Displacement of a *cis*-Olefin from a *trans*-Olefin Complex: $CpRu(CO)_2$(*trans*-olefin)$^+$

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Received June 6, 2007

Ruthenium(II)−olefin complexes $CpRu(CO)_2(\eta^2$-*trans*-olefin$)^+$ (Cp = η^5-C_5H_5; olefin = *trans*-3-hexene, *trans*-2-pentene, *trans*-3-octene, *trans*-4-octene, *trans*-5-decene) have been synthesized and characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopies. The reactions of these complexes with a wide range of ligands (L) result in the formation of $CpRu(CO)_2(L)^+$ and the release of both *cis*- and *trans*-olefins: $[CpRu(CO)_2$(*trans*-olefin)$]BF_4$ + L → $[CpRu(CO)_2(L)]BF_4$ + *cis*/*trans*-olefin. The relative amounts of *cis*- and *trans*-olefin released are controlled by several factors: identity and amount of the incoming ligand L, identity of the olefin, temperature, and solvent. For 4-substituted pyridines, the *cis*/*trans* ratio increases as the electron-donating ability of the 4-substituent increases: F_3C (18/82) < H (67/33) < CH_3 (74/26) < CH_3O (76/24). Increases in temperature, solvent polarity, and olefin side-chain length reduce the *cis*/*trans* ratio. A mechanism is proposed to account for the isomerization of *trans*-olefin ligands to their *cis* isomers during the substitution process.

Introduction

In a recent paper,[1] we reported a kinetic and mechanistic investigation of the substitution of a *cis*- or *trans*-3-hexene ligand in $Cp'Ru(CO)_2(\eta^2$-3hx$)^+$ by PPh_3 (eq 1).

$$Cp'Ru(CO)_2(\eta^2\text{-3hx})^+ + PPh_3 \rightarrow Cp'Ru(CO)_2(PPh_3)^+ + 3hx \quad (1)$$

For $Cp' = \eta^5$-C_5H_5(Cp), 3hx = *cis*-3-hexene (c3hx)

For $Cp' = \eta^5$-C_5Me_5(Cp*), 3hx = *cis*- or *trans*-3-hexene (c3hx or t3hx)

At 40.0 °C in $CDCl_3$ solution, the reaction of $CpRu(CO)_2(\eta^2$-c3hx$)^+$ follows a rate law that is dominated by a term (with $k_1 = 1.96 \times 10^{-6}$ s^{-1}) that is independent of the PPh_3 concentration. This first-order term suggested a mechanism involving a rate-determining dissociation of the *cis*-3-hexene followed by a rapid reaction of the unsaturated $CpRu(CO)_2^+$ intermediate with PPh_3. The analogous $Cp^*Ru(CO)_2(\eta^2$-c3hx$)^+$ complex also reacts predominately by a dissociative mechanism, but the rate ($k_1 = 21.8 \times 10^{-6}$ s^{-1}) is 11 times faster than for the $CpRu(CO)_2(\eta^2$-c3hx$)^+$ complex, which suggests a steric acceleration by the larger Cp* ligand. The reaction of the *trans*-3-hexene complex $Cp^*Ru(CO)_2(\eta^2$-t3hx$)^+$ with PPh_3 follows only a dissociative path, and the rate ($k_1 = 208 \times 10^{-6}$ s^{-1}) is 9.5 times faster than that of the analogous *cis*-3-hexene complex $Cp^*Ru(CO)_2(\eta^2$-c3hx$)^+$. The much faster rate of t3hx dissociation, as compared with c3hx, was attributed to repulsions between the Cp* ligand and an ethyl group in the *trans*-3-hexene ligand, which *must* have an ethyl group directed toward the Cp* ligand in all orientations of the coordinated t3hx; in contrast, both ethyl groups of the c3hx ligand in $Cp^*Ru(CO)_2(\eta^2$-c3hx$)^+$ are likely to be directed away from the Cp*.

Scheme 1. Equilibrium Data for Four Different Olefins

cis-2-butene	$\underset{100\ °C}{\overset{I_2\ \text{vapor}}{\rightleftharpoons}}$	*trans*-2-butene	K = 2.70, 73% *trans*[2]
cis-2-pentene	$\underset{100\ °C}{\overset{NO_2\ \text{vapor}}{\rightleftharpoons}}$	*trans*-2-pentene	K = 3.35, 77% *trans*[3]
cis-3-hexene	$\underset{25\ °C}{\overset{WCl_6/EtOH/C_2H_5AlCl_2}{\rightleftharpoons}}$	*trans*-3-hexene	K = 6.17, 86% *trans*[4]
cis-4-octene	$\underset{25\ °C}{\overset{WCl_6/EtOH/C_2H_5AlCl_2}{\rightleftharpoons}}$	*trans*-4-octene	K = 4.90, 83% *trans*[4]

In all of the above reactions, the liberated olefin retains the same *cis* or *trans* isomeric structure that was present in the reacting $Cp'Ru(CO)_2(\eta^2$-3hx$)^+$ complex. In contrast to these reported results, we observed that the *trans*-3-hexene ligand in $CpRu(CO)_2(\eta^2$-t3hx$)^+$ is substituted by PPh_3 and other ligands to give $CpRu(CO)_2(PPh_3)^+$, but the liberated olefin was a mixture of c3hx and t3hx (eq 2).

$$CpRu(CO)_2(\eta^2\text{-t3hx})^+ + PPh_3 \rightarrow CpRu(CO)_2(PPh_3)^+ + \text{c3hx and t3hx} \quad (2)$$

The liberation of c3hx is surprising for at least two reasons: (1) common mechanisms for olefin substitution do not explain the observed olefin isomerization, (2) the formation of c3hx from t3hx is a process that is thermodynamically unfavorable. Thermodynamic data for several *cis* ↔ *trans* isomerizations (Scheme 1) illustrate quantitatively (at the stated temperatures) the greater stability of *trans*-olefins.

In this paper, we describe investigations of reactions of $CpRu(CO)_2(\eta^2$-*trans*-olefin$)^+$ complexes with PPh_3 and a variety of other ligands (L) to give the $CpRu(CO)_2(L)^+$ complex[5] and the

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10.1021/om7005535 CCC: $37.00
Publication on Web 08/21/2007

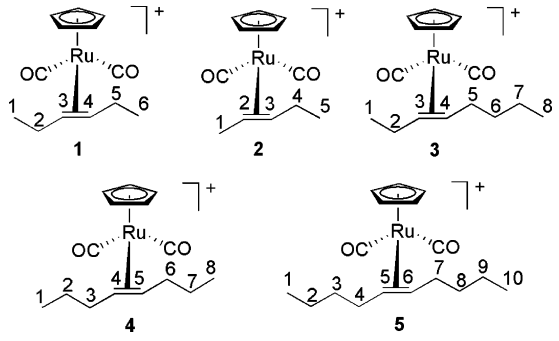

Figure 1. Structures of compounds **1**−**5**. Carbon and hydrogen labels correspond to NMR assignments given in the Experimental Section.

liberated *cis*- and/or *trans*-olefin. A mechanism is proposed to account for the isomerization of the coordinated *trans*-olefin to its *cis* isomer during the substitution process.

Results

Synthesis and Structural Characterization of the [CpRu(CO)$_2$(*trans*-olefin)]$^+$BF$_4^-$ Complexes. These complexes were all prepared in 75−85% yields by the abstraction of Cl^- from $CpRu(CO)_2Cl$ in the presence of the desired olefin (eq 3).

$$CpRu(CO)_2Cl + \text{olefin} \xrightarrow[-AgCl]{AgBF_4,\ CH_2Cl_2} [CpRu(CO)_2(\eta^2\text{-olefin})]BF_4 \quad (3)$$

1, olefin = t3hx = *trans*-3-hexene

2, olefin = t2pt = *trans*-2-pentene

3, olefin = t3oct = *trans*-3-octene

4, olefin = t4oct = *trans*-4-octene

5, olefin = t5dec = *trans*-5-decene

The general structures of the synthesized compounds are shown in Figure 1. Compounds **1** and **3**−**5** were isolated as light tan solids, whereas compound **2** was isolated as a dark brown solid. All of the compounds are stable toward air and moisture in the solid state for at least 8 weeks and are also stable in solution for several days when exposed to air. Compounds **1**−**5** all have ν(CO) bands in their IR spectra at 2078 and 2035 cm^{-1}. These values are approximately 27 cm^{-1} higher than those in the starting complex, $CpRu(CO)_2Cl$ (2055, 2003 cm^{-1}).

