η^1-Vinylidene to η^2-Alkyne Isomerization of Tungsten and Molybdenum Complexes

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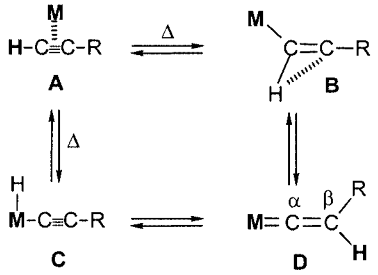
The thermal isomerizations of η^1-vinylidene complexes [(η^5-C_5H_5)(CO)(NO)W=C=CHR] [**5a**, R = $Si(CH_3)_2C(CH_3)_3$; **5c**, R = $C(CH_3)_3$] as well as [(η^5-C_5H_5)(CO)(NO)Mo=C=CHC$(CH_3)_3$] (**8**), to the corresponding η^2-1-alkyne complexes [(η^5-C_5H_5)(CO)(NO)W(η^2-H–C≡C–R)] [**7a**, R = $Si(CH_3)_2C(CH_3)_3$; **7c**, R = $C(CH_3)_3$] and [(η^5-C_5H_5)(CO)(NO)Mo{η^2-H–C≡C–CHC$(CH_3)_3$}] (**9**) has been investigated. Activation parameters for the isomerization of **5a** in [D$_6$]benzene and **8** in [D$_8$]toluene and [D$_5$]ethanol were determined. In [D$_8$]toluene η^1-vinylidene complex **5a** undergoes a single step 1,2-shift of the silyl group from C_β to C_α. However, complex **8** shows dichotomous behavior. The isomerization **8** → **9**, dependent upon the solvent applied, occurs by means of two different pathways: in a nonpolar solvent, **8** tautomerizes via the 1,2-migration of the hydrogen atom to **9** and in ethanol this tautomerization proceeds by a multi-step process via deprotonation-protonation and subsequent reductive elimination.

Introduction

A great deal of attention has been devoted to the isomerization of transition metal η^1-vinylidene and η^2-1-alkyne complexes over the past two decades.[1] Thus, it is now well established that the thermodynamic stabilities and properties of such derivatives are essentially a function of the nature of both the metal center and its ancillary ligands.[1,2] It is well-known that η^1-vinylidene complexes of electron-rich transition metals are thermodynamically more stable than the corresponding η^2-1-alkyne derivatives.[1,3] This fact is widely used in the preparation of η^1-vinylidene complexes.[4]

The mechanism of the η^2-1-alkyne → η^1-vinylidene rearrangement has been extensively studied both experimentally and theoretically.[2,4,5–8] Two alternative pathways are discussed so far in the literature (Scheme 1): via either an intramolecular 1,2-hydrogen shift (A−B−D)[2,4e,6a,6b] or by the formation of a hydride alkynyl species C and concomitant 1,3-hydrogen shift.[4a,4c,4d,4f,5a,8,6b] Electron-rich metal complexes favor the A−C−D[4a,4d,8b] pathway whereas electron poor complexes prefer the A−B−D[4e,5a,6a] pathway.

The reaction order for the 1,3-hydrogen shift is also a matter of active debate. Recent experimental and theoretical studies demonstrated a bimolecular mode for this process[4c,4a,4d,9] while others support a unimolecular reaction.[2]



Scheme 1. Alternative pathways for the η^2-1-alkyne → η^1-vinylidene rearrangement

The isomerization of η^1-vinylidene transition metal complexes into the corresponding η^2-alkyne complexes has rarely been described in the literature.[5] Bly et al.[5g,5h] have observed the isomerization of the cationic complexes [Fe(=C=CR^{1}R^2)(η^5-C_5H_5)$(CO)_2$]$^+$OTf$^-$ to the corresponding η^2-alkyne derivatives [Fe(η^2-R^{1}C≡CR^2)(η^5-C_5H_5)$(CO)_2$]$^+$OTf$^-$ by an alkyl shift from the β- to α-carbon atom. In the same way, Connelly et al.[5b,5g,5i] have observed η^1-vinylidene → η^2-alkyne rearrangements induced by one-electron oxidation of the 18-electron complexes [M=C=C$(SiMe_3)_2$(η^6-C_6R_6)$(CO)_2$]$^+$ (M = Cr, Mo).

To shed some light on the mechanism of the η^1-vinylidene → η^2-alkyne isomerization we have studied the thermal isomerization of the tungsten η^1-vinylidene complexes **5a−c**, as well as of the molybdenum derivatives **8**.

Results

Synthesis and Characterization of 5a,b

The reaction of the tungsten carbonyl complex **1** with lithium alkynyl **2a,b** in THF at −30 °C led to a deep green

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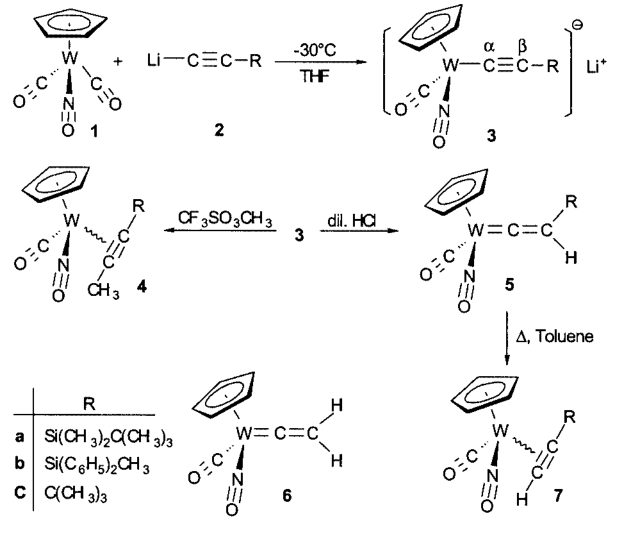
solution of the lithium metalate **3a,b** (Scheme 2). Treatment of this solution with dilute HCl resulted, after purification through chromatography, in the formation of the η^1-vinylidene complexes **5a,b** as a mixture of two rotamers. It is interesting to note that, after protonation the C−Si bond is cleaved, in the course of the reaction of **3b**, yielding the η^1-vinylidene complex **6** (21% yield).[10] This behavior has precedents in the literature, i.e., the formation of [CpRu=C=CH$_2$(dippe)][BPh$_4$] from [CpRuCl(dippe)] with H−C≡C−SiMe$_3$,[4g] and the formation of [CpFe=C=CH$_2$(dppm)][BF$_4$] from [CpFe−C≡C−SiMe$_3$(dppm)].[11]



Scheme 2. Synthesis of vinylidene complexes **5** and **6** from the tungsten complexes **1**

Compound **5a** is an orange crystalline solid, whereas **5b** is a dark red oil. These η^1-vinylidenes can be stored under argon at −20 °C for several months. Their unequivocal characterization was achieved by means of standard spectroscopic techniques and, in particular, by the ^{13}C NMR signal at $\delta = 331-335$ ppm that is characteristic for the α-carbon atom of the η^1-vinylidene moiety.

