtree, R. H. *Organometallics* **1999**, *18*, 1615. (d) Esteruelas, M. A.; Oliván, M.; Oñate, E.; Ruiz, N.; Tajada, M. *Organometallics* **1999**, *18*, 2953. (e) Hampton, C. R. S. M.; Butler, I. R.; Cullen, W. R.; James, B. R.; Charland, J. P.; Simpson, J. *Inorg. Chem.* **1992**, *31*, 5509. (f) Sellmann, D.; Barth, I.; Moll, M. *Inorg. Chem.* **1990**, *29*, 176. (g) Richmond, T. G. *Coord. Chem. Rev.* **1990**, *105*, 221.

performed the protonation of [RuH(Cl)(PPh$_3$)$_2$(NBD)] with HOTf in the presence of CH$_3$CN. It is expected that [RuH(CH$_3$CN)(PPh$_3$)$_2$(NBD)]$^+$ would be produced if intermediate [RuH(HCl)(PPh$_3$)$_2$(NBD)]$^+$ (**B**) was formed due to protonation of the chloride ligand and that [RuCl(CH$_3$CN)(PPh$_3$)$_2$(NBD)]$^+$ would be produced if intermediate [Ru(Cl)(H$_2$)(PPh$_3$)$_2$(NBD)]$^+$ (**A**) is formed due to protonation of the hydride ligand. In C$_6$D$_6$ or CD$_2$Cl$_2$ in the presence of CH$_3$CN, [RuH(Cl)(PPh$_3$)$_2$(NBD)] reacted rapidly with HOTf to give [RuH(CH$_3$CN)(PPh$_3$)$_2$(NBD)]OTf (**7**) as the only product (eq 2). A control experiment

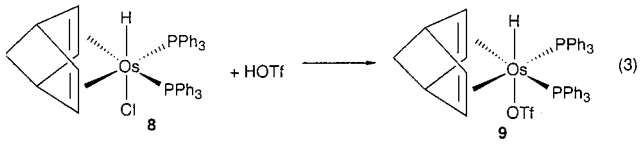


(2)

shows that [RuH(Cl)(PPh$_3$)$_2$(NBD)] is unreactive toward CH$_3$CN alone. The result strongly suggests that protonation of chloride could occur readily. Exclusive formation of [RuCl(CH$_3$CN)(PPh$_3$)$_2$(NBD)]$^+$ (rather than [RuH(CH$_3$CN)(PPh$_3$)$_2$(NBD)]$^+$) in the protonation of [RuH(Cl)(PPh$_3$)$_2$(NBD)] in the presence of CH$_3$CN may also imply that protonation of the chloride ligand is kinetically more favorable than protonation of the hydride ligand.

Although it could not be completely excluded, formation of norbornene is also unlikely related to direct protonation of the NBD ligand or the ruthenium center in [RuH(Cl)(PPh$_3$)$_2$(NBD)] (**1**). Direct protonation of the NBD ligand in **1** would initially produce both intermediates **C** and **D**, from which a mixture of nortricyclene and norbornene would be produced (see Scheme 2). However, only norbornene could be detected experimentally in the protonation reaction. In addition, in the protonation of complexes such as [Ni(COD)$_2$],[25] [Fe(CO)$_3$(η^4-cycloheptatrienone)],[26] [Mo(MeC≡CH)$_2$(dppe)$_2$],[27] and [VCp$_2$(MeC≡CMe)],[28] where the coordinated olefin or alkyne ligands are attacked directly by protons,[29] the protons are added to the olefin or alkyne ligands from the "solvent side". Thus deuteration may occur at the exo position of norbornene if norbornene was produced through direct protonation of the NBD ligand in **1**. However, the deuterium is incorporated only at the endo position of norbornene in the protonation of **1** with DOTf. Initial protonation of the ruthenium center in **1** to give dihydride species [RuH$_2$(Cl)(PPh$_3$)$_2$(NBD)]$^+$ followed by proton transfer would also produce both intermediates **C** and **D**, which would eventually give a mixture of nortricyclene and norbornene. Since only norbornene is produced in the protonation reaction, it is therefore unlikely that such a process is involved in the formation of norbornene. In addition, formation of the dihydride species [RuH$_2$(Cl)(PPh$_3$)$_2$(NBD)]$^+$ is not supported by theoretical studies (see discussion later).

Protonation of [OsH(Cl)(PPh$_3$)$_2$(NBD)]. With the hope to detect the reaction intermediate, we have studied the protonation reaction of [OsH(Cl)(PPh$_3$)$_2$(NBD)] (**8**). Protonation of [OsH(Cl)(PPh$_3$)$_2$(NBD)] (**8**) with a limiting amount of HOTf in benzene or dichloromethane only produced [OsH(OTf)(PPh$_3$)$_2$(NBD)] (**9**)[19] (eq 3). If excess of HOTf was used, a complicated mixture of phosphorus-containing species was produced. Neither norbornene or nortricyclene was observed in the protonation reactions.