In the room-temperature ^{1}H NMR spectrum of **1**, there is a marked shift upfield from 5.46 ppm to 4.86 ppm for the olefinic protons upon coordination to the metal, which is also observed for all of the other complexes (**2**−**5**) and for $CpRu(CO)_2(\eta^2$-olefin)$^+$ complexes reported in the literature.[5,6] Two multiplets at 2.23 and 1.64 ppm in the ^{1}H NMR spectrum of **1** are assigned to the methylene protons, and a single triplet peak at 1.17 ppm is assigned to the methyl protons. ^{1}H−^{1}H COSY experiments showed that the two methylene peaks are coupled to each other, indicating that the two methylene protons on the same carbon are different from one another. The presence of two methylene peaks also shows that the olefin remains bound to the metal in solution, as rapid dissociation and reassociation would make the CH_2 protons equivalent. The presence of only one methyl signal in the room-temperature spectrum indicates that the olefin is rotating rapidly about the metal−olefin bond, as a nonfluxional *trans*-olefin would exhibit two methyl signals due to the inequivalence of the two ethyl groups (Figure 2). An ^{1}H NMR spectrum recorded at −35 °C showed that the olefin was still rotating at low temperature, as no broadening of the peaks from the olefin was observed. In the ^{13}C NMR spectrum of **1**, two peaks for the CO ligands are observed at 197.02 and 192.58 ppm, which is consistent with the asymmetry imposed by the *trans*-olefin. The resonance for the olefinic carbons 3 and 4 is observed at 85.15 ppm, which is significantly upfield shifted from that of the free olefin (131.30 ppm). Peaks for the methylene and methyl carbon atoms appear at 32.89 and 18.12 ppm, respectively.

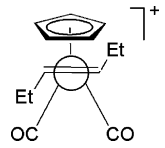

Figure 2. View down the Ru−olefin bond showing the inequivalency of the *trans* ethyl groups.

In **2**, the two methylene peaks appear as multiplets at 2.15 and 1.64 ppm and are coupled to each other. A doublet at 1.93 ppm may be assigned to the methyl group attached directly to the olefin carbon (C_2), while the other methyl signal appears as a triplet at 1.17 ppm. In the ^{13}C NMR spectrum, the two CO resonances are observed at 197.11 and 192.58 ppm, and the olefinic carbon peaks appear upfield at 86.89 (C_3) and 79.94 (C_2) ppm. Due to the asymmetry of the *trans*-2-pentene ligand in **2**, the NMR results do not indicate whether or not the olefin is rotating rapidly. However, considering that the olefins in compounds **1**, **4**, and **5** were all found to be rotating rapidly on the NMR time scale at room temperature, it seems likely that this is also the case for **2**.

The ^{1}H NMR spectrum of **3** shows a multiplet for the olefinic protons at 4.88 ppm and three multiplets at 2.25, 1.69, and 1.56 ppm for methylene protons. As in the ^{13}C NMR spectrum of **2**, **3** exhibits two peaks for the CO ligands (197.06, 192.55 ppm) and two peaks for the olefinic carbons (85.91 (C_3), 83.96 (C_4) ppm). The ^{1}H and ^{13}C NMR spectra of **4** and **5** have features similar to those of the other complexes, which indicate rapid rotation of the olefin at room temperature on the NMR time scale.

Displacement of the Olefin in the [CpRu(CO)$_2$(*trans*-olefin)]$^+$BF$_4^-$ Complexes. Although the reaction of Cp*Ru(CO)$_2$(t3hx)$^+$ with PPh_3 gave Cp*Ru(CO)$_2$(PPh$_3$)$^+$ and free t3hx,[1] the same reaction with $CpRu(CO)_2$(t3hx)$^+$ gave $CpRu(CO)_2(PPh_3)^+$ and both *cis*- and *trans*-3-hexene. It was the surprising formation of *cis*-3-hexene that led to the present study of reactions (eq 4) of $CpRu(CO)_2$(*trans*-olefin)$^+$ complexes with

$$[CpRu(CO)_2(\textit{trans}\text{-olefin})]BF_4 + L \rightarrow [CpRu(CO)_2(L)]BF_4 + \textit{cis}\text{- and }\textit{trans}\text{-olefin} \quad (4)$$

a variety of ligands (L). It was evident that the coordinated t3hx was isomerizing partially to c3hx during the substitution reaction. In order to determine whether free t3hx isomerizes on its own to c3hx under the conditions of the reaction, an NMR tube containing free t3hx dissolved in CD_2Cl_2 was flame-sealed and placed in a constant-temperature bath at 50 °C. After 7 days, the ^{1}H NMR spectrum showed no indication of c3hx formation, eliminating thermal isomerization as a pathway for the formation

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Table 1. *cis*/*trans* Ratios of 3-Hexene Obtained from Reactions of $CpRu(CO)_2(t3hx)^+$ According to Eq 4 at 25 °C in CD_2Cl_2

entry	ligand (L)[a]	pK_a	reaction time (h)	*cis*/*trans* ratio[b]
1	PPh_3[c]	2.73	1200	44/56
2	PPh_2Me[c]	4.57	312	43/57
3	$PPhMe_2$[c]	6.50	144	0/100
4	PMe_3[d]	8.65	144	0/100
5	PCy_3[c]	9.70	480	13/87
6	$P(OMe)_3$[d]		1440	0/100
7	$P(OEt)_3$[d]		720	0/100
8	$P(OPh)_3$[c]		1440	0/100
9	pyridine[c]	5.23	960	78/22
10	2-bromopyridine[e]	0.90	1440	6/94
11	2-benzoylpyridine[e]	2.60	1440	20/80
12	2-hydroxypyridine[c]	0.75	1440	27/73
13	3-bromopyridine[e]	2.91	1440	34/66
14	4-methoxypyridine[d]	6.62	480	83/17

[a] 50-fold concentration as compared with that of $CpRu(CO)_2(t3hx)^+$ (**1**). [b] The *cis*/*trans* ratios were determined at the indicated times when all of $CpRu(CO)_2(t3hx)^+$ (**1**) had reacted. Only reactions 10−13 were stopped before **1** had reacted completely. [c] Moderate amount of decomposition. [d] Large amount of decomposition. [e] Small amount of decomposition.

of c3hx. To examine the possibility that the reacting ligand (L) catalyzes the isomerization, 50-fold excesses of PPh_3 and 4-picoline were added to NMR tubes containing t3hx in CD_2Cl_2. The tubes were flame-sealed under inert gas and placed in a 50 °C water bath. As no c3hx was observed in either tube after at least a week, the PPh_3 and 4-picoline ligands did not catalyze the isomerization. To test for the possibility that the isomerization occurs in the complex or is catalyzed by a product of metal complex decomposition, an NMR tube loaded with $CpRu(CO)_2(t3hx)^+$ (**1**) dissolved in CD_2Cl_2 and flame-sealed under inert gas was heated in a 50 °C water bath. After one week, **1** was still present in solution with no evidence for the formation of c3hx or release of free t3hx; this experiment also showed the considerable thermal stability of the olefin complex. These experiments show that the formation of free c3hx from coordinated t3hx must occur during the substitution reaction (eq 4).