Upon treatment of the deep green solution of lithium metalate **3a,b** with methyltrifluoromethanesulfonate at −30 °C, the η^2-alkynes **4a,b** were obtained (Scheme 2). We suppose that the alkylation of the metalate anion occurs at the β-carbon atom generating the corresponding η^1-vinylidene complexes, which then isomerize by migration of the silyl group to **4a,b**. Structural assignment of the η^2-alkynes **4a,b** are based on NMR spectroscopic data and by the characteristic C≡C stretching vibration in IR spectra, respectively.[12]

Isomerization of η^1-Vinylidene Complexes

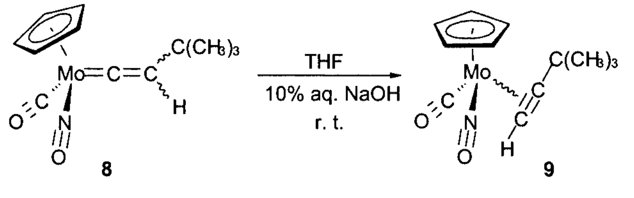
Molybdenum-vinylidene complex **8** and tungsten derivatives **5a,b** rearrange under refluxing toluene to the corresponding η^2-alkyne complexes **9** and **7a,b**. Whereas the tungsten η^1-vinylidene complex **5c** with a *tert*-butyl group at the β-carbon atom, is much more stable than **5a,b** and **8** and rearranges very poorly upon heating at 110 °C to the corresponding η^2-alkyne complex **7c**. The η^1-vinylidene/η^2-alkyne ratios of the interconversion of **8**, **5a,b** and **5c** after heating in toluene for 24 h are reported in Table 1. Longer reaction times lead to the decomposition of **5b** and **5c**. Interestingly the isomerization rate of **8** is highly dependent on the nature of the solvent. In ethanol as the solvent the transformation occurs quantitatively after heating for 2 h at 79 °C.[13]

Table 1. Product ratios of the thermal interconversion of the η^1-vinylidenes **8**, **5a−c** after 24 h at 110 °C

η^1-Vinylidene complexes	Product ratio[a] η^2-alkyne: η^1-vinylidene[b]
[Mo{=C=CHC(CH$_3$)$_3$}(η^5-C$_5$H$_5$)-(CO)(NO)] (**8**)	100:0
[W{=C=CHSi(CH$_3$)$_2$C(CH$_3$)$_3$}(η^5-C$_5$H$_5$)-(CO)(NO)] (**5a**)	79:21
[W{=C=CHSi(C$_6$H$_5$)$_2$CH$_3$}(η^5-C$_5$H$_5$)-(CO)(NO] (**5b**)	63:37
[W{=C=CHC(CH$_3$)$_3$}(η^5-C$_5$H$_5$)(CO)-(NO)] (**5c**)	6:94

[a] All reactions were carried out in toluene. [b] The product ratios were determined by measuring the relative peak integration of the ^{1}H NMR signals of the η^2-alkyne and η^1-vinylidene complexes in the crude product spectra.

Also a quantitative isomerization to **9** is observed by treating the THF solution of **8** at room temperature with 10% aqueous NaOH for 20 min (Scheme 3).



Scheme 3. Base-catalyzed isomerization of vinylidene complexes **8**

Kinetic Studies

a) Isomerization in a Nonpolar Solvent

The isomerization rates of **8** to **9** were measured at fixed temperatures between 80 °C and 140 °C in [D$_8$]toluene while the rate of transformation of **5a** to **7a** was measured between 130 °C and 150 °C in [D$_6$]benzene by varying the starting concentration of the η^1-vinylidene complexes.[14] The results indicate that the η^1-vinylidene → η^2-alkyne isomerization is first-order. The first-order rate constants measured at five different temperatures are listed in Table 2 and 3. From the Eyring plot, we derived the activation parameters for **8** → **9**: $\Delta H^{\#} = 29.0 \pm 0.5$ (kcal·mol^{-1}) and $\Delta S^{\#} = -1.8 \pm 0.2$ (cal/mol·K) and for **5a** → **7a**: $\Delta H^{\#} = 27.2 \pm 0.4$ (kcal·mol^{-1}) and $\Delta S^{\#} = -9.7 \pm 0.9$ (cal/mol·K). For the rearrangement of [RuCp(H−C≡C−Me)(PMe$_3$)$_2$]PF$_6$ to [RuCp(=C=CHMe)(PMe$_3$)$_2$]PF$_6$ the kinetic study in CH$_3$CN by Bullock gave $\Delta H^{\#} = 23.4 \pm 0.3$ kcal·mol^{-1} and $\Delta S^{\#} = 3.9 \pm 0.9$ (cal/mol·K).[15]

Table 2. Rates of the isomerization and kinetic deuterium isotope effect of **5a** to **7a** and **5a-D** to **7a-D** in [D$_6$]benzene

Temp. (°C)	10^4k_H (s^{-1})	r[a]	10^4k_D (s^{-1})	r[a]	k_H/k_D
130	1.174	0.999	0.957	0.999	1.227
135	1.731	0.999	1.482	0.999	1.168
140	2.706	0.998	2.310	0.999	1.172
145	4.037	0.999	3.414	0.999	1.182
150	6.067	0.999	4.939	0.999	1.228
					average: 1.196 ± 0.030

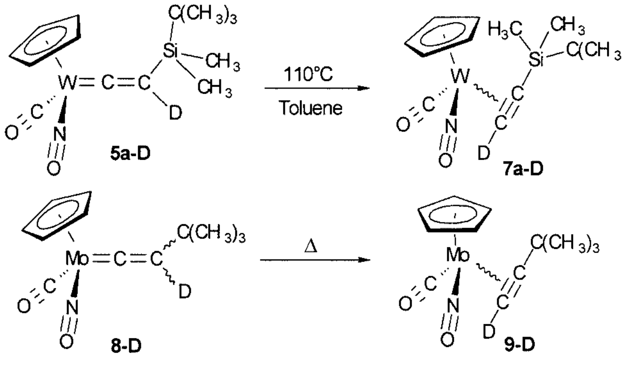
[a] Correlation coefficient for the first-order plot.

