# Activation of $\eta^5$-Cyclopentadienyl Ligands toward Nucleophilic Attack through $\eta^5 \rightarrow \eta^3$ Ring Slippage. Kinetics, Thermodynamics, and NMR Spectroscopy

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*Summary: The kinetics of the reactions of the complexes* $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(L)]CF_3SO_3$ *(L = $CH_3CN$, pyridine, thiourea) with $PMe_3$ have been studied in acetone. The novel reaction products* $[Ru(\eta^3\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(PMe_3)(L)]CF_3SO_3$ *formed are fluxional in solution due to an intramolecular enantiomeric equilibrium likely proceeding through a five-coordinate* $\eta^1\text{-}C_5H_5$ *intermediate.*



Of the various bonding modes the cyclopentadienyl ligand can adopt in organotransition metal complexes, the $\eta^5$, $\eta^3$, and $\eta^1$ fashions are of particular interest, in view of their ability to interconvert through ring slippage.[1] A decrease in hapticity implies a decrease in the number of electrons donated to the metal and creates vacant sites for further reactions to utilize. This feature is arguably the key property for understanding the catalytic efficiency of cyclopentadienyl complexes.

For a number of years the $\eta^3\text{-}C_5H_5$ ligand itself proved to be a controversial species, until it was detected in the X-ray structure of $W(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)(CO)_2$.[2] In contrast to available reports on $\eta^5$ to $\eta^1$ slippage,[1,3] direct observation of an $\eta^5$ to $\eta^3$ interconversion is still outstanding. Nevertheless, the possibility of the occurrence of $\eta^3$ intermediates has been postulated frequently as a mechanistic rationale for a number of organometallic rearrangement reactions,[4] simply to adhere to the 18e rule. Among such reactions are α- and β-hydrogen abstractions,[5,6] photochemically induced C−H, Si−H, and C−C bond cleavages,[7] cyclopentadienyl ligand transfers,[8] and ligand substitution.[3d,9] Surprisingly, for inter- or intramolecular nucleophilic attack at $C_5H_5$ ligands,[10] transient $\eta^3$ or $\eta^1$ coordination has hitherto not been considered, despite the fact that $\eta^5\text{-}C_5H_5$ is known to be rather inert toward nucleophilic attack.[11] However, the $\eta^3$ or $\eta^1$ modes should appreciably enhance the reactivity of the $C_5H_5$ ligand. Unfortunately, the few reports dealing with additions, substitutions, and migrations of nucleophiles onto the $C_5H_5$ ligand do not allow any definite conclusions to be drawn as to the involvement of ring slippages.[10] Here we report the synthesis and characterization of the novel $\eta^3\text{-}C_5H_5$ complexes $[Ru(\eta^3\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(PMe_3)(L)]CF_3SO_3$ (L = $CH_3CN$, pyridine, thiourea), which are precursors of the 1,1′-disubstituted ruthenocene $[Ru(\eta^5\text{-}C_5H_4PMe_3)(\eta^5\text{-}C_5H_4OH)]CF_3SO_3$ (**10**), formed by endo migration of $PMe_3$ (Scheme 1).[12] Thus, kinetic and thermodynamic

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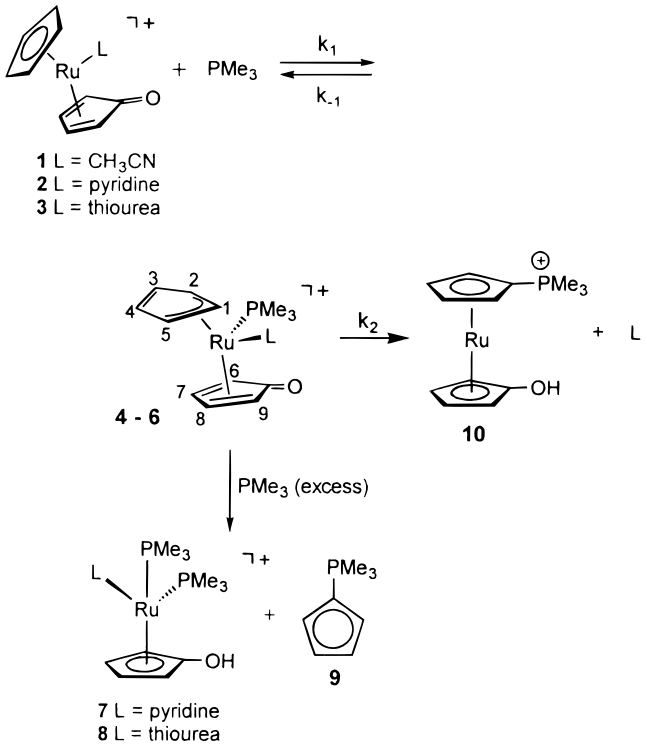
**Scheme 1**