(3)

Theoretical Study. Several interesting questions arise from the experimental results. (i) We have proposed that the intermediate [RuH(HCl)(PPh$_3$)$_2$(NBD)]$^+$ (**B**) is possibly involved in the formation of norbornene in the protonation of **1** (Scheme 2). Unfortunately, we have not been able to detect the intermediate. One may ask whether intermediate **B** is a reasonable species and whether proton transfer from the Ru−H and coordinated HCl to the NBD ligand in **B** is kinetically feasible. (ii) Protonation of [RuH(X)P$_4$] (P = phosphines) usually leads to the formation of the dihydrogen complexes [Ru(X)(H$_2$)P$_4$]$^+$. Thus one might expect that protonation of [RuH(Cl)(PPh$_3$)$_2$(NBD)] could also produce the dihydrogen complex [Ru(Cl)(H$_2$)(PPh$_3$)$_2$(NBD)]$^+$ (**A**). However, the dihydrogen complex **A** was not observed experimentally in the protonation of [RuH(Cl)(PPh$_3$)$_2$(NBD)]. Apparently the dihydrogen complex **A** is also not involved in the hydrogenation of NBD. One may ask why hydrogenation of NBD could not proceed through the dihydrogen intermediate **A**. (iii) Protonation of [RuH(Cl)(PPh$_3$)$_2$(NBD)] with HOTf led to the formation of [RuH(OTf)(PPh$_3$)$_2$(NBD)] along with norbornene. However, protonation of [OsH(Cl)(PPh$_3$)$_2$(NBD)] with HOTf only produced [OsH(OTf)(PPh$_3$)$_2$(NBD)]. One may ask why the protonation products for the ruthenium system are so different from those of the osmium system.

To answer these questions, theoretical calculations based on the B3LYP density functional theory have been carried out to examine the structural and energetic aspects of the possible reaction pathways involving the model hydrochloride complex [RuH(HCl)(PH$_3$)$_2$(NBD)]$^+$ (**10Ru**) and the model dihydrogen species [Ru(Cl)(H$_2$)(PH$_3$)$_2$(NBD)]$^+$ (**10Ru′**).

Figure 2 shows the two possible reaction pathways, which start from **10Ru** (path 1) and **10Ru′** (path 2), respectively, together with the calculated free energies for the reactants, intermediates, transition states, and the assumed products (**12Ru** and **12Ru′**). The reaction energies are also given in parentheses. The calculated reaction energies and free energies give consistent trends in the relative stabilities among the different species. Our calculations are based on the gas-phase model. The results are used to simulate the reactions in solution. It is therefore more appropriate to use the calculated free energies, which consider the entropy effect as well as the thermal/zero-point energy corrections, in discussing the relevant energetics. Path 1 starts from **10Ru** with the first hydrogen transfer from H$_a$ to

(25) Åkermark, B.; Martin, J. Nyström, J. E.; Strömberg, S.; Svensson, M.; Zetterberg, K.; Zuber, M. *Organometallics* **1998**, *17*, 5367.
(26) Hunt, D. F.; Farrant, G. C.; Rodeheaver, G. T. *J. Organomet. Chem.* **1972**, *38*, 349.
(27) Henderson, R. A.; Oglieve, K. E.; Salisbury, P. *J. Chem. Soc., Dalton Trans.* **1995**, 2479.
(28) Henderson, R. A.; Lowe, D. J.; Salisbury, P. *J. Organomet. Chem.* **1995**, *489*, C22.
(29) For additional examples of direct protonation of olefin and alkyne ligands, see: Henderson, R. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 946, and references therein.