Table 3. Rates of the isomerization and kinetic deuterium isotope effect of **8** to **9** and **8-D** to **9-D** in [D$_8$]toluene

Temp. (°C)	10^5k_H (s^{-1})	r[a]	10^5k_D (s^{-1})	r[a]	k_H/k_D
80.0	0.558	0.999	0.280	0.999	2.0
90.2	1.733	0.998	0.920	0.998	1.9
106.2	11.483	0.999	5.266	0.999	2.2
121.4	43.883	0.998	22.070	0.998	2.0
139.6	236.516	0.999	123.489	0.999	1.9
					average: 2.00 ± 0.2

[a] Correlation coefficient for the first-order plot.

Principally the isomerization of **5a** to **7a** can occur either by migration of the silyl group or of the hydrogen atom from C$_\beta$ to C$_\alpha$, however, a priori it is not possible to differentiate between one or the other reaction path. In order to distinguish between these two possibilities, we determined the kinetic deuterium isotope effect for the conversion of [(η^5-C$_5$H$_5$)(CO)(NO)W=C=CDSi(CH$_3$)$_2$C(CH$_3$)$_3$] (**5a-D**) to [(η^5-C$_5$H$_5$)(CO)(NO)W{η^2-DC≡CSi(CH$_3$)$_2$C(CH$_3$)$_3$}] (**7a-D**) and as a comparison the kinetic deuterium isotope effect for the transformation **8-D** to **9-D** (Scheme 4).



Scheme 4. Thermal isomerization of **5a-D** and **8-D**

The $k_{5a \to 7a}/k_{5a\text{-}D \to 7a\text{-}D}$ in [D$_8$]toluene was found to be 1.20 ± 0.03 and $k_{8 \to 9}/k_{8\text{-}D \to 9\text{-}D}$ = 2.00 ± 0.2 (Table 2 and 3), both effects show very minor temperature dependency. The kinetic isotope effect for the former reaction is in the range of normal secondary isotope effects,[16] and is the result of a hybridization change from sp^2 to sp of the C$_\beta$ of the η^1-vinylidene ligand in the transition state during the migration of the silyl group. Contrary, for the later isomerization, k_H/k_D suggests that the bond to the isotopically substituted hydrogen atom is being broken in the rate-determining step. The 1,2-shift of the silyl group is also supported by the comparison of the isomerization ability of **5a** and **5b** versus **5c** where the reaction rate decreases in the order: Si(CH$_3$)$_2$C(CH$_3$)$_3$ > Si(C$_6$H$_5$)$_2$(CH$_3$) > C(CH$_3$)$_3$.[17]

b) Isomerization in Ethanol

In order to obtain more information on the mechanism of the η^1-vinylidene → η^2-alkyne isomerization we examined the isomerization of **8** in ethanol as the solvent. The isomerization rate of **8** in C$_2$D$_5$OH, measured in a 0.1 M solution at fixed temperatures between 60 °C and 100 °C, is much faster than the reaction rate in [D$_8$]toluene. The pseudo first-order rate constants are listed in Table 4. From Eyring plots we have obtained the activation parameters for the isomerization **8** → **9** in C$_2$D$_5$OH, $\Delta S^{\#} = -21.3 \pm 0.5$ (cal/mol·K) and $\Delta H^{\#} = 19.6 \pm 1.6$ kcal·mol^{-1}. Compared to the isomerization in [D$_8$]toluene, the most striking point of the thermodynamics of the reaction, is the high negative value of $\Delta S^{\#}$ in C$_2$D$_5$OH. This leads one to suppose, that in toluene and ethanol two different mechanisms govern the reaction. This presumption is further strongly supported by the large differences of the kinetic isotope effect for $k_{8 \to 9}$ measured in C$_2$D$_5$OH and $k_{8\text{-}D \to 9\text{-}D}$ in C$_2$D$_5$OD versus the $k_{8 \to 9}/k_{8\text{-}D \to 9\text{-}D}$ measured in [D$_8$]toluene as the solvent. The $k_{8 \to 9}/k_{8\text{-}D \to 9\text{-}D}$ ratio also shows a large temperature dependency in ethanol contrary to the value in toluene. From extrapolation of the reaction rate the values k_H/k_D = 15.7 at 60 °C and k_H/k_D = 7.1 at 100 °C, are obtained.

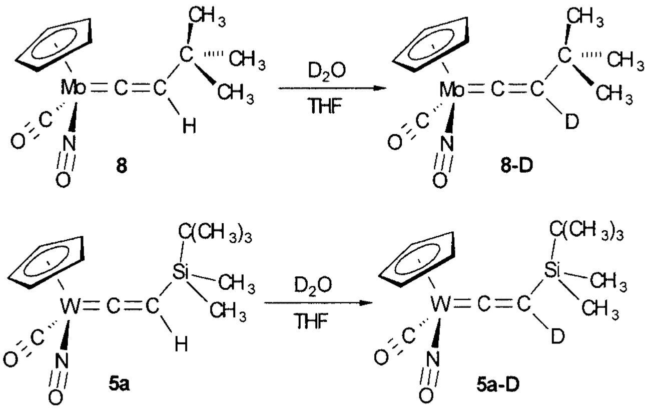
Table 4. Rates of the isomerization and kinetic deuterium isotope effect of **8** to **9** in [D$_5$]ethanol and **8-D** to **9-D** in [D$_6$]ethanol (k_H/k_D = 15.7 at 60 °C and 7.1 at 100 °C)

8 → 9			**8-D → 9-D**		
Temp. (°C)	10^4 k_H (s^{-1})	r[a]	Temp. (°C)	10^4 k_D (s^{-1})	r[a]
59.0	1.070	0.998	83.7	0.717	0.998
69.0	2.200	0.998	94.4	2.233	0.999
79.3	4.450	0.999	106.2	5.417	0.998
88.5	8.833	0.999	116.2	12.867	0.999
97.6	24.920	0.998	125.0	25.68	0.999

[a] Correlation coefficient for the first-order plot.