In Tables 1 and 2 are shown percent ratios of *cis*- and *trans*-3-hexene that are formed in reactions (eq 4) of $CpRu(CO)_2(t3hx)^+$ (**1**) with various ligands at 25 and 50 °C, respectively, in CD_2Cl_2 using large excesses of the ligand (L). Due to the long reaction times at 25 °C and the high temperature of the 50 °C experiments, considerable decomposition is seen in the ^1H NMR spectra of many of the reactions. This decomposition is attributed to both breakdown of the ligand in the deuterated solvent and the formation of several Ru products, as evidenced by the presence of multiple Cp peaks. Approximate amounts of decomposition for each reaction are noted in Tables 1 and 2. The reactions were run long enough (Tables 1 and 2) such that all of the $CpRu(CO)_2(t3hx)^+$ (**1**) had reacted, except where the reaction time was excessively long, as in entries 10−13 in Table 1. In an experiment wherein **1** was reacted with a 50-fold excess of PPh_3 at 50 °C and the *cis*/*trans* ratio was determined after 12, 24, or 48 h, it was found that the *cis*/*trans* ratio is the same after the reaction is approximately 25%, 50%, and 100% complete, respectively.

It is notable that the reaction times at 50 °C (Table 2) are much shorter than those at 25 °C (Table 1) by several hundred hours for the same ligand, and the *cis*/*trans* ratio for every ligand is lower at 50 °C than at 25 °C. The *cis*/*trans* ratios for the reactions of PPh_3 and pyridine were determined at several temperatures between 25 and 50 °C in order to document in greater detail the decreasing *cis*/*trans* ratio as the temperature is increased (Table 3). In principle, an even lower temperature would give still higher *cis*/*trans* ratios, but the reactions would be even slower than the 50 days already required at 25 °C for the reaction of PPh_3.

Kinetic studies of the reactions of **1** with PPh_2Me and 4-picoline using ligand/**1** ratios from 30 up to 70 were conducted at 50 °C in CD_2Cl_2 under pseudo-first-order conditions. The rates of reactions of both ligands did not depend on the concentration of L, giving similar rate constants at all concentrations; the k_1 values averaged 3.1×10^{-5} s^{-1} for PPh_2Me and 2.2×10^{-5} s^{-1} for 4-picoline (see Supporting Information). While the rates do not depend on the ligand concentration, the rate constant for PPh_2Me is slightly higher than that for 4-picoline, which suggests some type of association between the complex and L. Inspection of Table 2 shows that many of the other ligands, such as 4-methoxypyridine, 2-picoline, and PPh_3, react at about the same rate, as indicated by their 48 h completion time. On the other hand many of the ligands, such as quinaldine, take longer than 48 h to react fully with **1**. These ligands are generally more bulky than those that react within 48 h.

For the P-donor ligands, PPh_3 reacts with **1** to give the free olefin with a *cis*/*trans* ratio of 44/56; PPh_2Me gives the same ratio (43/57), but PCy_3 gives a much smaller ratio (13/87) (Table 1). The smaller and more basic phosphines, $PPhMe_2$ and PMe_3, attack the olefin, initially forming an η^1-complex, $CpRu(CO)_2[CH(Et)CH(Et)PR_3]^+$, as established by ^1H NMR studies, which exhibit two upfield multiplets for the formerly olefinic protons (4.86 ppm) at 3.02 and 2.78 ppm for $PR_3 = PPhMe_2$ and at 2.98 and 2.49 ppm for $PR_3 = PMe_3$. These values are similar to those of $CpFe(CO)_2[CH_2CH_2PPh_3]^+$, which exhibits two upfield multiplets at 3.34 and 1.42 ppm.[7] In $CpRu(CO)_2[CH(Et)CH(Et)PPhMe_2]^+$, overlapping triplets at 0.92 and 0.91 ppm indicate the inequivalence of the two ethyl groups of the olefin after phosphine attack has occurred. These η^1-complexes of both $PPhMe_2$ and PMe_3 give only free *trans*-3-hexene and $CpRu(CO)_2(PR_3)^+$ within 144 h at 25 °C. The phosphites react with **1** to yield only free *trans*-3-hexene. Among the P-donor ligands (entries 1−8 in Table 1), those that give the highest *cis*/*trans* ratios are moderately basic (PPh_3, PPh_2Me). Those that are less basic ($P(OR)_3$) or more basic ($PPhMe_2$, PMe_3) give much lower *cis*/*trans* ratios.

Pyridine gives a much higher *cis*/*trans* ratio (78/22 at 25 °C and 67/33 at 50 °C) than any of the P-donor ligands. For the reactions of **1** with substituted pyridines at 50 °C, the *ortho*-substituted pyridines, 2-bromopyridine (3/97), 2-benzoylpyridine (14/86), 2-methoxypyridine (20/80), and 2-picoline (58/42), all give lower *cis*/*trans* ratios than pyridine (67/33). The *meta*-substituted pyridine, 3-bromopyridine (22/78), yields a ratio higher than that of 2-bromopyridine but still much lower than pyridine. The highest ratios are obtained with the pyridines, 4-picoline (74/26) and 4-methoxypyridine (76/24), that have electron-donating *para*-substituents, while 4-CF_3pyridine gives a low ratio (18/82). On the basis of the data from the *para*-substituted pyridine reactions, it is obvious that substituents that increase the basicity of the nitrogen, such as the methyl group in 4-picoline (p$K_a = 5.98$) and the methoxy group in 4-methoxypyridine (p$K_a = 6.62$), increase the *cis*/*trans* ratio as compared with pyridine (p$K_a = 5.23$). Conversely, the electron-withdrawing CF_3 group in 4-CF_3-pyridine reduces the basicity of the nitrogen, resulting in a lower yield of the *cis*-olefin. These electronic effects also appear to influence the *cis*/*trans* ratios obtained from reactions of the *ortho*-substituted pyridines where

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Table 2. *cis*/*trans* Ratios of 3-Hexene Obtained from Reactions of $CpRu(CO)_2(t3hx)^+$ According to Eq 4 at 50 °C in CD_2Cl_2

entry	ligand (L)	excess of L	pK_a	reaction time (h)	*cis*/*trans* ratio[a]
15	PPh_3[b]	10×	2.73	48	8/92
16	PPh_3[b]	50×	2.73	48	29/71
17	PPh_3[b]	100×	2.73	48	31/69
18	4-picoline[b]	10×	5.98	48	45/55
19	4-picoline[b]	50×	5.98	48	74/26
20	4-picoline[b]	100×	5.98	48	73/27
21	pyridine[b]	50×	5.23	48	67/33
22	pyridine	pure	5.23	48	40/60
23	2-bromopyridine[c]	50×	0.90	96	3/97
24	2-benzoylpyridine[c]	50×	2.60	96	14/86
25	2-methoxypyridine[b]	50×	3.06	96	20/80
26	2-picoline[c]	50×	6.00	48	58/42
27	3-bromopyridine[c]	50×	2.91	72	22/78
28	4-CF_3pyridine[c]	50×		48	18/82
29	4-methoxypyridine[d]	50×	6.62	48	76/24
30	$(BnNEt_3)Br$[c]	50×		48	0/100
31	$(BnNEt_3)Cl$[c]	50×		48	32/68
32	piperidine[d]	50×	11.3	0.5	0/100
33	DMAP[d]	50×	9.2	12	0/100
34	*N*-methylmorpholine[d]	50×	7.38	72	55/45
35	quinoline[d]	50×	4.90	72	44/56
36	pyrazole[d]	50×	2.48	144	0/100
37	imidazole[d]	50×	6.95	144	68/32
38	quinaldine[d]	50×	5.42	144	32/68
39	indoline[d]	50×	4.9	192	30/70
40	2,2′-bipyridyl[d]	50×		96	25/75
41	4,4′-dimethyl-2,2′-bipyridyl[d]	50×		96	32/68
42	benzophenone imine[d]	50×		48	48/52
43	2,2′,4,4′-tetramethyl-3-pentanone imine[d]	50×		48	15/85

[a] The *cis*/*trans* ratios were determined at the indicated times when all of $CpRu(CO)_2(t3hx)^+$ (**1**) had reacted. [b] Moderate amount of decomposition. [c] Small amount of decomposition. [d] Large amount of decomposition.