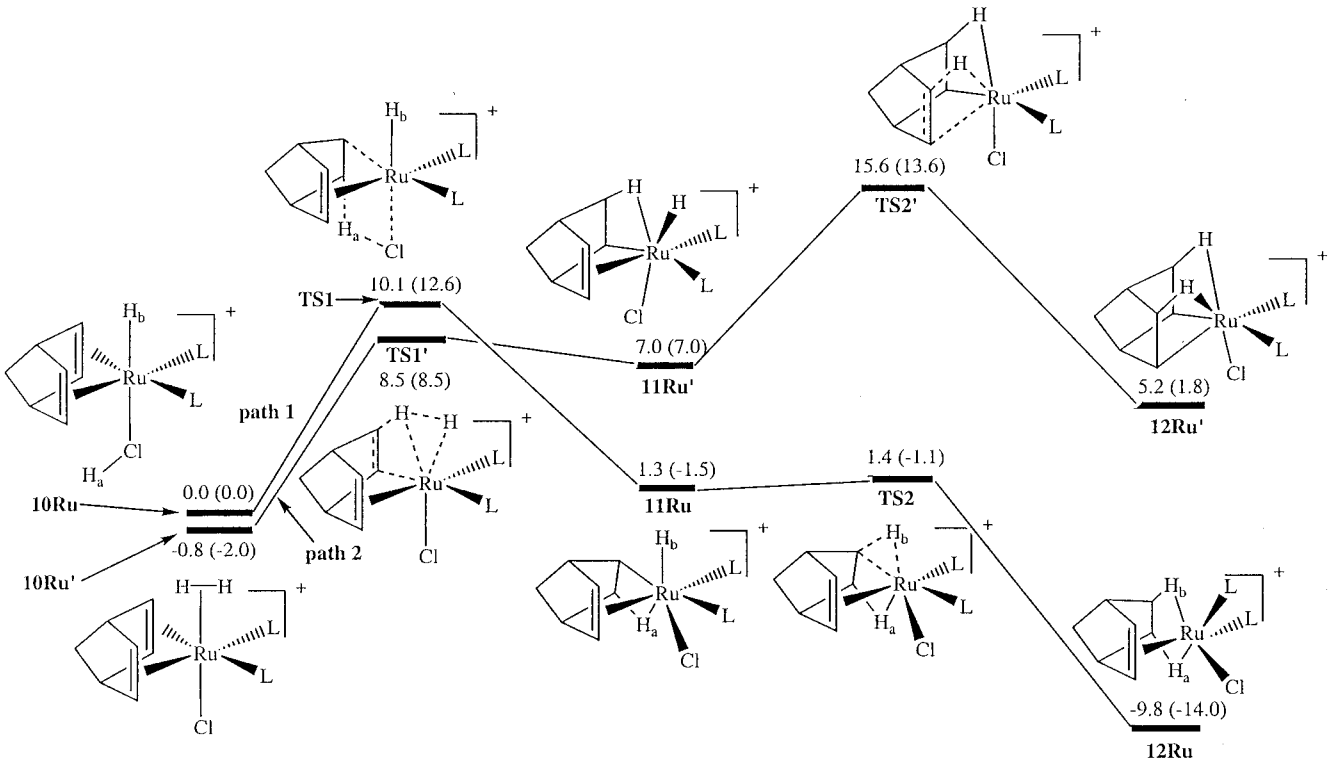


Figure 2. Schematic illustration of the two studied reaction pathways together with calculated relative free energies (kcal/mol) and reaction energies (kcal/mol, in parentheses) for species involved in the reaction.

form intermediate **11Ru**. Then the second hydrogen transfer from H_b completes the hydrogenation and gives a coordinated norbornene complex **12Ru**. Path 2 starts from **10Ru′** with the hydrogen transfer from one hydrogen atom of the dihydrogen ligand to form intermediate **11Ru′**. The second hydrogen transfer forms a precursor complex **12Ru′**, which can give a nortricyclene by reductive elimination.

The reaction from the dihydrogen complex **10Ru′** (path 2) overcomes a barrier of 9.3 kcal/mol through **TS1′**, forming the relatively unstable intermediate (**11Ru′**). Climbing another barrier of 8.6 kcal/mol for the second hydrogen transfer, one gets the complex **12Ru′** (a precursor to nortricyclene). Since the overall reaction from **10Ru′** to **12Ru′** is endothermic, formation of **12Ru′** from **10Ru′** is unlikely. The finding is consistent with the experimental result that no nortricylene was produced in the protonation of $[RuH(Cl)(PPh_3)_2(NBD)]$. In addition, it is noted that **11Ru′** could not undergo reductive elimination to give norbornene because the alkyl and the hydride ligands are not cis to each other. Thus it is unlikely that norbornene is formed from the dihydrogen intermediate $[Ru(Cl)(H_2)(PPh_3)_2(NBD)]^+$ in the protonation of $[RuH(Cl)(PPh_3)_2(NBD)]$.

From the relative free energies (Figure 2), it is interesting to see that the hydrochloride complex **10Ru** is only slightly less stable than the dihydrogen complex **10Ru′**, indicating that intermediate $[RuH(HCl)(PPh_3)_2(NBD)]^+$ (**B**) is indeed a reasonable species. For the reaction starting from **10Ru** (path 1), the barrier of the first hydrogen transfer is slightly higher (10.1 kcal/mol) when compared to that of path 2. The second hydrogen transfer is almost barrierless. The overall reaction of path 1 is exothermic. Clearly, the reaction from the hydrochloride complex (path 1) is both thermodynamically and kinetically favorable. These results are consistent with the experimental observation that the NBD ligand of $[RuH(Cl)(PPh_3)_2(NBD)]$ is hydrogenated to produce norbornene after the protonation of the hydride complex. In addition, these results also support the proposition that the chloride is indeed assisting the hydrogenation process by positioning a hydrogen at an approximate position to the olefin ligand through a HCl ligand.