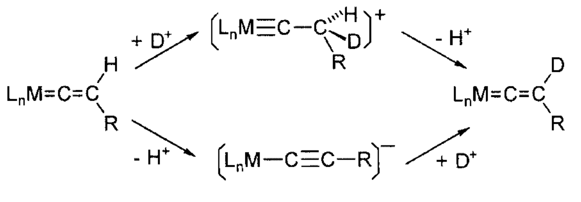
H/D Exchange

The η^1-Vinylidene derivatives **8** and **5a** undergo H/D exchange at the C_β atom without isomerization. Treatment of tetrahydrofuran solutions of **5a** at room temperature and **8** at 45 °C with D_2O produces the corresponding deuterated derivatives **8-D** and **5a-D** (Scheme 5).



Scheme 5. H/D exchange of vinylidene complexes **8** and **5a**

Besides the deprotonation-deuteration pathway, it is conceivable that the H/D exchange occurs by the prior addition of deuterium to yield a carbyne derivative (Scheme 6).



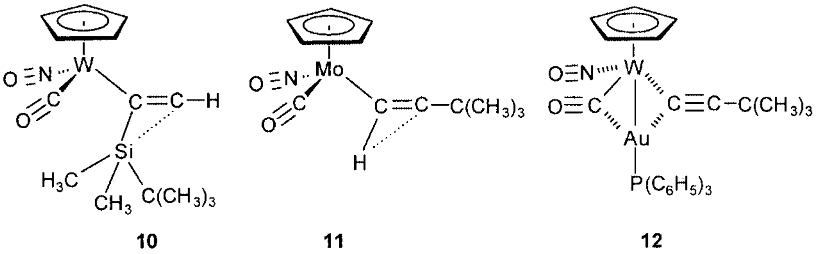
Scheme 6. Alternative mechanisms for the H/D exchange of vinylidene complexes

Theoretical studies on vinylidene transition metal complexes have identified the electron density on the C_β atom,[18] and the protonation of vinylidene complexes to the carbyne derivatives occurs via another mechanism.[9,19] In order to distinguish between these two possibilities we investigated the exchange rate in the presence of D_2O and C_6D_5OD, respectively. While after 3 h at 45 °C the H/D exchange in 10 molar D_2O/[D_8]THF was complete, no exchange occurred in the presence of C_6D_5OD. The result of this experiment clearly shows that the H/D exchange occurs by a dissociative pathway.

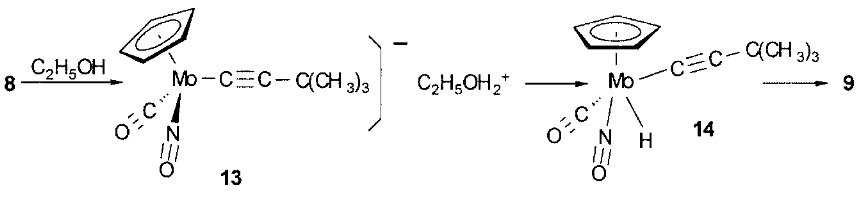
Discussion

Our kinetic study of the isomerization of **8** → **9** and **5a** → **7a** suggests that the η^1-vinylidene → η^2-alkyne isomerization of the molybdenum and tungsten complexes studied here, follows two different pathways.

In nonpolar solvents such as toluene or benzene, starting from the η^1-vinylidene **5a**, a 1,2-shift of the silyl group takes place by forming the transition state **10** (Scheme 7). Slippage processes of the silyl group as well as the metal, followed by C−Si σ bonding and π coordination of the metal center generated the η^2-alkyne complexes **7**. The magnitude of the kinetic isotope effect and the activation entropy observed for the isomerization **5a** → **7a** are in good agreement with an isomerization mechanism of least motion; namely, the 1,2-silyl group shifts in a concerted fashion.[20,21] In the same manner the thermal tautomerization of **8** in nonpolar solvents occurs by a 1,2-migration of the hydrogen atom leading to the transition state **11**, followed by a slippage of the metal to yield the η^2-1-alkyne complex **9**. The observed kinetic isotope effect supports the isomerization pathway, **D**→**B**→**A** (Scheme 1) with an asymmetrically bonded transition state in a single-step hydrogen or silyl transfer reaction for both transformations depicted as **10** and **11**.[22,23]



Scheme 7. Postulated transition states **10** and **11** and structure of gold complexes **12**



Scheme 8. Postulated mechanism for the isomerization of vinylidene complexes **8** in ethanol

Additionally we have recently synthesized and structurally characterized the gold-tungsten complex **12** which has similar structural features to **10** and **11** and shows a fluxional behavior.[24]

Contrary to the isomerization in nonpolar solvents, the kinetic data of the isomerization **8** → **9** in ethanol suggests a two-step dissociation-addition process (Scheme 8). The high value of $k_{\mathbf{8}\rightarrow\mathbf{9}}/k_{\mathbf{8\text{-}D}\rightarrow\mathbf{9\text{-}D}}$ and its temperature dependency supports this mode of isomerization and suggests that it is even more likely that a tunneling process takes place for this reaction.[22,23] According to this data we suppose that the tautomerization of **8** occurs via a deprotonation step generating the η^1-alkynyl complex **13** followed by the protonation on molybdenum to the hydrido-alkynyl complex **14** which undergoes reductive elimination to the η^2-1-alkyne isomer **9**. The NaOH catalyzed isomerization of **8** (see Scheme 3) is in agreement with this hypothesis as it supports a deprotonation-protonation process. All attempts to isolate the hydrido-alkynyl complex were unsuccessful.

The tautomerization of η^2-1-alkyne via hydrido-alkynyl complexes is often postulated in the literature as a concerted 1,3-hydrogen shift.[1,4f] However, this mechanism was found to be, in general, energetically too costly.[4b,4h] Our results, however, support the findings that isomerization via a hydrido-alkynyl complex proceeds in a nonconcerted fashion.