Table 3. *cis*/*trans* Ratios of 3-Hexene Obtained from Reactions of $CpRu(CO)_2(t3hx)^+$ According to Eq 4 at Various Temperatures in CD_2Cl_2

entry	temp (°C)	ligand (L)[a]	pK_a	reaction time (h)	*cis*/*trans* ratio[b]
44	25	PPh_3[c]	2.73	1200	44/56
45	30	PPh_3[c]	2.73	525	41/59
46	40	PPh_3[c]	2.73	96	36/64
47	50	PPh_3[c]	2.73	48	29/71
48	25	pyridine[c]	5.23	960	78/22
49	30	pyridine[c]	5.23	525	79/21
50	40	pyridine[c]	5.23	96	75/25
51	50	pyridine[c]	5.23	48	67/33

[a] 50-Fold concentration as compared with that of $CpRu(CO)_2(t3hx)^+$ (**1**). [b] The *cis*/*trans* ratios were determined at the indicated times when all of $CpRu(CO)_2(t3hx)^+$ (**1**) had reacted. [c] Moderate amount of decomposition.

the electron-withdrawing Br group gives the lowest ratio (3/97), and the electron-donating and relatively small CH_3 group gives the largest ratio (58/42).

Considering the effectiveness of pyridines at achieving high *cis*/*trans* 3-hexene ratios, other nitrogen-containing ligands were tested at 50 °C. Ligands with high pK_a values (piperidine, 11.3; *p*-dimethylaminopyridine, DMAP, 9.2) or low pK_a values (pyrazole, 2.48) did not yield any of the *cis*-olefin during the course of the reactions but instead gave multiple Cp peaks in the ^{1}H NMR spectra as well as very dark solutions with piperidine and *p*-dimethylaminopyridine. Heterocyclic ligands with moderate pK_a values gave a wide range of *cis*/*trans* ratios: imidazole (68/32), *N*-methylmorpholine (55/45), quinoline (44/56), quinaldine (32/68), and indoline (30/70). The polycyclic ring structures of quinoline, quinaldine, and indoline increase the steric bulk around the nitrogen donor atom, which is perhaps the basis of the lower *cis*/*trans* ratios than those for the smaller heterocycles. The 2,2′-bipyridyl (25/75) and 4,4′-dimethyl-2,2′-bipyridyl (32/68) ligands with aryl groups in the *ortho* position of the pyridine give lower ratios than pyridine (67/33). The slightly higher ratio for 4,4′-dimethyl-2,2′-dipyridyl is probably due to the electron-donating methyl groups at the 4 and 4′ positions. The two imines, benzophenone imine and 2,2′,4,4′-tetramethyl-3-pentanone imine, react with **1** to give *cis*/*trans* ratios of 48/52 and 15/85, respectively. The much lower ratio for 2,2′,4,4′-tetramethyl-3-pentanone imine may be attributed to the steric bulk of this ligand.

The chloride anion in $(BnNEt_3)Cl$ reacts with **1** to give a 32/68 *cis*/*trans* ratio as well as generating $CpRu(CO)_2Cl$. The bromide anion in $(BnNEt_3)Br$, on the other hand, reacts with **1** to give solely *trans*-3-hexene and $CpRu(CO)_2Br$. Two ligands containing sulfur donor atoms, thiophene and diethyl sulfide, did not react with **1** at 25 °C even after 336 h.

In order to determine whether or not other *trans*-olefins in $CpRu(CO)_2(\eta^2$-*trans*-olefin$)^+$ can be isomerized to the *cis*-olefin upon displacement by various ligands, complexes of 2-pentene (**2**), *trans*-3-octene (**3**), *trans*-4-octene (**4**), and *trans*-5-decene (**5**) were reacted with selected phosphine and pyridine ligands (Table 4). Compounds **2** and **3** react with PPh_3 to give *cis*/*trans* ratios of 17/83 and 26/74, respectively, which are slightly lower than that obtained for **1** (29/71). Similarly, **2** and **3** react with 4-methoxypyridine to give ratios (75/25 and 71/29, respectively), that again are slightly lower than for **1** (76/24). On the other hand, the reactions of **4** and **5** with PPh_3 give only the *trans*-olefin. However, **4** and **5** do react with 4-picoline to give both *cis*- and *trans*-olefins, as evidenced by two peaks in the ^{1}H NMR spectrum at 5.48 and 5.44 ppm for **4** and 5.47 and 5.43 ppm for **5**, but exact *cis*/*trans* ratios could not be determined due to overlapping peaks. The larger sizes of the *n*-propyl and *n*-butyl groups in *trans*-4-octene and *trans*-5-decene in **4** and **5** are presumably responsible for the poor *trans*-to-*cis* conversion, especially when reacted with a bulky ligand such as PPh_3. For complexes **2** and **3**, at least one of the alkyl groups in the olefin is a relatively small methyl or ethyl. It is interesting that the *trans*-3-octene, with ethyl and *n*-butyl groups, in **3** reacts with PPh_3 to give some of the *cis*-olefin, while the *trans*-4-octene,

Table 4. *cis*/*trans* Ratios of Olefin Obtained from Reactions of $CpRu(CO)_2$(*trans*-olefin)$^+$ According to Eq 4 at 50 °C in CD_2Cl_2

entry	compound	olefin	ligand[a]	pK_a	*cis*/*trans* ratio[b]
52	**1**	*trans*-3-hexene	PPh_3[c]	2.73	29/71
53	**2**	*trans*-2-pentene	PPh_3[c]	2.73	17/83
54	**3**	*trans*-3-octene	PPh_3[c]	2.73	26/74
55	**4**	*trans*-4-octene	PPh_3[c]	2.73	0/100
56	**5**	*trans*-5-decene	PPh_3[c]	2.73	0/100
57	**1**	*trans*-3-hexene	4-methoxypyridine[d]	6.62	76/24
58	**2**	*trans*-2-pentene	4-methoxypyridine[d]	6.62	75/25
59	**3**	*trans*-3-octene	4-methoxypyridine[d]	6.62	71/29
60	**1**	*trans*-3-hexene	4-picoline[c]	5.98	73/27
61	**4**	*trans*-4-octene	4-picoline[c]	5.98	*e*
62	**5**	*trans*-5-decene	4-picoline[c]	5.98	*e*

[a] 50-Fold concentration as compared with that of $CpRu(CO)_2$(*trans*-olefin)$^+$. [b] The *cis*/*trans* ratios were determined at the indicated times when all of $CpRu(CO)_2$(*trans*-olefin)$^+$ had reacted. [c] Moderate amount of decomposition. [d] Large amount of decomposition. [e] Exact ratio could not be determined due to peak overlap in the ^{1}H NMR spectrum but is estimated to be 50/50 based on inspection.

Table 5. *cis*/*trans* Ratios of 3-Hexene Obtained from Reactions of $CpRu(CO)_2(t3hx)^+$ According to Eq 4 at 50 °C in Various Solvents

entry	solvent	nucleophile[a]	pK_a	reaction time (h)	*cis*/*trans* ratio[b]
63	CD_2Cl_2	PPh_3[c]	2.73	48	29/71
64	$CDCl_3$	PPh_3[c]	2.73	48	26/74
65	DMSO-d_6	PPh_3[d]	2.73	48	15/85
66	acetone-d_6	PPh_3[d]	2.73	72	0/100
67	CD_2Cl_2	4-picoline[c]	5.98	48	74/26
68	$CDCl_3$	4-picoline[c]	5.98	48	57/43
69	acetone-d_6	4-picoline[e]	5.98	48	32/68
70	CD_3OD	4-picoline[d]	5.98	48	9/91

[a] 50-Fold concentration as compared with that of $CpRu(CO)_2(t3hx)^+$ (**1**). [b] The *cis*/*trans* ratios were determined at the indicated times when all of $CpRu(CO)_2(t3hx)^+$ (**1**) had reacted. [c] Moderate amount of decomposition. [d] Small amount of decomposition. [e] Large amount of decomposition.

with two *n*-propyl groups, in **4** does not give any *cis*-olefin. In the reactions of 4-picoline with **4** and **5**, the *trans*-to-*cis* conversion occurs despite the bulkiness of the olefins. This may be due to the smaller size of 4-picoline as compared with PPh_3.