data for a facile and reversible $\eta^5$ to $\eta^3$ transformation are presented for the first time.

Reaction of $PMe_3$ with $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(L)]CF_3SO_3$ (**1**−**3**)[12a,13] in acetone affords the novel complexes $[Ru(\eta^3\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(PMe_3)(L)]CF_3SO_3$ (**4**−**6**) in quantitative yield at −90 °C (L = $CH_3CN$) and at −20 °C (L = pyridine, thiourea) (Scheme 1).[14] With equimolar amounts of each reagent the reactions are complete on mixing. At room temperature **4** has only a transient existence, rapidly forming **10** ($t_{1/2}$ of **4** = 0.1 s), whereas **5** and **6** react within about 2 h to give a mixture of **10** and $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3OH\text{-}2\text{-}PMe_3)]CF_3SO_3$.[12c] It is noteworthy that in the presence of ≥5 equiv of $PMe_3$, **5** and **6** are cleanly converted to the half-sandwich complexes $[Ru(\eta^5\text{-}C_5H_4OH)(PMe_3)_2(L)]CF_3SO_3$ (**7**, **8**) and free $C_5H_4PMe_3$ (**9**)[15] in quantitative yield, as monitored by $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy.

The identity of the intermediates **4**−**6** was established by $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and, in the case of **5**, also by elemental analysis.[14] Complexes **5** and **6** were tentatively, but incorrectly, formulated as $[Ru(\eta^5\text{-}C_5H_4O)((1\text{−}4\text{-}\eta)\text{-}5\text{-}endo\text{-}L\text{-}C_5H_5)(PMe_3)]CF_3SO_3$ (L = pyridine, thiourea) on the basis of more limited NMR evidence.[12c] The $^1H$ and $^{13}C\{^1H\}$ NMR spectra of **4**−**6** are consistent with binding of cyclopentadienyl in an $\eta^3$ fashion. In the $^1H$ NMR spectra of **4**−**6** the olefinic hydrogens $H^{3,4}$ absorb at about 5.5 ppm, the terminal allylic hydrogen atoms $H^{2,5}$ at about 3.8 ppm, and the central allyl hydrogen $H^1$, except for **5**, at about 4.4 ppm.