Experimental Section

General Remarks: All reactions were carried out under argon (99.99%, by Messer−Griesheim) with the use of standard Schlenk techniques. Solvents were purified by standard methods and distilled under argon prior to use. Literature methods were used to prepare $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)]$ and $[(\eta^5\text{-}C_5H_5)W(CO)_2(NO)]$,[25] (*tert*-butyldimethylsilyl)acetylene,[26] (methyldiphenylsilyl)acetylene,[26] $[(\eta^5\text{-}C_5H_5)(CO)(NO)Mo{=}C{=}CHC(CH_3)_3]$ (**8**);[12] **7c**, and **5c**[12] and $[(\eta^5\text{-}C_5H_5)(CO)(NO)W{=}C{=}CHSi(CH_3)_2C(CH_3)_3]$ (**5a**).[27] All other compounds were commercially available. NMR spectra were obtained with a Bruker AM 400 spectrometer (^{1}H NMR, 400.13 MHz. ^{13}C NMR, 100.61 MHz). Proton and carbon chemical shifts are reported in ppm relative to the residual proton resonance (δ = 7.24 ppm) or the carbon multiplet (δ =77.0 ppm) of the NMR solvent $CDCl_3$. When [D$_6$]benzene is used as solvent for a ^{1}H NMR spectrum, the shifts are reported in ppm relative to the residual proton resonance at δ = 7.17 ppm. ^{13}C DEPT experiments were run with the Bruker AM 400 spectrometer. MS measurements (70 eV) were performed with a Varian MAT 311-A. IR spectra were recorded with a Bruker FT-IR IFS 85. Microanalyses were done with a Carlo Erba 1104 elemental analyzer.

Synthesis of the Vinylidene Complexes. $[(\eta^5\text{-}C_5H_5)(CO)(NO)W{=}C{=}CHSi(C_6H_5)_2CH_3]$ (5b): At −78 °C *n*BuLi (3 mL, 4.5 mmol; a solution of 1.5 mmol/mL in hexane) was added to a solution of (methyldiphenylsilyl)acetylene (1.00 g, 4.5 mmol) in THF (10 mL). This solution was added dropwise to $[(\eta^5\text{-}C_5H_5)(CO)_2(NO)W]$ (1.0 g, 3.0 mmol) in THF (60 mL) at −30 °C, whereby the color changed from orange to deep green. The reaction mixture was stirred for 4 h at −30 °C. Addition of 1 mL of concentrated HCl diluted with 20 mL of water led to a dark red solution. After the reaction mixture was allowed to reach room temperature, the THF was removed under reduced pressure. The residue was extracted with diethyl ether, washed with saturated aqueous sodium chloride and dried with magnesium sulfate. The dark red oil was filtered through silica gel (*n*-pentane/diethyl ether, 5:1) to remove decomposition products. Chromatography on silica gel (*n*-pentane/diethyl ether, 5:1) yielded 341 mg (21%) of **5b** as dark red oil and 230 mg (15%) of the unsubstituted vinylidene complex **6** as orange crystals.[12]

Compound 5b: Two rotamers (5:2) were found in the NMR spectra. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 7.65−7.38 (m, 10 H, C_6H_5), 6.02 and 5.93 (2 s, 2:5, 1 H, $C_\beta H$), 5.73 and 5.40 (2 s, 2:5, 5 H, Cp), 0.71 and 0.69 (2 s, 5:2, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 334.9 and 333.6 [$^1J_{C-W}$ = 183.1 Hz, C_α], 212.3 ($^1J_{C-W}$ = 202.6 Hz), 212.0 (CO), 136.0−127.9 (C_6H_5), 118.3 and 117.2 [$^2J_{C-W}$ = 34.5 Hz, C_β], 95.4 and 95.3 (Cp), −2.0 and −2.2 (CH_3) ppm. IR (KBr): ṽ = 1990 (s, C=O), 1636 (s, N≡O), 1595 (s, C=C) cm^{-1}. MS (70 eV): *m*/*z* = 529 [M$^+$, ^{184}W], 501 [M$^+$ − CO], 471 [M$^+$ − CO − NO]. $C_{21}H_{19}NO_2SiW$: calcd. C 47.65, H 3.62, N 2.65; found C 47.28, H 3.32, N 2.89. High-resolution mass spectrum: *m*/*z* calcd. for $C_{21}H_{19}NO_2Si^{182}W$ [M$^+$] 527.0668, found 527.0667.

Compound 6: ^{1}H NMR ($CDCl_3$, 25 °C): δ = 5.87 (s, 5 H, Cp), 5.28 ($^3J_{W\text{-}H}$ = 6 Hz), 5.21 [2 d, 2 H, $^2J_{H,H}$ = 19 Hz, CH_2] ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 341.2 (C_α), 209.9 (CO), 112.2 (C_β), 96.3 (Cp) ppm. IR (KBr): ṽ = 1998 (CO), 1635 (NO), 1591 (C=C) cm^{-1}. IR (CCl_4): ṽ = 2008 (CO), 1654 (NO), 1618 (C=C) cm^{-1}. MS (70 eV): *m*/*z* = 333 [M$^+$, ^{184}W], 305 [M$^+$ − CO], 275 [M$^+$ − CO − NO]. $C_{14}H_{11}NO_2W$: calcd. C 28.86, H 2.12, N 4.21; found C 29.17, H 1.74, N 4.29. High-resolution mass spectrum: *m*/*z* calcd. for $C_{14}H_{11}NO_2{}^{186}W$ [M$^+$] 335.0021, found 335.0027.