One of the reviewers was concerned that the proposed intermediates **11Ru** and **11Ru′** are questionable because of no known examples of seven-coordinate Ru(IV) complexes featuring agostic interactions. On the basis of the potential energy profiles given in Figure 2, we can see that these intermediates are very reactive and easily converted into **12Ru** for **11Ru** and **10Ru′** for **11Ru′**. These results are consistent with the fact that seven-coordinate Ru(IV) complexes featuring agostic interactions have not yet been characterized. It should be noted that seven-coordinate Ru(IV) complexes are not unusual, as several of them have been characterized by X-ray diffraction.[30] The formally seven-coordinate Os(IV) complex $[OsH_2(\eta^3\text{-}C_6H_9)(P^iPr_3)_2]^+$ with an agostic interaction has been recently reported.[31] Therefore, we feel reasonable to propose **11Ru** and **11Ru′** as very reactive intermediates in the reaction routes. The calculated Ru···H−C distance (1.817 Å) in **11Ru′** was also considered as unreasonably short. This could be because there is still some sort of attraction between the hydride ligand and the agostic hydrogen in the intermediate. As the intermediate is very unstable, such an unusual structural feature is possible.

(30) See for example: (a) Given, K. W.; Mattson, B. M.; Pignolet, L. H. *Inorg. Chem.* **1976**, *15*, 3152. (b) Mattson, B. M.; Pignolet, L. H. *Inorg. Chem.* **1977**, *16*, 488.

(31) Castillo, A.; Esteruelas, M. A.; Oñate, E.; Ruiz, N. *J. Am. Chem. Soc.* **1997**, *119*, 9691.

Calculations on other intermediate structures, such as nonagostic species with 16 electrons and dihydride structure, were not successful. Starting with a structure having the agostic hydrogen atom away from Ru at a distance of 2.5 Å, the optimizations always lead to **11Ru** and **11Ru′**. By fixing the distance at 2.5 Å, the partially optimized structures are calculated to be ca. 7 kcal/mol higher in energy than the fully optimized intermediates. These partially optimized structures experience extremely unfavorable metal−carbon interactions because of the geometric requirement with the norbornenyl ligand. Although many 16-electron Ru complexes are known, these complexes are normally five-coordinate and adopt a square-pyramidal structure having one vacant ligand site. Instead of having 16-electron intermediates without agostic interactions, the strong tendency to have the agostic interactions with an 18-electron configuration in the currently studied intermediates is apparently due to the different ligand number as well as the different ligand environment. Therefore a reductive elimination through the nonagostic species with 16 electrons would require a higher activation energy. An attempt to find a concerted process by simultaneously transferring the two hydrogen atoms to one of the two olefin bonds in the NBD ligand was also not successful.

One might also consider the possibility of the rearrangement from **11Ru′** (derived from protonation of hydride) to **11Ru** (derived from protonation of chloride), which gives the reaction outcome independent of the initial protonation sites. However, such a rearrangement is unlikely on the basis of the following considerations. **11Ru′** is quite unstable relative to **11Ru** and **10Ru′**. The conversion of **11Ru′** back to **10Ru′** through **TS1′** has a very low barrier (only 1.5 kcal/mol). In contrast, the rearrangement from **11Ru′** to **11Ru** involves drastic movement of ligands. An appreciable activation energy from **11Ru′** to **11Ru** would prevent such a rearrangement from occurring.

Another possible pathway starting from hydrochloride complex **10Ru** is that the hydride (H_b) transfer occurs prior to the hydrogen from the hydrochloride ligand. The intermediate from such a pathway is calculated to be 13.0 kcal/mol higher in energy than **10Ru**. It is expected that the corresponding transition state has an even higher energy. Therefore, this possible pathway can be eliminated. As mentioned previously, direct protonation at the ruthenium center of **1** would give dihydride species [RuH$_2$(Cl)(NBD)(PPh$_3$)$_2$]$^+$, which may also lead to the formation of norbornene. To test this possibility, the structure of the model complex [RuH$_2$(Cl)(PH$_3$)$_2$(NBD)]$^+$ was optimized. However, the optimized structure turns to **10Ru** or **10Ru′**. The dihydride complex [RuH$_2$(Cl)(NBD)(PH$_3$)$_2$]$^+$ was not found to be a transition state in the conversion of **10Ru** to **12Ru** either. This result suggests that [RuH$_2$(Cl)(PH$_3$)$_2$(NBD)]$^+$ is unlikely to be involved in the formation of norbornene.

Figure 3 shows the calculated structures with selected structural parameters of those species involved in the studied reactions. The hydrochloride complex (**10Ru**) has a very long Ru−Cl distance (2.838 Å) due to the trans influence of the hydride ligand and the low donor ability of the HCl ligand**.** The dihydrogen complex **10Ru′** shows a short H−H distance (0.834 Å). Both intermediates **11Ru** and **11Ru′** can be described as pentagonal-bipyramidal (PB) in which the olefin and one of the phosphine ligands form the axle of the PB structure. In **11Ru**, the chloride and the agostic ligands can be viewed as trans to the hydride ligand on the equatorial plane of the PB structure. Such an arrangement provides an optimal coordination because the two weaker bonds (Ru−Cl and Ru−agostic) occupy the coordination sites trans to the strong trans-influence hydride ligand. The stability of intermediate **11Ru** suggests that the Ru−H and Ru−C σ bonds prefer to be cis to each other. Indeed, the Ru−H and Ru−C σ bonds on the equatorial plane of the PB structure in **11Ru** are shorter than the corresponding ones in **11Ru′**. The high stability of the norbornene complex (**12Ru**) is related to its octahedral arrangement of all the ligands. The precursor complex **12Ru′** is highly strained because of the presence of three four-membered rings in the structure.