The *cis*/*trans*-olefin product ratios from reactions (eq 4) of $CpRu(CO)_2(t3hx)^+$ with PPh_3 and 4-picoline are highly dependent on the nature of the solvent (Table 5). Reactions in relatively low polarity and poorly coordinating solvents (CD_2Cl_2 and $CDCl_3$) give the highest *cis*/*trans* ratios (entries 63, 64, 67, 68). In polar, coordinating solvents (DMSO-d_6, acetone-d_6, and methanol-d_6), the *cis*/*trans* ratios are considerably lower. DMSO is sufficiently strongly coordinating that it displaces the olefin when **1** is dissolved in DMSO. This reaction gives a 15/85 *cis*/*trans* ratio of 3-hexenes, the same ratio that was observed in the presence of PPh_3 (entry 65) in DMSO solvent.

Discussion

For the purpose of considering possible mechanisms for reactions (eq 4) of $CpRu(CO)_2$(*trans*-olefin)$^+$ with various ligands, it is useful to consider previously reported reactions of $CpFe(CO)_2(\eta^2$-olefin$)^+$ (olefin = ethylene, propene, styrene, *trans*-2-butene) with various ligands such as alkoxides, amines, mercaptans, phosphines, and phosphites.[7] The reaction of $CpFe(CO)_2(\eta^2$-ethylene$)^+$ with PPh_3 gives the η^1 product $CpFe(CO)_2(CH_2CH_2PPh_3)^+$, resulting from PPh_3 attack on the ethylene. For the analogous propene and styrene complexes, formation of the η^1 PPh_3 adduct competes with displacement of the olefin to give $CpFe(CO)_2(PPh_3)^+$ (**6**), which becomes the sole product upon warming to 65 °C, as the PPh_3 adducts are not stable at high temperatures. More specific to our studies is the reaction of the *trans*-2-butene complex with PPh_3, which gives only **6** and free olefin, which was not identified as *cis* or *trans*. In this reaction, there was no ^{1}H NMR evidence for the formation of the η^1-adduct, $CpFe(CO)_2[CH(Me)CH(Me)PPh_3]^+$.

In reactions of $CpRu(CO)_2(\eta^2$-t3hx$)^+$ (**1**) with phosphine ligands, formation of the PR_3 adduct, $CpRu(CO)_2[CH(Et)CH(Et)PR_3]^+$, is observed in the ^{1}H NMR spectrum within 5 min of adding PMe_3 or $PPhMe_2$. As in the Fe series, the adducts are not stable and transform in CH_2Cl_2 over the course of 144 h at 25 °C to $CpRu(CO)_2(PR_3)^+$ (**7**) and free t3hx. In an attempt to isolate an η^1-adduct, **1** was reacted with benzenethiol in the presence of K_2CO_3 at 0 °C in CH_3CN, as thiols had been shown to give only η^1 adducts when *tert*-butylmercaptan was reacted with either $CpFe(CO)_2(\eta^2$-$CH_2CH_2)^+$ or $CpFe(CO)_2(\eta^2$-CH_2-$CHMe)^+$. A reaction occurred at 0 °C within 2 h to give a product with ν(CO) bands in the IR spectrum at 2009 and 1946 cm^{-1} in CH_3CN. The ^{1}H NMR spectrum obtained in CD_2Cl_2 showed two upfield multiplets at 3.45 and 3.12 ppm for the former olefinic protons and two triplets for the methyl groups at 1.03 and 0.91 ppm. These values support the formulation of the compound as $CpRu(CO)_2[CH(Et)CH(Et)SPh]$ (**8**), the only product. A similar Fe complex, $CpFe(CO)_2[CH_2CH_2SBu^t]$, exhibits ν(CO) bands at 2012 and 1949 cm^{-1} in CH_3CN solvent and multiplets for the CH_2 groups at 2.55 and 1.48 ppm in C_6D_6 in the ^{1}H NMR spectrum.[7] The previously reported amine adduct, $CpRu(CO)_2(CH_2CH_2NH_3)^+$, exhibits ν(CO) bands at 2012 and 1950 cm^{-1}, and the ^{1}H NMR spectrum shows two multiplets at 3.43 and 1.70 ppm for the methylene groups.[8] Although attempts to isolate and purify **8** were unsuccessful, the IR and ^{1}H NMR spectral data are consistent with a structure in which PhS^- has added to the t3hx ligand. This result together with evidence for the formation of η^1 adducts in reactions of **1** with PMe_3 and $PPhMe_2$ suggests a possible pathway for reaction 4 that involves the addition of ligand (L) to the coordinated olefin in $CpRu(CO)_2(t3hx)^+$.

In reactions of nucleophiles with metal complexes containing η^2-olefins,[9,10] the rate law generally includes first-order dependences on the complex and the nucleophile concentrations, which suggests a mechanism involving nucleophilic attack on the η^2-olefin. However, in the reactions (eq 4) of $CpRu(CO)_2(t3hx)^+$, the rates do not depend on the concentration of the ligand (L = PPh_2Me or 4-picoline), which suggests a mechanism that is not simple nucleophilic attack of L on the olefin. Also, the similar rate constants for the reactions of **1** with PPh_3 (3.1×10^{-5} s^{-1}) and 4-picoline (2.2×10^{-5} s^{-1}) at 50.0 °C in CD_2Cl_2 solvent suggest that the incoming ligand does not greatly affect the rate of the reaction. On the other hand, the mechanism

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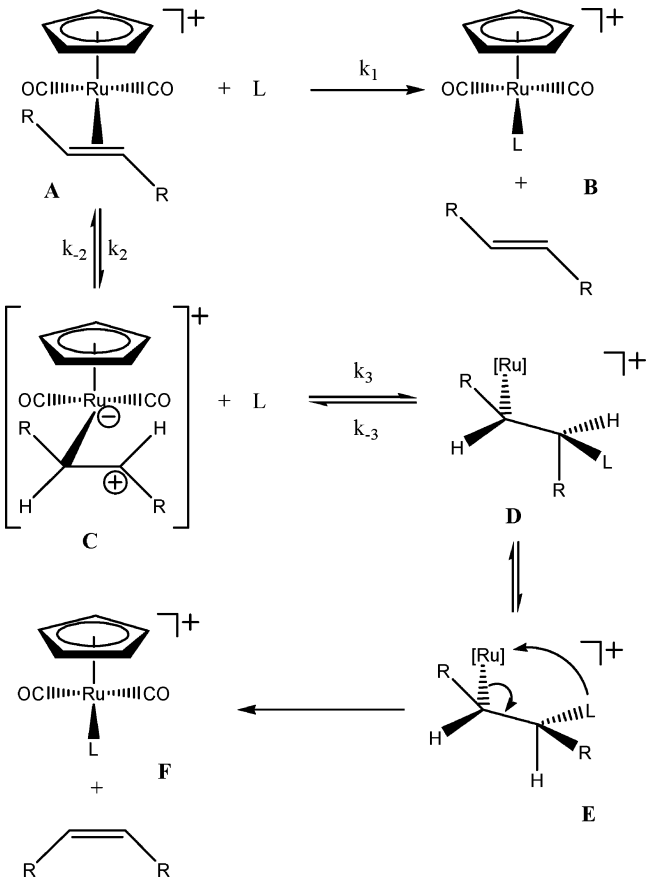
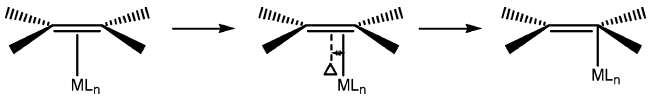
Scheme 2. Mechanism for the Reaction in Eq 4



Scheme 3. Slipping of ML_n Fragment along Olefin π−Bond by Distance Δ



must account for the fact that the *cis*/*trans* 3-hexene product ratios in the reactions are different for PPh_3 and 4-picoline. It must also account for the observation that the double bond does not migrate along the carbon chain of the olefin during the *trans*-to-*cis* isomerization process. We propose the mechanism shown in Scheme 2 for these reactions.