$[(\eta^5\text{-}C_5H_5)(CO)(NO)W{=}C{=}CDSi(CH_3)_2C(CH_3)_3]$ (5a-D): A solution of vinylidene **5a** (300 mg) in THF (5 mL) and D_2O (5 mL) was stirred for 2 h at room temperature. After removal of THF and D_2O under reduced pressure, the residue was dried under vacuum for several hours. Spectroscopically pure orange crystals of **5a-D** were obtained (m.p. 60 °C). $C_{14}DH_{20}NO_2SiW$: calcd. C 37.51, H 4.50, N 3.12; found C 37.32, H 4.53, N 3.28. Two rotamers were found in the NMR spectra. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 5.76 (s, 5 H, Cp), 0.91 and 0.89 [2 s, 3:2, 9 H, $C(CH_3)_3$], 0.13, 0.10 and 0.09 (3 s, overlapping, diastereotopic methyl groups, 6 H, $Si[CH_3)_2C(CH_3)_3]$ ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 333.0 and 331.0 (C_α), 213.8 and 212.0 (CO), 118.5 ($^1J_{C-D}$ = 20.8 Hz) and 117.5 ($^1J_{C-D}$ = 22.2 Hz) (C_β), 95.4 and 95.2 (Cp), 26.1 [$C(CH_3)_3$], 17.6 and 17.1 [$C(CH_3)_3$], −4.4, −4.5 and −4.8 [$Si(CH_3)_2C(CH_3)_3$] ppm. IR (KBr): ṽ = 1999 and 1975 (s, C=O), 1635 and 1617 (s, N≡O), 1584 (s, C=C) cm^{-1}. MS (70 eV): *m*/*z* = 448 [M$^+$, ^{184}W], 420 [M$^+$ − CO]. High-resolution mass spectrum: *m*/*z* calcd. for $C_{14}DH_{20}NO_2Si^{182}W$ [M$^+$] 446.0887, found 446.0884.

Synthesis of the η^2-Alkyne Complexes. $[(\eta^5\text{-}C_5H_5)(CO)(NO)W\{\eta^2\text{-}H_3C{-}C{\equiv}C{-}Si(CH_3)_2C(CH_3)_3\}]$ (4a): The preparation of **4a** is analogous to that of **5a**, but, instead of diluted HCl, (0.5 mL, 4.5 mmol) trifluoromethanesulfonate was used. This solution was stirred for 1 h at −30 °C. After usual workup the dark red oil was chromatographed on silica gel (*n*-pentane/diethyl ether, 3:1) to yield 927 mg (67%) of **4a** as orange crystals (m.p. 119 °C). $C_{15}H_{23}NO_2SiW$: calcd. C 39.06, H 5.03, N 3.04; found C 39.02, H 4.73, N 2.78. Two rotamers were found in the NMR spectra. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 5.65 and 5.60 ppm (2 s, 6:1, 5 H, Cp), 2.92 and 2.87 (2 s, 1:6, 3 H, C≡CCH$_3$), 0.96 and 0.90 [2 s, 6:1, 9 H, $C(CH_3)_3$], 0.30 ($^2J_{H-Si}$ = 6.3 Hz), 0.24 and 0.16 [3 s, overlapping, diastereotopic methyl groups, 6 H, $Si(CH_3)_2C(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 220.0 (CO), 122.5 (alkyne C), 95.9 and 95.8 (Cp), 90.7 (alkyne C), 26.6 and 26.5 [$C(CH_3)_3$], 20.6 and 18.6 [$C(CH_3)_3$], 18.2 and 15.7 ($C{\equiv}CCH_3$), −3.8 and −3.9 [$Si(CH_3)_2C(CH_3)_3$] ppm. IR (KBr): $\tilde{\nu}$ = 1986 (s, C=O), 1827 (m, $C{\equiv}C$), 1558 (s, $N{\equiv}O$) cm^{-1}. MS (70 eV): *m*/*z* = 461 [M^+, ^{184}W], 433 [$M^+ - CO$]. High-resolution mass spectrum: *m*/*z* calcd. for $C_{15}H_{23}NO_2Si^{182}W$ [M^+] 459.0981, found 459.0974.

[$(\eta^5\text{-}C_5H_5)(CO)(NO)W\{\eta^2\text{-}H_3C{-}C{\equiv}C{-}Si(C_6H_5)_2CH_3\}$] (4b): The preparation was carried out as described for **4a**, but, instead of (*tert*-butyldimethylsilyl)acetylene, (1.00 g, 4.5 mmol) (methyldiphenylsilyl)acetylene was used. After usual workup the dark red oil was chromatographed on silica gel (*n*-pentane/diethyl ether, 7:1) to yield 760 mg (47%) of **4b** as a dark red oil. $C_{22}H_{21}NO_2SiW$: calcd. C 48.63, H 3.90, N 2.58; found C 48.90, H 3.58, N 2.77. Two rotamers were found in the NMR spectra. ^1H NMR ($CDCl_3$, 25 °C): δ = 7.62−7.33 (m, 10 H, C_6H_5), 5.57 and 5.37 [2 s, 1:8, $^2J_{H-W}$ = 9.5 Hz, , 5 H, Cp], 2.88 and 2.82 (2 s, 8:1, 3 H, $C{\equiv}CCH_3$), 0.83 ($^2J_{H-Si}$ = 6.6 Hz) and 0.79 [2 s, 8:1, 3 H, $Si(C_6H_5)_2CH_3$] ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 219.1 ($^1J_{C-W}$ = 183.1 Hz) and 217.5 (CO), 136.8−127.8 (C_6H_5), 127.4 [$^1J_{C-W}$ = 13.9 Hz, alkyne C], 96.0 and 95.8 (Cp), 90.7 [$^1J_{C-W}$ = 38.9 Hz, alkyne C], 20.4 and 15.5 ($C{\equiv}CCH_3$), −2.0 ($^1J_{C-Si}$ = 56.9 Hz) and −2.9 [$Si(C_6H_5)_2CH_3$] ppm. IR (KBr): $\tilde{\nu}$ = 1966 (s, C=O), 1806 (s, $C{\equiv}C$), 1575 (s, $N{\equiv}O$) cm^{-1}. MS (70 eV): *m*/*z* = 543 [M^+, ^{184}W], 515 [$M^+ - CO$], 485 [$M^+ - CO - NO$]. High-resolution mass spectrum: *m*/*z* calcd. for $C_{22}H_{21}NO_2Si^{182}W$ [M^+] 541.0820, found 541.0817.