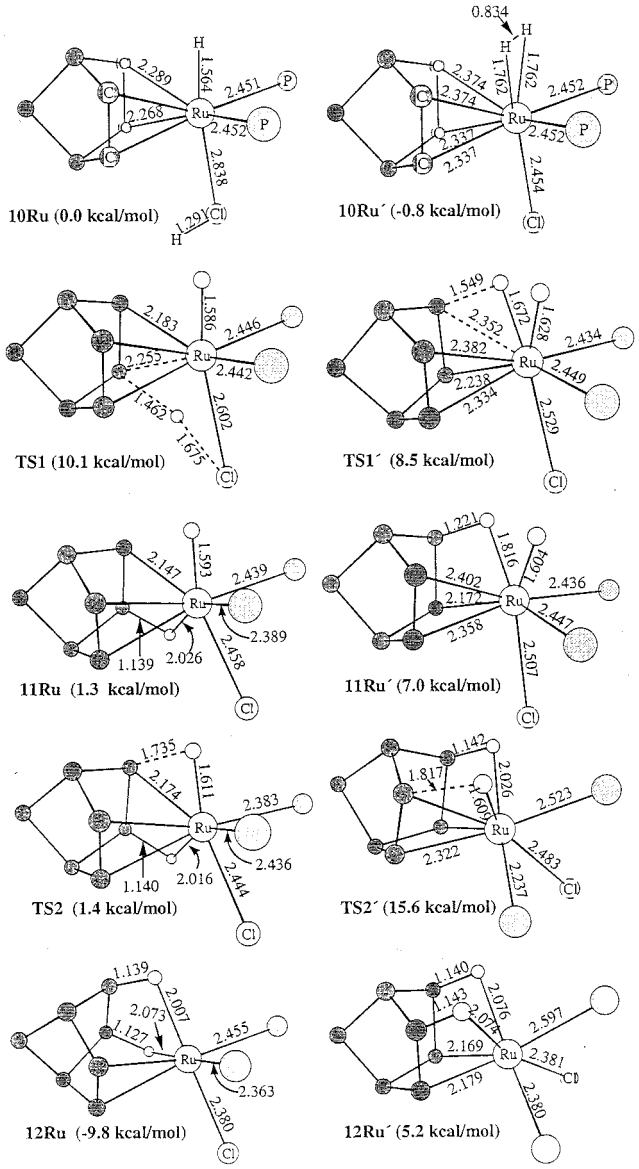


Figure 3. Optimized structures with selected structural parameters (and relative stability). The hydrogen atoms, which are not directly involved in the hydrogenation, have been omitted for the purpose of clarity.

While the protonation of [RuH(Cl)(PPh$_3$)$_2$(NBD)] with HOTf leads to the formation of [RuH(OTf)(PPh$_3$)$_2$(NBD)]

along with norbornene, protonation of $[OsH(Cl)(PPh_3)_2(NBD)]$ with HOTf gives only the substitution product $[OsH(OTf)(PPh_3)_2(NBD)]$. There are two possible explanations for the experimental observation. The corresponding reaction from the analogous hydrochloride complex **10Os** might have a much higher reaction barrier. Calculations of the corresponding reaction give a free energy barrier of 8.4 kcal/mol and do not support this explanation. However, the calculation results show that the norbornene complex **12Os** is thermodynamically less stable by 2.1 kcal/mol when compared to **10Os**. Therefore, the second possible explanation can be related to the fact that the competing substitution (Cl^- by OTf^-) reaction in $[OsH(Cl)(PPh_3)_2(NBD)]$ could be more favorable. Indeed the substitution reaction free energy is calculated to be −5.5 kcal/mol, which is thermodynamically much more favorable than the corresponding hydrogenation reaction giving **12Os**. The hydrogenation free energy is 2.1 kcal/mol, which is 7.6 kcal/mol higher than the substitution reaction. For $[RuH(Cl)(PPh_3)_2(NBD)]$, the substitution reaction free energy (−8.2 kcal/mol) is, however, calculated to be slightly higher by 1.6 kcal/mol than the hydrogenation free energy (−9.8 kcal/mol). These results are in agreement with the experimental observation that the Os complex involves only the substitution reaction, while the Ru complex undergoes the hydrogenation reaction as well as the substitution reaction. On the basis of the results of our calculations, a plausible explanation for the different reactivities of the Os and Ru complexes can be provided here. The third-row transition metal has more diffuse d orbitals, leading to a stronger metal−olefin interaction. Osmium−olefin complexes are expected to be more stable when compared to the corresponding ruthenium−olefin complexes, and therefore, the Os−NBD bonds remain intact in the reactions.