This mechanism involves two olefin substitution pathways; both are first order in the complex and independent of the ligand (L) concentration. The k_1 pathway is a simple dissociation of the *trans*-olefin followed by rapid addition of L to the unsaturated Ru intermediate. This pathway gives only the *trans*-olefin product. The k_2 pathway begins with a rate-determining slippage of the η^2-olefin to give a dipolar η^1-olefin intermediate **C**, which can either return to **A** or undergo attack by L on the side of the olefin opposite the Ru to give olefin adduct **D**. Rotation around the C−C bond in **D** places the L group near the metal, where it can transfer to the Ru and release the *cis*-olefin. Rotation around the C−C bond converts **D** to **E** and also moves the *trans* R groups to a *cis* arrangement, thereby setting up the release of the *cis*-olefin in the final step (**E** → **F**). In this mechanism, the relative rates of the k_1, k_2/k_{-2}, and k_3/k_{-3} steps control the *cis*/*trans*-olefin product ratio. In the following paragraphs is a more detailed discussion of the mechanism and the experimental observations that pertain to this mechanism.

The mechanism in Scheme 2 predicts that the *cis*/*trans* ratio will remain the same throughout the course of the reaction when using a large excess of the ligand L. This result was observed in the reaction of **1** with a 50-fold excess of PPh_3 when the *cis*/*trans* ratio was determined to be the same after 12, 24, and 48 h. At all three times, the *cis*/*trans* ratio was 29/71, which is identical to that in entry 16 (Table 2). In other experiments, **1** was reacted with PPh_3 and 4-picoline in CD_2Cl_2 at 50 °C using 10-, 50-, and 100-fold excesses in order to establish the effect of ligand concentration on the *cis*/*trans* ratio (entries 15−20). For both PPh_3 and 4-picoline, the *cis*/*trans* ratio increases as the ligand concentration increases from 10-fold to 50-fold excess, but the *cis*/*trans* ratio remains relatively unchanged as the amount of ligand is increased further to 100-fold excess. This means, in the context of the proposed mechanism, that the dissociative pathway predominates at a 10-fold excess, as the low concentration of L results in a relatively slow rate for the conversion of **C** to **D**. At higher concentrations (50- and 100-fold), this step is fast, as compared with k_{-2}, which means that the *cis*/*trans* ratios are controlled by the rates of the k_1 and k_2 steps, which are both independent of the concentration of L. Thus, the dependence of the *cis*/*trans* ratios on the concentration of L can be reasonably explained by the proposed mechanism. Not only is the *cis*/*trans* ratio dependent on the concentration of the ligand, but the specific identity of the ligand is also important. On the basis of the data in Table 2, high *cis*/*trans* ratios are favored by ligands whose conjugate acids have pK_a values between 2 and 6. Ligands with pK_a values outside of this range give either very low amounts of the *cis*-olefin or none at all. Highly basic amines (methylamine, dimethylamine, dibenzylamine) gave only decomposition of the metal complex accompanied by release of the *trans*-olefin. This is in stark contrast to $CpFe(CO)_2(\eta^2\text{-}CH_2CH_2)^+$, which reacts with both methylamine and dimethylamine to give the corresponding η^1-amine adducts $CpFe(CO)_2(CH_2CH_2NHR_2)^+$.[7] These reactions were conducted at −10 °C or below, which suggests that decomposition may occur at higher temperatures. This would be consistent with our temperature studies (Table 3), which showed a decrease in the *cis*/*trans* ratio as the temperature is increased. In contrast to the decomposition of **1** observed with strongly basic ligands, weakly basic ligands such as ethyl sulfide and thiophene do not react at all with **1**.

Among the ligands (L) that give significant amounts of the *cis*-olefin product, both electronic and steric properties of the ligand influence the *cis*/*trans* ratio. For reactions of **1** with the series of *para*-substituted pyridines, the *cis*/*trans* ratio decreases, using a 50-fold excess of ligand, as the substituent becomes less electron-donating (Table 2): MeO (76/24) > Me (74/26) > H (67/33) > CF_3 (18/82). This is the expected trend from the proposed mechanism where the k_3 step would be faster for the more nucleophilic pyridines, which would lead to higher yields of the *cis*-olefin.

Pyridines with *ortho* substituents uniformly give lower *cis*/*trans* 3-hexene ratios than *para*- or *meta*-substituted pyridines (Tables 1 and 2). The steric effect of an *ortho*-substituent would be expected to reduce the rate of attack in the k_3 step of the proposed mechanism, which would result in a lower *cis*/*trans* ratio.

The size of the R groups in the *trans*-olefin (RHC═CHR) ligand also plays a major role in determining the amount of *cis*-olefin that is produced in the reaction of **1** with PPh_3 (Table 4). Those olefins (*trans*-3-hexene, *trans*-2-pentene, and *trans*-3-octene) with at least one ethyl or methyl R group give similar *cis*/*trans* ratios, whereas olefins (*trans*-4-octene and *trans*-5-decene) with larger R groups (*n*-propyl or *n*-butyl) yield none of the *cis*-olefins. Such an effect of large R groups is not sur-

prising because they would decrease the rate of ligand addition to **C** in the k_3 step, especially with bulky ligands such as PPh_3. However, if the ligand is the less bulky 4-picoline, both compounds **4** and **5** react to yield some of the *cis*-olefin (entries 61, 62). An exact *cis*/*trans* ratio could not be obtained for these latter two reactions due to overlap of the *cis*- and *trans*-olefin peaks, but the ratio is estimated to be about 50/50 based on inspection. Therefore, even internal olefins with large R groups can yield *cis*-olefin if the correct incoming ligand is chosen.

Although PPh_3 and PCy_3 react with **1** at rates that are similar to pyridine, PMe_3 and $PPhMe_2$ react much more rapidly (within 5 min) to give the η^1 complexes $CpRu(CO)_2[CH(Et)CH(Et)PR_3]^+$, which were identified by their ^1H NMR spectra. The much greater rate of these reactions means that they must proceed by a mechanism that is different than either the k_1 or k_2 pathways in Scheme 2. These highly basic and sterically small ligands are likely to react by direct nucleophilic attack on the coordinated olefin to give the η^1 complex. The $CpRu(CO)_2[CH(Et)CH(Et)PR_3]^+$ complexes convert at 25 °C over a period of about 144 h to $CpRu(CO)_2(PR_3)^+$ and the free *trans*-olefin. Although it is not clear how these η^1-intermediate complexes yield the *trans*-olefin, they cannot follow the **E** → **F** pathway, which would be expected to give the *cis*-olefin.

Conclusions

Reactions (eq 4) of the η^2-*trans*-olefin complexes $CpRu(CO)_2(\eta^2$-*trans*-olefin$)^+$ with pyridine and phosphine ligands (L) to give $CpRu(CO)_2(L)^+$ and free *cis*- and *trans*-olefins is surprising because as much as 83% of the *trans*-olefin isomerizes to the thermodynamically less stable *cis* isomer during the substitution process. The driving force for this *trans*-to-*cis* isomerization must be the greater stability of the $CpRu(CO)_2(L)^+$ product as compared with the $CpRu(CO)_2(\eta^2$-*trans*-olefin$)^+$ reactant. This isomerization is also not accompanied by migration of the double bond along the hydrocarbon chain. In other metal complexes where *cis*/*trans* isomerization and double-bond migration are observed (often catalytic reactions),[11] a mechanism involving a metal hydride intermediate is proposed (and sometimes detected). In eq 4, H_2 or other sources of hydrogen are not present, and it seems unlikely that the $CpRu(CO)_2(\eta^2$-*trans*-olefin$)^+$ complexes themselves would form an allyl-hydride intermediate $CpRu(CO)(H)(\eta^3$-allyl$)^+$, which would be expected to give olefin products in which the double bond has migrated.