[$(\eta^5\text{-}C_5H_5)(CO)(NO)W\{\eta^2\text{-}H{-}C{\equiv}C{-}Si(CH_3)_2C(CH_3)_3\}$ (7a): A solution of vinylidene **5a** (300 mg) in toluene (30 mL) was heated for 24 h under reflux. After removal of the solvent under reduced pressure at room temperature, the dark red oily residue was chromatographed on silica gel (*n*-pentane/diethyl ether, 7:1) to yield 152 mg (51%) of **7a** as orange crystals (m.p. 66 °C). $C_{14}H_{21}NO_2SiW$: calcd. C 37.60, H 4.73, N 3.13; found C 37.87, H 4.57, N 2.90. Two rotamers were found in the NMR spectra. ^1H NMR ($CDCl_3$, 25 °C): δ = 8.74 ($^2J_{H-W}$ = 7.8 Hz) and 8.12 [2s, 1:5, $^2J_{H-W}$ = 8.8 Hz, 1 H, $C{\equiv}CH$], 5.67 and 5.62 (2 s, 5:1, 5 H, Cp), 0.97 and 0.93 [2 s, 5:1, 9 H, $C(CH_3)_3$], 0.32 ($^2J_{H-Si}$ = 6.1 Hz), 0.27, 0.25 (6.0 Hz) and 0.18 [4 s, diastereotopic methyl groups, 5:1:5:1, 6 H, $Si(CH_3)_2C(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 219.2 and 218.4 [$^1J_{C-W}$ = 178.4 Hz, CO], 121.9 and 115.7 [$^1J_{C-W}$ = 15.4 Hz, $C{\equiv}CH$], 105.1 ($^1J_{C-W}$ = 40.3 Hz) and 97.1 ($C{\equiv}CH$), 95.9 (Cp), 26.5 and 26.4 [$C(CH_3)_3$], 18.2 and 17.8 [$C(CH_3)_3$], −3.6 ($^1J_{C-Si}$ = 52.2 Hz), −4.1 ($^1J_{C-Si}$ = 54.5 Hz), −4.5 and −4.8 [$Si(CH_3)_2C(CH_3)_3$] ppm. IR (KBr): $\tilde{\nu}$ = 1965 (s, C=O), 1713 (m, $C{\equiv}C$), 1565 (s, $N{\equiv}O$) cm^{-1}. MS (70 eV): *m*/*z* = 447 [M^+, ^{184}W], 419 [$M^+ - CO$]. High-resolution mass spectrum: *m*/*z* calcd. for $C_{14}H_{21}NO_2Si^{182}W$ [M^+] 445.0825, found 445.0824.

[$(\eta^5\text{-}C_5H_5)(CO)(NO)W\{\eta^2\text{-}H{-}C{\equiv}C{-}Si(C_6H_5)_2CH_3\}$] (7b): The preparation of **7b** is analogous to that of **7a**, but, instead of complex **5a**, vinylidene **5b** (300 mg) was used. Chromatography on silica gel (*n*-pentane/diethyl ether, 7:1) yielded 60 mg (20%) of **7b** as dark red oil and 40 mg (13%) of the starting material **5b** as orange crystals. $C_{21}H_{19}NO_2SiW$: calcd. C 47.65, H 3.62, N 2.65; found C 47.20, H 3.34, N 2.86. Two rotamers were found in the NMR spectra. ^1H NMR ($CDCl_3$, 25 °C): δ = 9.10 ($^2J_{H-W}$ = 7.4 Hz) and 8.54 ($^2J_{H-W}$ = 8.8 Hz) (2s, 1:5, 1 H, $C{\equiv}CH$), 7.64 and 7.33 (m, 10 H, C_6H_5), 5.59 and 5.38 (2 s, 5:1, 5 H, Cp), 0.84 ($^2J_{H-Si}$ = 6.5 Hz) and 0.83 (2 s, 5:1, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 217.6 ($^1J_{C-W}$ = 177.6 Hz) and 217.0 (CO), 136.4−126.7 (C_6H_5), 120.1 [$^1J_{C-W}$ = 15.3 Hz, $C{\equiv}CH$], 105.2 [$^1J_{C-W}$ = 40.2 Hz, $C{\equiv}CH$], 96.0 and 95.9 (Cp), −1.9 ($^1J_{C-Si}$ = 58.3 Hz), −2.9 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 1983 (s, C=O), 1699 (m, $C{\equiv}C$), 1594 (s, $N{\equiv}O$) cm^{-1}. MS (70 eV): *m*/*z* = 529 [M^+, ^{184}W], 501 [$M^+ - CO$], 471 [$M^+ - CO - NO$]. High-resolution mass spectrum: *m*/*z* calcd. for $C_{21}H_{19}NO_2Si^{182}W$ [M^+] 527.0668, found 527.0681.

[$(\eta^5\text{-}C_5H_5)(CO)(NO)W\{\eta^2\text{-}H{-}C{\equiv}C{-}C(CH_3)_3\}$] (7c): The preparation of **7c** is analogous to that of **7a**, but, instead of complex **5a**, vinylidene **5c** (1000 mg) was used. Chromatography on silica gel with 10:1 *n*-pentane/diethyl ether yielded 24 mg (2%) of **7c** as light orange crystals and 563 mg (56%) of the starting material **5c** as orange crystals. $C_{12}H_{15}NO_2W$: calcd. C 37.04, H 3.89, N 3.60; found C 37.32, H 3.70, N 3.40. Two rotamers were found in the NMR spectra. ^1H NMR ($CDCl_3$, 25 °C): δ = 7.45 ($^2J_{H-W}$ = 8.0 Hz) and 6.98 ($^2J_{H-W}$ = 9.2 Hz) (2 s, 1:6, 1 H, $C{\equiv}CH$), 5.77 and 5.68 (2 s, 6:1, 5 H, Cp), 1.35 and 1.32 [2 s, 6:1, 9 H, $C(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 215.5 (CO), 133.7 ($^1J_{C-W}$ = 52.0 Hz) and 124.4 ($^1J_{C-W}$ = 13.6 Hz) (alkyne C), 96.4 and 96.0 (Cp), 91.0 ($^1J_{C-W}$ = 43.1 Hz) and 88.1 ($^1J_{C-W}$ = 8.9 Hz) (alkyne C), 36.4 and 34.6 [$C(CH_3)_3$], 31.9 and 31.0 [$C(CH_3)_3$] ppm. IR (KBr): $\tilde{\nu}$ = 1977 (s, C=O), 1736 (m, $C{\equiv}C$), 1556 (s, $N{\equiv}O$) cm^{-1}. MS (70 eV): *m*/*z* = 389 [M^+, ^{184}W], 361 [$M^+ - CO$]. High-resolution mass spectrum: *m*/*z* calcd. for $C_{12}H_{15}NO_2{}^{182}W$ [M^+] 387.0585, found 387.0553.