Summary and Conclusion. $[RuH(Cl)(PPh_3)_2(NBD)]$ in C_6D_6 reacted with HOTf to give $[RuH(OTf)(PPh_3)_2(NBD)]$, norbornene, and $[RuCl_2(PPh_3)_2]_2$. In dichloromethane, $[RuH(Cl)(PPh_3)_2(NBD)]$ reacted with HOTf to give $[RuH(OTf)(PPh_3)_2(NBD)]$, norbornene, and the trimetallic complex $[Ru_3Cl_5(PPh_3)_6]OTf$. In contrast, protonation of $[OsH(Cl)(PPh_3)_2(NBD)]$ in C_6D_6 or CD_2Cl_2 with HOTf gave only $[OsH(OTf)(PPh_3)_2(NBD)]$. The fact that norbornene was not produced in the protonation of $[OsH(Cl)(PPh_3)_2(NBD)]$ can be attributed to the stronger osmium−olefin interaction. In the protonation of $[RuH(Cl)(PPh_3)_2(NBD)]$, the norbornene is likely produced through the intermediate $[RuH(HCl)(PPh_3)_2(NBD)]^+$. The involvement of $[RuH(HCl)(PPh_3)_2(NBD)]^+$ in the formation of norbornene is supported by theoretical calculations based on the B3LYP density functional theory.

Experimental Section

All manipulations were carried out under nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen from sodium-benzophenone (hexane, ether, THF) or calcium hydride (CH_2Cl_2). The starting materials $[RuH(Cl)(PPh_3)_2(NBD)]$[16] and $[OsH(Cl)(PPh_3)_2(NBD)]$[19] were prepared according to literature methods. All other reagents were used as purchased from Aldrich Chemical Co. Microanalyses were performed by M-H-W Laboratories (Phoenix, Az). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were collected on a JEOL EX-400 spectrometer (400 MHz) or a Bruker ARX-300 spectrometer (300 MHz). ^1H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts relative to 85% H_3PO_4.

Protonation of $[RuH(Cl)(PPh_3)_2(NBD)]$ with HOTf in C_6D_6. To an NMR tube charged with $[RuH(Cl)(PPh_3)_2(NBD)]$ (20 mg, 0.027 mmol) and C_6D_6 (0.5 mL) was added 0.015 mL of C_6D_6 solution of HOTf ($HOTf/C_6D_6$ = 1:8, 0.019 mmol HOTf) through a microsyringe. The solution was allowed to stand for 1 h, and then NMR spectra were collected. ^1H NMR (300.13 MHz, C_6D_6): δ −13.47 (t, $J(PH)$ = 22.5 Hz, $[Ru\mathit{H}(OTf)(PPh_3)_2(NBD)]$), −8.74 (t, $J(PH)$ = 24.0 Hz, $[Ru\mathit{H}(Cl)(PPh_3)_2(NBD)]$), 1.05−1.74 (m, CH_2 of norbornene, $[RuH(Cl)(PPh_3)_2(NBD)]$ and $[RuH(OTf)(PPh_3)_2(NBD)]$), 2.91 (s, bridge-head CH of norbornene), 3.33−4.60 (m, bridge-head CH and =CH of $[RuH(Cl)(PPh_3)_2(NBD)]$ and $[RuH(OTf)(PPh_3)_2(NBD)]$), 6.12 (s, =CH of norbornene), 7.04−7.74 (m, PPh_3). $^{31}P\{H\}$ NMR (121.50 MHz, C_6D_6): δ 39.8 (s, $[RuH(Cl)(PPh_3)_2(NBD)]$), 41.5 (s, $[RuH(OTf)(PPh_3)_2(NBD)]$), 52.6 (s) and 59.7 (broad, $[RuCl_2(PPh_3)_2]_2$). The ratio of norbornene to $[RuH(OTf)(PPh_3)_2(NBD)]$ was determined to be 1:2.1 on the basis of the integration of the norbornene olefinic ^1H signal at 6.12 ppm and the hydride signal of $[RuH(OTf)(PPh_3)_2(NBD)]$ at −13.47 ppm. The ^1H NMR and ^{31}P NMR spectra showed no appreciable change after the solution was allowed to stand for 19 h. The volatile portion of the reaction mixture can be separated by vacuum transfer. A ^1H NMR spectrum of the vacuum-transferred solution shows that norbornene is the only volatile organic product formed in the reaction.

Protonation of $[RuH(Cl)(PPh_3)_2(NBD)]$ with DOTf in C_6H_6. The procedure was similar to that described above except that DOTf and C_6H_6 were used instead. The volatile portion of the reaction mixture was separated by vacuum transfer. The separated organic solution was treated with Proton Sponge and then was subjected to vacuum transfer again. The ^2D NMR spectrum (61.25 MHz) of the resulting solution showed a singlet at 0.89 ppm.