For the above reasons, it appears that the formation of *cis*-olefins in eq 4 occurs by a new mechanism (Scheme 2). A key step (k_2) in the proposed pathway to the *cis*-olefin product involves rate-determining slippage of the η^2-bonded olefin in **A** to an η^1-dipolar complex (**C**). Such a slippage was previously proposed by Roald Hoffman to account for the increased reactivity of coordinated olefins toward nucleophiles.[12] This activation, which was supported by computational analysis, stems from slippage of the olefin away from a symmetrical bonding mode.

As the extent of slippage (Δ) increases, the η^2-coordination of the olefin begins to resemble an η^1 σ-complex with the carbon furthest from the metal building up a positive charge, causing it to be activated to attack by nucleophiles. Computational analysis performed on the $CpFe(CO)_2^+$ fragment,[13] which is analogous to our system, showed that this fragment should strongly activate olefins toward nucleophilic attack. Experimental support for this activation was found in the higher reactivity of $CpFe(CO)_2[\eta^2$-$CH_2{=}CH(OMe)]^+$, in which the olefin is unsymmetrically bonded to the Fe, as compared with that of $CpFe(CO)_2(\eta^2$-$CH_2{=}CH_2)^+$.[14] In the mechanism in Scheme 2, the olefin-slipping step (k_2) is proposed to be rate-determining, which has not been suggested for other reactions involving nucleophilic attack on coordinated olefins.

Although the mechanism in Scheme 2 reasonably accounts for the experimental results, the most important result of these studies is the observation that the simple process of substituting a *trans*-olefin in a metal complex by another ligand may result in the formation of the free *cis*-olefin. This represents a new pathway for the *trans*-to-*cis* isomerization of olefins that may occur in transition metal complex-catalyzed reactions of olefins, where substituting ligands are often present in solution. However, it should be noted that this isomerization does not occur in all olefin substitution reactions. Even the reaction (eq 1) of $Cp^*Ru(CO)_2(t3hx)^+$ with PPh_3 liberates only *trans*-3-hexene, which can be explained by the much faster rate of t3hx dissociation in the sterically crowded Cp* complex (208×10^{-6} s^{-1} at 40.0 °C) by the k_1 pathway, as compared with the rate of t3hx substitution in the analogous Cp complex **1** (27×10^{-6} s^{-1} at 50.0 °C).[1] Also, the reaction (eq 1) of $CpRu(CO)_2(c3hx)^+$ with PPh_3 gives only *cis*-3-hexene,[1] which is more difficult to understand because the rate of c3hx dissociation ($k_1 = 1.96 \times 10^{-6}$ s^{-1} at 40.0 °C) is slower than the substitution in the t3hx complex **1** (27×10^{-6} s^{-1} at 50.0 °C); this suggests that the olefin slippage step (k_2) in the mechanism (Scheme 2) is slower for c3hx than t3hx. Moreover, many substituting ligands (L) (Tables 1 and 2) produce no or little *cis*-olefin. The lack of olefin isomerization in these reactions shows that the *trans*-to-*cis* isomerization observed in the present study depends sensitively on the metal complex, the specific *trans*-olefin, and the substituting ligand L.

Experimental Section

Methods and Materials. All reactions were carried out under an inert atmosphere of dry argon using standard Schlenk techniques. Diethyl ether, methylene chloride, and hexanes were purified on alumina using a Solv-Tek solvent purification system, similar to that reported by Grubbs.[15] The olefins *trans*-3-hexene (t3hx), *trans*-2-pentene (t2pt), *trans*-3-octene (t3oct), *trans*-4-octene (t4oct), and *trans*-5-decene (t5dec) were purchased from Sigma-Aldrich Chemical Co. and used as received. All deuterated solvents were purchased from Cambridge Isotope Laboratories. Solution infrared spectra were recorded on a Nicolet-560 spectrometer using a NaCl cell with a 0.1 mm path length. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer using the deuterated solvents as internal references. Elemental analyses were performed on a Perkin-Elmer 2400 Series II CHNS/O analyzer. The compound $CpRu(CO)_2Cl$ was prepared according to reported methods.[16]

General Procedure for Preparations of the $[CpRu(CO)_2(\eta^2$-olefin$)]BF_4$ Complexes (1−5). To a mixture of dry CH_2Cl_2 (20 mL) containing $AgBF_4$ (75.6 mg, 0.388 mmol) was added $CpRu(CO)_2Cl$ (100 mg, 0.388 mmol) and 1.2 mmol of the olefin (olefin

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= t3hx, t2pt, t3oct, t4oct, t5dec). The solution was stirred at room temperature for 4 to 6 h until the reaction was complete, as indicated by the disappearance of the ν(CO) bands for $CpRu(CO)_2Cl$ in the IR spectrum. The solution was filtered to remove AgCl and concentrated in vacuo to approximately 1 mL. Then, 20 mL of hexanes was added to precipitate the tan solid product, which was isolated by filtration and washed with hexanes (3 × 5 mL) to remove excess olefin. Isolated yields were typically 75−85%. The products were further purified by recrystallization from CH_2Cl_2/ether.

Characterization of Compounds 1−5. [CpRu(CO)$_2$(η^2-t3hx)]BF$_4$ (1). ^{1}H NMR (CD_2Cl_2, 400 MHz, 293 K): δ 5.87 (s, 5H, C_5H_5), 4.86 (m, 2H, $H_{3,4}$), 2.23 (m, 2H, $H_{2,5}$), 1.64 (m, 2H, $H_{2,5}$), 1.17 (t, $^3J_{HH}$ = 7.6 Hz, 6H, $H_{1,6}$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, 293 K): δ 197.02 (C≡O), 192.58 (C≡O), 91.78 (C_5H_5), 85.15 ($C_{3,4}$), 32.89 ($C_{2,5}$), 18.12 ($C_{1,6}$). IR (CH_2Cl_2): ν(CO) (cm^{-1}) 2078 (s), 2035 (s). Anal. Calcd for $C_{13}H_{17}BF_4O_2Ru$: C, 39.71; H, 4.37. Found: C, 40.07; H, 4.77.

Uncoordinated t3hx. ^{1}H NMR (CD_2Cl_2, 400 MHz, 293 K): δ 5.46 (m, 2H, $H_{3,4}$), 2.01 (m, 4H, $H_{2,5}$), 0.98 (t, $^3J_{HH}$ = 7.6 Hz, 6H, $H_{1,6}$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, 293 K): δ 131.30 ($C_{3,4}$), 26.31 ($C_{2,5}$), 14.34 ($C_{1,6}$).

Uncoordinated c3hx. ^{1}H NMR ($CDCl_3$, 400 MHz, 293 K): δ 5.35 (m, 2H, $H_{3,4}$), 2.05 (m, 4H, $H_{2,5}$), 0.97 (t, $^3J_{HH}$ = 7.6 Hz, 6H, $H_{1,6}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz, 293 K): δ 131.08 ($C_{3,4}$), 20.55 ($C_{2,5}$), 14.48 ($C_{1,6}$).

[CpRu(CO)$_2$(η^2-t2pt)]BF$_4$ (2). ^{1}H NMR (CD_2Cl_2, 400 MHz, 293 K): δ 5.87 (s, 5H, C_5H_5), 4.98 (m, 2H, $H_{2,3}$), 2.15 (m, 1H, H_4), 1.93 (d, $^3J_{HH}$ = 5.2 Hz, 3H, H_1), 1.64 (m, 1H, H_4), 1.17 (t, $^3J_{HH}$ = 7.6 Hz, 3H, H_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, 293 K): δ 197.11 (C≡O), 192.58 (C≡O), 91.77 (C_5H_5), 86.89 (C_3), 79.94 (C_2), 32.80 (C_4), 24.90 (C_1), 17.91 (C_5). IR (CH_2Cl_2): ν(CO) (cm^{-1}) 2078 (s), 2035 (s). Anal. Calcd for $C_{12}H_{15}BF_4O_2Ru$: C, 38.02; H, 3.99. Found: C, 37.69; H, 3.99.

Uncoordinated t2pt. ^{1}H NMR (CD_2Cl_2, 400 MHz, 293 K): δ 5.43 (m, 2H, $H_{2,3}$), 1.99 (m, 2H, H_4), 1.64 (m, 3H, H_1), 0.95 (t, $^3J_{HH}$ = 7.6 Hz, 3H, H_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, 293 K): δ 133.72 (C_3), 124.14 (C_2), 26.19 (C_4), 18.19 (C_1), 14.33 (C_5).