Isomerization of 8 to 9 with NaOH: 10% aqueous NaOH (3 mL) was added to a solution of **8** (0.4 mmol) in THF (10 mL). After the reaction mixture was stirred for 20 min at room temperature, the organic layer was separated and the solvent was removed under reduced pressure. The residue was dissolved in diethyl ether and dried with $MgSO_4$. The diethyl ether was removed under reduced pressure, and the ^1H NMR spectrum of the residue was collected. **8** was 100% isomerized to **9**.

Treatment of 8 with D_2O and C_6D_5OD: **8** (0.6 mL, 0.1 mmol) and D_2O (0.2 mL, 10 mmol) in [D_8]THF (1 mL) were heated at 45 °C. At regular time intervals the probe was cooled to −20 °C, which was followed by the measuring of the relative peak integration of the ^1H NMR $C_\beta{-}H$ signal [([D_8]THF) δ = 5.93 and 5.91 ppm] of **8**. After 3 h the H/D exchange was complete. The same experiment with perdeuterated phenol (C_6D_5OD) instead of D_2O showed no exchange.

[$(\eta^5\text{-}C_5H_5)(CO)(NO)Mo\{\eta^2\text{-}H\text{-}C{\equiv}C\text{-}C(CH_3)_3\}$] (9): At −30 °C, a solution of 7.5 mmol of (*tert*-butylethynyl)lithium in THF (15 mL) was added dropwise to an orange solution of (η^5-C_5H_5)Mo-$(CO)_2(NO)$ (1.24 g, 5 mmol) in THF (50 mL). The progress of the reaction was monitored by IR spectroscopy. After complete disappearance of [$(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)$], at 5 °C, saturated aq. sodium carbonate (30 mL) was added to the deep green reaction mixture, whereby the color changed to red. The solution was concentrated under vacuum and extracted with diethyl ether. The organic layer was dried with $MgSO_4$. The diethyl ether was removed under reduced pressure and the residue was chromatographed (silica gel, pentane) to yield 714 mg (47%) of **9**, as orange crystals, m.p. 71−72 °C (dec, pentane:dichloromethane, 10:1). $C_{12}H_{15}MoNO_2$: calcd. C 47.85, H 5.02, N 4.65; found C 47.84, H 4.83, N 4.72. Two rotamers (ratio 1:5). ^1H NMR ($CDCl_3$, 25 °C): δ = 6.69 and 6.09 ppm (2 s, 1:5, 1 H, $C{\equiv}CH$), 5.65 and 5.55 (2 s, 5:1, 5 H, Cp), 1.37 and 1.34 [2 s, 5:1, 9 H, $C(CH_3)$]. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 226.7 (C=O), 128.0 ($C{\equiv}C$), 97.0 and 96.7 (Cp), 80.5 ($C{\equiv}C$), 35.8 [$C(CH_3)_3$], 32.2 and 31.3 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 1982 (C=O), 1785 ($C{\equiv}C$), 1581 (N=O) cm^{-1}. MS (70 eV): *m*/*z* = 301 [M^+, ^{96}Mo], 273 [$M^+ - CO$], 243 [$M^+ - CO - NO$]. High resolution mass spectrum calcd. for $C_{12}H_{15}{}^{92}MoNO_2$ [M^+]: *m*/*z* = 297.0171, found *m*/*z* = 297.0141.

Kinetic Studies of the η^1-Vinylidene → η^2-Alkyne Isomerization of 8 → 9; 8-D → 9-D in $[D_8]$Toluene and 5a → 7a and 5a-D → 7a-D in $[D_6]$Benzene: A typical experiment was done in the following way. **8** or **8-D** (0.8 mL, 0.1 M) in $[D_8]$toluene as well as a weighted amount of the vinylidene **5a** or **5a-D** (in the range of 20−120 mg) in $[D_6]$benzene (0.8 mL) (measured with a gas-tight syringe) were placed in a dried sealable NMR tube. The solution was freeze-pump-thaw degassed and the NMR tube was sealed under vacuum. The sample was then placed into a thermostat at a fixed temperature (reproducibility ± 0.1 °C). At regular time intervals, the tube was removed and the reaction quenched at room temperature. The reaction time was followed by measuring the relative peak integration of the ^{1}H NMR of the cyclopentadienyl signals of **8** (δ = 5.18 and 5.16 ppm); **9** (δ = 5.06 and 4.92 ppm); **8-D** (δ = 5.18 and 5.16 ppm); **9-D** (δ = 5.06 and 4.92 ppm); *tert*-butyl signals of **5a** (δ = 0.95 ppm); **7a** (δ = 1.01 and 0.99 ppm); **5a-D** (δ = 0.94 ppm) and **7a-D** (δ = 1.01 and 0.99 ppm).

First-order rate constants were derived from least-squares best-fit lines of the ln(%) versus time plots. The uncertainty in the isomerization rate constants was derived from the slope of the best-fit line. Uncertainties in the activation enthalpies and entropies were calculated from the uncertainties in the slope of the best-fit line of the Eyring plot.

Kinetic Studies of the η^1-Vinylidene → η^2-Alkyne. Isomerization of 8 → 9 in $[D_5]$Ethanol and 8-D → 9-D in $[D_6]$Ethanol: The kinetic studies of isomerization of **8** → **9** in $[D_5]$ethanol and **8-D** → **9-D** in $[D_6]$ethanol are analogous to that for the isomerization of **8** → **9** and **8-D** → **9-D** in $[D_8]$toluene. The time course of the reaction was followed by measuring the relative peak integration of the ^{1}H NMR of cyclopentadienyl signals **8** [(C_2D_5OH) δ = 5.83 and 5.81 ppm], **9** [(C_2D_5OH) δ = 5.70 and 5.60 ppm], **8-D** [(C_2D_5OD) δ = 5.82 and 5.81 ppm] and **9-D** [(C_2D_5OD) δ = 5.67 and 5.59 ppm]. Uncertainties in the activation enthalpies and entropies were calculated from the uncertainties in the slope of the best-fit line of the Eyring plot.

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