Protonation of $[RuH(Cl)(PPh_3)_2(NBD)]$ with HOTf in CD_2Cl_2. To an NMR tube charged with $[RuH(Cl)(PPh_3)_2(NBD)]$ (20 mg, 0.027 mmol) and CD_2Cl_2 (0.5 mL) was added 0.015 mL of CD_2Cl_2 solution of HOTf ($HOTf/CD_2Cl_2$ = 1:8, 0.019 mmol) through a microsyringe. The solution was allowed to stand for 5 h, and then NMR spectra were collected. ^1H NMR (300.13 MHz, CD_2Cl_2): δ −13.8 (br, $[Ru\mathit{H}(OTf)(PPh_3)_2(NBD)]$), −9.46 (brt, $J(PH)$ = 24 Hz, $[Ru\mathit{H}(Cl)(PPh_3)_2(NBD)]$), 0.88−1.70 (m, CH_2 of norbornene, $[RuH(Cl)(PPh_3)_2(NBD)]$ and $[RuH(OTf)(PPh_3)_2(NBD)]$), 2.80 (s, bridge-head CH of norbornene), 3.33−4.60 (m, bridge-head CH and =CH of $[RuH(Cl)(PPh_3)_2(NBD)]$ and $[RuH(OTf)(PPh_3)_2(NBD)]$), 6.00 (s, =CH of norbornene), 7.01−7.70 (m, PPh_3). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2): δ 39.9 (s, $[RuH(Cl)(PPh_3)_2(NBD)]$), 40.3 (s, $[Ru_3Cl_5(PPh_3)_6]OTf$), 41.6 (br, $[RuH(OTf)(PPh_3)_2(NBD)]$). The ratio of norbornene to $[RuH(OTf)(PPh_3)_2(NBD)]$ was determined to be 1:1.8 based on the integration of the norbornene olefinic ^1H signal at 6.00 ppm and the hydride signal of $[RuH(OTf)(PPh_3)_2(NBD)]$ at −13.8 ppm. The ^1H NMR and ^{31}P NMR spectra showed no appreciable change after the solution was allowed to stand for 19 h. The volatile portion of the reaction mixture can be separated by vacuum transfer. A ^1H NMR spectrum of the vacuum-transferred solution shows that norbornene is the only volatile organic product formed in the reaction.

Protonation of $[RuH(Cl)(PPh_3)_2(NBD)]$ with DOTf in CH_2Cl_2. The procedure was similar to that described above except that DOTf and CH_2Cl_2 were used instead. The volatile portion of the reaction mixture was separated by vacuum transfer. The separated organic solution was treated with Proton Sponge and then was subjected to vacuum transfer again. The ^2D NMR spectrum (61.25 MHz) of the resulting solution showed a singlet at 0.93 ppm.

$[Ru_3Cl_5(PPh_3)_6]OTf$. A mixture of $[RuH(Cl)(PPh_3)_2(NBD)]$ (0.84 g, 1.11 mmol) and HOTf (0.4 mL, 4.5 mmol) in dichloromethane (20 mL) and water (20 mL) was stirred for 72 h. The

aqueous layer was then removed with a syringe. The dichloromethane layer was washed with 30 mL of water. The solvent was then removed completely under vacuum to give a brown solid, 20 mL of diethyl ether was added, and the mixture was stirred for 20 min. The brown solid was collected on a filter frit, washed with diethyl ether (3 × 10 mL), and dried under vacuum. Yield: 0.72 g, 88.3%. Anal. Calcd for $C_{109}H_{90}Cl_5F_3O_3P_6SRu_3$: C, 59.42; H, 4.12. Found: C, 59.24; H, 4.40. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 6.34−7.69 (m, broad, PPh_3). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ 40.2 (s).

[Ru$_3$Cl$_5$(PPh$_3$)$_6$]BPh$_4$. [Ru$_3$Cl$_5$(PPh$_3$)$_6$]OTf (0.5 g, 0.23 mmol) and $NaBPh_4$ (0.5 g, 1.46 mmol) in methanol (40 mL) were stirred for 1 h to give a brown solid, which was collected on a filter frit, washed with methanol (3 × 10 mL), and dried under vacuum. Yield: 0.48 g, 88.9%. Anal. Calcd for $C_{132}H_{110}BCl_5P_6Ru_3$: C, 66.80; H, 4.67. Found: C, 66.90; H, 4.70. ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 6.3−7.7 (m, broad, PPh_3). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2): δ 40.3 (s).

Protonation of [RuH(Cl)(PPh$_3$)$_2$(NBD)] with DOTf in CD$_2$Cl$_2$ in the Presence of CD$_3$CN. To an NMR tube charged with [RuH(Cl)(PPh$_3$)$_2$(NBD)] (20 mg), CD_2Cl_2 (0.7 mL), and CD_3CN (50 μL) was added DOTf (10 μL) through a microsyringe. The ^{1}H and $^{31}P(^1H)$ NMR spectra of the reaction mixture showed only the signals of $[RuH(CH_3CN)(PPh_3)_2(NBD)]^+$. ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ −8.74 (t, J(PH) = 22.4 Hz, 1 H, RuH), 0.78 (s, 2 H, CH_2), 3.04 (s, 2 H, =CH), 3.42 (s, 1 H, CH), 3.56 (s, 1 H, CH), 3.63 (s, 2 H, =CH), 6.95−7.44 (m, PPh_3). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2): δ 45.2 (s).