[CpRu(CO)$_2$(η^2-t3oct)]BF$_4$ (3). ^{1}H NMR (CD_2Cl_2, 400 MHz, 293 K): δ 5.86 (s, 5H, C_5H_5), 4.88 (m, 2H, $H_{3,4}$), 2.25 (m, 2H, $H_{2,5}$), 1.69 (m, 1H, H_2), 1.56 (m, 3H, $H_{5,6}$), 1.41 (m, 2H, H_7), 1.18 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H_1), 0.93 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H_8). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, 293 K): δ 197.06 (C≡O), 192.55 (C≡O), 91.76 (C_5H_5), 85.91 (C_3), 83.96 (C_4), 39.40 (C_5), 36.14 (C_6), 32.93 (C_2), 22.70 (C_7), 18.15 (C_1), 14.10 (C_8). IR (CH_2Cl_2): ν(CO) (cm^{-1}) 2078 (s), 2035 (s). Anal. Calcd for $C_{15}H_{21}BF_4O_2Ru$: C, 42.77; H, 5.03. Found: C, 41.82; H, 4.61.

Uncoordinated t3oct. ^{1}H NMR (CD_2Cl_2, 400 MHz, 293 K): δ 5.42 (m, 2H, $H_{3,4}$), 1.99 (m, 4H, $H_{2,5}$), 1.33 (m, 4H, $H_{6,7}$), 0.96 (t, $^3J_{HH}$ = 7.6 Hz, 3H, H_1), 0.89 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H_8). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, 293 K): δ 132.43 (C_3), 129.94 (C_4), 32.85 (C_5), 32.49 (C_6), 26.22 (C_2), 22.82 (C_7), 14.42 (C_1), 14.34 (C_8).

[CpRu(CO)$_2$(η^2-t4oct)]BF$_4$ (4). ^{1}H NMR (CD_2Cl_2, 400 MHz, 293 K): δ 5.86 (s, 5H, C_5H_5), 4.90 (m, 2H, $H_{4,5}$), 2.24 (m, 2H, $H_{3,6}$), 1.56 (m, 6H, $H_{2,3,6,7}$), 0.99 (t, $^3J_{HH}$ = 7.2 Hz, 6H, $H_{1,8}$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, 293 K): δ 197.09 (C≡O), 192.51 (C≡O), 91.74 (C_5H_5), 84.59 ($C_{4,5}$), 41.65 ($C_{3,6}$), 27.43 ($C_{2,7}$), 13.87 ($C_{1,8}$). IR (CH_2Cl_2): ν(CO) (cm^{-1}) 2078 (s), 2035 (s).

Uncoordinated t4oct. ^{1}H NMR (CD_2Cl_2, 400 MHz, 293 K): δ 5.41 (m, 2H, $H_{4,5}$), 1.96 (m, 4H, $H_{3,6}$), 1.37 (m, 4H, $H_{2,7}$), 0.89 (t, $^3J_{HH}$ = 7.2 Hz, 6H, $H_{1,8}$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, 293 K): δ 130.93 ($C_{4,5}$), 35.33 ($C_{3,6}$), 23.41 ($C_{2,7}$), 14.01 ($C_{1,8}$).

[CpRu(CO)$_2$(η^2-t5dec)]BF$_4$ (5). ^{1}H NMR (CD_2Cl_2, 400 MHz, 293 K): δ 5.86 (s, 5H, C_5H_5), 4.88 (m, 2H, $H_{5,6}$), 2.25 (m, 2H, $H_{4,7}$), 1.56 (m, 6H, $H_{3,4,7,8}$), 1.41 (m, 4H, $H_{2,9}$), 0.93 (t, $^3J_{HH}$ = 7.2 Hz, 6H, $H_{1,10}$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, 293 K): δ 197.09 (C≡O), 192.53 (C≡O), 91.74 (C_5H_5), 84.57 ($C_{5,6}$), 39.45 ($C_{4,7}$), 36.19 ($C_{3,8}$), 22.77 ($C_{2,9}$), 14.09 ($C_{1,10}$). IR (CH_2Cl_2): ν(CO) (cm^{-1}) 2078 (s), 2035 (s).

Uncoordinated t5dec. ^{1}H NMR (CD_2Cl_2, 400 MHz, 293 K): δ 5.40 (m, 2H, $H_{5,6}$), 1.98 (m, 4H, $H_{4,7}$), 1.33 (m, 8H, $H_{2,3,8,9}$), 0.89 (t, $^3J_{HH}$ = 7.2 Hz, 6H, $H_{1,10}$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, 293 K): δ 130.92 ($C_{5,6}$), 32.90 ($C_{4,7}$), 32.51 ($C_{3,8}$), 22.82 ($C_{2,9}$), 14.34 ($C_{1,10}$).

General Procedure for Reactions of the CpRu(CO)$_2$(*trans*-olefin)$^+$ Complexes with Nucleophiles/Ligands Resulting in Displacement of the Olefin. A 0.010 mmol sample of the complex (**1**−**5**) was placed in a 22 cm NMR tube. The tube was then moved into a glovebox, and a 0.70 mL aliquot of deuterated solvent (CD_2Cl_2, acetone-d_6, $CDCl_3$, CD_3OD, or DMSO-d_6) was added to the NMR tube by calibrated syringe. An excess of the nucleophile was then added (10×−100×) to the NMR tube, which was subsequently capped with a rubber septum. After removal from the glovebox, the NMR tube was then flame-sealed and placed in a constant-temperature bath at 50.0 ± 0.1 °C. The tube was removed from the bath periodically. and the spectrum was recorded on a Bruker DRX-400 spectrometer at room temperature using the deuterated solvent as the internal lock and standard. The tube was then returned to the bath within a 10 min period. After the bound olefin peak had disappeared, the NMR tube was opened and attached to a vacuum line along with an empty NMR tube. After the sample was frozen with liquid nitrogen, it was evacuated along with the empty NMR tube. The vacuum was turned off, and the sample tube was allowed to warm to room temperature, thereby transferring the liquid into the empty NMR tube that was immersed in liquid nitrogen. This process transferred the deuterated solvent, the free olefin(s), and sometimes excess nucleophile to the originally empty NMR tube. A ^{1}H NMR spectrum of the contents of the tube showed diagnostic peaks (see above) for the olefinic protons of the free *cis* and *trans* isomers, which were integrated to give the relative amounts of the *cis* and *trans* isomers. All reactions listed were done in duplicate. The relative amounts of *cis* and *trans* isomers that were obtained from each trial were reproducible to within 3% or less.

Kinetic Studies of the Reactions of CpRu(CO)$_2$(t3hx)$^+$ with PPh$_3$ and 4-Picoline. A 0.010 mmol sample of complex **1** was placed in a 22 cm NMR tube. The tube was then moved into a glovebox, and a 0.70 mL aliquot of CD_2Cl_2 was added to the NMR tube by calibrated syringe. An excess of the nucleophile was then added (30×−70×) to the NMR tube, which was subsequently capped with a rubber septum. After removal from the glovebox, the NMR tube was then flame-sealed and placed in a Bruker DRX-400 spectrometer maintained at a constant temperature of 50.0 ± 0.1 °C. Spectra were recorded on the Bruker DRX-400 spectrometer at specific intervals using the deuterated solvent as the internal lock and standard. The olefin methyl peaks were integrated using XWIN-NMR software. Rate constants, k_{obs}, were obtained from the slopes of first-order least-squares plots of ln(1 + [product]/[reactant]) versus time.[17] All trials were done in duplicate.

Acknowledgment. This project was supported by the National Research Initiative of the USDA Cooperative State Research, Education, and Extension Service, grant number 2003-35504-12846.

Supporting Information Available: Table of rate constants for reactions in eq 4. This material is available free of charge via the Internet at http://pubs.acs.org.

OM7005535

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