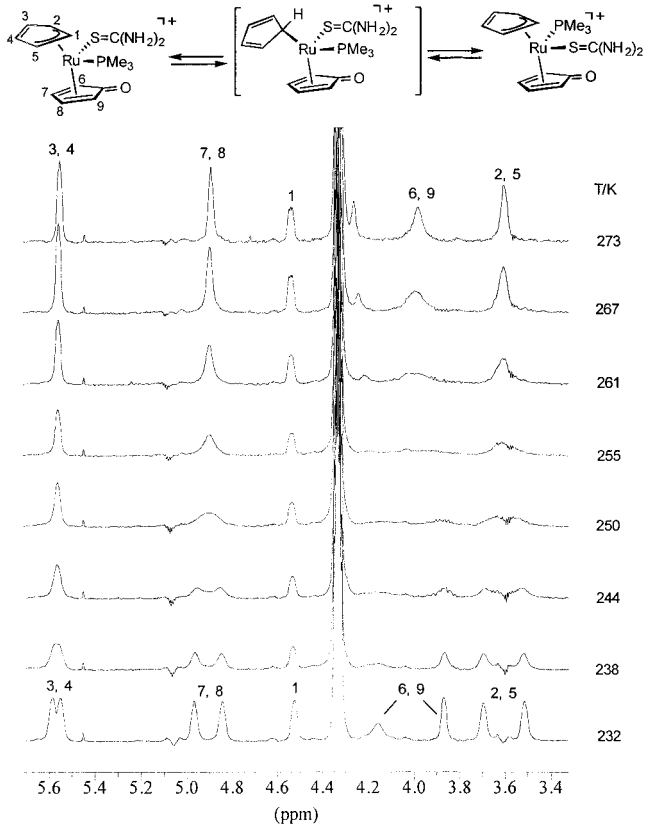



**Figure 1.** Variable-temperature 250 MHz $^1H$ NMR spectra of $[Ru(\eta^3\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(PMe_3)(S{=}C(NH_2)_2)]CF_3SO_3$ (**6**) in $CD_3NO_2$.

The hydrogen atom $H^1$ of the latter experiences a shift of about −1.1 ppm relative to those of the analogous complexes **4** and **6** due to anisotropic shielding by the aromatic ring current of the pyridine placing the $\eta^3$-$C_5H_5$ ligand in an *endo* orientation (as drawn in Scheme 1 and Figure 1). Only in this conformation is $H^1$ situated above the pyridine ring.

The first step of Scheme 1 (in the case of L = $CH_3CN$ also the formation of **10**) has been studied in detail by means of stopped-flow spectrophotometry with the results summarized in Table 1. The bimolecular rate law and the large negative activation entropies calculated from values of $k_1$ ($\Delta S^{\ddagger}$ = −24.8 to −27.8 cal $K^{-1}$ $mol^{-1}$) are in accord with the formation of **4**−**6** being an associative process. The activation enthalpies ($\Delta H^{\ddagger}$ = 4.9−7.5 kcal $mol^{-1}$) are surprisingly small, in view of the loss of aromaticity involved, and this may be taken to reflect the importance of Ru−P bond development in the activation process. Although there are no absolute Ru−P bond dissociation energies available in the literature, the activation enthalpies for $PMe_3$ dissociation from $Ru(\eta^5\text{-}C_5Me_5)(PMe_3)_2X$ (X = various anionic N, S, and C donor ligands, halides) provide approximate minimum Ru−P bond strengths which are on the order of 23−47 kcal $mol^{-1}$.[16] By the same token, the activation enthalpy for the reverse step ($k_{-1}$) is relatively high. When the data are combined for both steps ($k_1$ and $k_{-1}$), the favorable equilibrium for formation of **4**−**6** is seen to be enthalpy driven ($\Delta H°$ = −12.7 to −16.3 kcal $mol^{-1}$). Thus, the additional Ru−P bond

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(14) Spectroscopic data for complexes **4**−**6** and microanalytical data for complex **5** are provided as Supporting Information. Complexes **4** and **6** could not be isolated in pure form in the solid state. Due to the poor solubility of **6**, the $^{13}C\{^1H\}$ NMR spectrum of this complex has been recorded with $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(S{=}C(NH_2)_2)]BAr'_4$ (Ar′ = 3,5-$C_6H_3(CF_3)_2$); **6′**).

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**Table 1. Kinetic and Thermodynamic Data for the Reaction of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(L)]CF_3SO_3$ (1−3) with $PMe_3$ in Acetone**

| L | param[a] | $\Delta H^{\ddagger}$ or $\Delta H°$ (kcal mol$^{-1}$) | $\Delta S^{\ddagger}$ or $\Delta S°$ (cal K$^{-1}$ mol$^{-1}$) | $k^b$ or $K^c$ (25 °C) |
|---|---|---|---|---|
| $CH_3CN$ | $k_1$ | 4.9 ± 0.2 | −27.8 ± 0.6 | 1400 M$^{-1}$ s$^{-1}$ |
| | $k_{-1}$ | 20.1 ± 1.0 | 9.8 ± 3.1 | 1.4 s$^{-1}$ |
| | $K$ | −15.2 ± 1.0 | −37.6 ± 3.2 | 1000 M$^{-1}$ |
| | $k_2$ | 20.8 ± 0.2 | 12.6 ± 0.7 | 6.6 s$^{-1}$ |
| pyridine | $k_1$ | 6.5 ± 0.2 | −24.8 ± 0.7 | 420 M$^{-1}$ s$^{-1}$ |
| | $k_{-1}$ | 22.8 ± 1.2 | 18.4 ± 3.7 | 1.2 s$^{-1}$ |
| | $K$ | −16.3 ± 1.2 | −43.2 ± 3.8 | 350 M$^{-1}$ |
| $S{=}C(NH_2)_2$ | $k_1$ | 7.5 ± 1.2 | −26.5 ± 4.0 | 33 M$^{-1}$ s$^{-1}$ |
| | $k_{-1}$ | 20.2 ± 2.6 | 10.8 ± 8.9 | 2 s$^{-1}$ |
| | $K$ | −12.7 ± 2.8 | −37.3 ± 9.8 | 17 M$^{-1}$ |