[RuH(CH$_3$CN)(PPh$_3$)$_2$(NBD)]BPh$_4$. CH_3CN (1.0 mL) was added to a CH_2Cl_2 (30 mL) solution of [RuH(OTf)(PPh$_3$)$_2$(NBD)] (1.41 g, 1.62 mmol). The solvent was removed completely under vacuum. MeOH (40 mL) was added to redissolve the solid. $NaBPh_4$ (0.50 g, 2.34 mmol) in MeOH (10 mL) was added. A large amount of white precipitate was formed. The white solid was collected on a filter frit, washed with water, and dried under vacuum. Yield: 1.49 g, 85.2%. Anal. Calcd for $C_{69}H_{62}BNP_2Ru$: C, 76.80; H, 5.80; N, 1.30. Found: C, 76.78; H, 5.37; N, 1.27. ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ −8.59 (t, J(PH) = 22.2 Hz, 1 H, RuH), 1.09 (s, 2 H, CH_2), 1.82 (s, 3 H, CH_3CN), 3.23 (s, 2 H, =CH), 3.46 (s, 1 H, CH), 3.49 (s, 1 H, CH), 3.61 (s, 2 H, =CH), 6.87−7.45 (m, 50 H, BPh_4, PPh_3). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2): δ 45.2 (s).

Protonation of [OsH(Cl)(PPh$_3$)$_2$(NBD)] with HOTf in C$_6$D$_6$. To an NMR tube charged with [OsH(Cl)(PPh$_3$)$_2$(NBD)] (20 mg, 0.024 mmol) and C_6D_6 (0.5 mL) was added HOTf (5 μL, 0.057 mmol) through a microsyringe. The solution was allowed to stand for 1 h, and then NMR spectra were collected. The NMR spectra showed signals of [OsH(OTf)(PPh$_3$)$_2$(NBD)]. ^{1}H NMR (300.13M Hz, C_6D_6): δ −17.57 (t, J(PH) = 21.0 Hz, 1 H Os*H*), 0.68 (s, 2 H, CH_2), 3.46 (s, 1 H, bridgehead CH), 3.63 (s, 2 H, =CH), 4.05 (s, 2 H, =CH), 4.86 (s, 1 H, bridgehead CH), 6.5−7.9 (m, PPh_3). $^{31}P\{^1H\}$ NMR (121.50 MHz, C_6D_6): δ 12.6 (s).

Crystallographic Analysis for [Ru$_3$Cl$_5$(PPh$_3$)$_6$]BPh$_4$·2.5CH$_2$Cl$_2$. Crystals suitable for X-ray diffraction study were grown by layering of hexane on a CH_2Cl_2 solution of [Ru$_3$Cl$_5$(PPh$_3$)$_6$]BPh_4. A brown prismatic single crystal with dimensions of 0.22 × 0.14 × 0.10 mm was mounted on a glass fiber, and diffraction data were collected on a Bruker SMART CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Intensity data were corrected for SADABS (Siemens Area Detector Absorption)[32] (from 0.757 to 1 on I). The structure was solved by direct methods and refined by full matrix least-squares on F^2 using the Bruker SHELXTL (Version 5.10)[33] program package. Non-hydrogen atoms of the cation were refined anisotropically. The phenyl rings of the BPh_4^- anion were treated as rigid groups and refined with isotropic parameters. The dichloromethane solvent molecules were disordered and refined isotropically with partial occupancy factors using fixed C−Cl distances restraints without addition of H atoms. The remaining H atoms were introduced at calculated positions and refined via a riding model. Further details are given in Table 1.

Computational Details. In the calculations, the PPh_3 ligands have been modeled using PH_3 groups. Geometry optimizations and frequency calculations have been performed for all species (reactants, precursors, intermediates, transition states, and assumed products) involved in the reactions using the Gaussian 98 program[34] installed on Pentium III personal computers with Linux (Redhat) operating systems. All calculations have been carried out at the B3LYP level of density functional theory. The LANL2DZ effective core potentials and basis sets[35] were used to describe Ru, Os, P, and Cl, while the standard 6-31G basis set was used for C and H atoms. Polarization functions[36] were added for Cl (ξ(d) = 0.514) and hydrogens (ξ(p) = 1.1) involved in the transfer processes.

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Supporting Information Available: Tables of crystallographic details, bond distances and angles, atomic coordinates and equivalent isotropic displace coefficients, and anisotropic displacement coefficients for [Ru$_3$Cl$_5$(PPh$_3$)$_6$]BPh_4. This material is available free of charge via the Internet at http://pubs.acs.org.

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