[a] Extraction of the three rate constants from the stopped-flow data was done as described previously.[12c] When the intermediate (**5**, **6**) did not form products on the time scale of the stopped-flow experiment, the plot of the observed pseudo-first-order rate constant vs the phosphine concentration gave $k_1$ as the slope and $k_{-1}$ as the intercept. [b] Calculated from the activation parameters. [c] Calculated from $k_1$ and $k_{-1}$.

makes **4**−**6** more stable than **1**−**3** and $PMe_3$, even at the expense of the change in the hapticity of the $C_5H_5$ ligand from $\eta^5$ to $\eta^3$.

Complexes **4**−**6** are chiral. If stereochemically rigid, the $\eta^3$-$C_5H_5$ moiety should exhibit five individual resonances in the $^1$H and $^{13}C\{^1H\}$ NMR spectra and the $\eta^4$-$C_5H_4O$ ligand four proton and five carbon resonances. At room temperature, however, the $\eta^3$-$C_5H_5$ ligand exhibits only three proton and carbon resonances (in a 2:1:2 ratio) and the cyclopentadienone ring shows only two hydrogen and three carbon resonances. Thus, these molecules are fluxional in solution. This process for **4** and **5** is in the fast-exchange region for 250 MHz $^1$H NMR, even at −90 °C in acetone-$d_6$. For **6**, when the temperature is lowered below about 0 °C, the signals of $H^{2,5}$, $H^{3,4}$, $H^{6,9}$, and $H^{7,8}$ broaden and eventually reemerge as eight distinct signals, uniquely defining **6** as a chiral metal complex (Figure 1). The following observations lend support to the conclusion that the underlying enantiomeric equilibrium is an intramolecular one. As seen in Figure 1, the signal of the allylic proton $H^1$ remains unaffected by the exchange process, advocating against an *exo*/*endo* equilibrium. The same conclusion is drawn from $^{13}C\{^1H\}$ NMR spectroscopy. Furthermore, site exchange by a dissociative process is also excluded by the observation that the temperature dependence of the line shapes is unaffected by addition of L or $PMe_3$. From the variable-temperature NMR studies, exchange rate constants were determined by visual comparison of the observed and computer-simulated spectra.[17] The rate constants derived from the different sets of coalescing resonances gave the same activation parameters. This points to the operation of a single exchange mechanism with $\Delta H^{\ddagger} = 12.3 \pm 0.4$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = -0.3 \pm 1.3$ cal K$^{-1}$ mol$^{-1}$. The rate constant (extrapolated to 298 K) of 5080 s$^{-1}$ is about 2300 times greater than $k_{-1}$ in Table 1, again signaling the absence of ligand dissociation in the enantiomeric conversion.

An intramolecular isomerization process requires a vacant coordination site with appropriate orbital geometry which may be brought about by rearranging **4**−**6** toward a five-coordinate pseudo four-legged piano-stool complex containing an $\eta^1$-$C_5H_5$ ligand (as drawn in Figure 1). For comparison, the activation enthalpies for intramolecular ligand rearrangements in the five-coordinate d$^6$ ruthenium complexes $Ru(PPh_3)_3Cl_2$ and $Ru(PPh_3)_3(H)(Cl)$ have been reported to be 10.0 ± 0.4 and 13.4 ± 0.6 kcal mol$^{-1}$, respectively.[18]

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**Supporting Information Available:** Text and tables giving spectroscopic and microanalytical data for **4**−**9** and details of the kinetic measurements (14 pages). Ordering information is given on any current masthead page.

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