J. Am. Chem. Soc. 1991, 113, 6082-6090

Direct Observation of α-Hydrogen Transfer from Alkyl to Alkylidyne Ligands in $(Me_3CCH_2)_3W{\equiv}CSiMe_3$. Kinetic and Mechanistic Studies of Alkyl–Alkylidyne Exchange

Kenneth G. Caulton,* Malcolm H. Chisholm,* William E. Streib, and Ziling Xue

Contribution from the Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405. *Received December 19, 1990*

Abstract: α-Hydrogen atoms in $(Me_3CCH_2)_3W{\equiv}CSiMe_3$ are found to migrate to the α-carbon atom of the alkylidyne ligand leading to the equilibrium $(Me_3CCH_2)_3W{\equiv}CSiMe_3$ (**2a**) $\rightleftarrows$ $(Me_3CCH_2)_2(Me_3SiCH_2)W{\equiv}CCMe_3$ (**2b**). The equilibrium has been observed to follow reversible first-order kinetics with $\Delta H^\circ = 2.3\ (0.5)$ kcal mol^{-1} and $\Delta S^\circ = 8.1\ (1.3)$ eu. The activation parameters for the conversion **2a** → **2b** are $\Delta H^\ddagger = 27.5\ (0.6)$ kcal mol^{-1} and $\Delta S^\ddagger = -2.0\ (1.7)$ eu and for the back-reaction **2b** → **2a** are $\Delta H^{\ddagger\prime} = 25.4\ (0.8)$ kcal mol^{-1} and $\Delta S^{\ddagger\prime} = -9.5\ (1.9)$ eu. Isomerizations involving $(Me_3CCD_2)_3W{\equiv}CSiMe_3$ (**2a**-d_6) and $(Me_3CCHD)_3W{\equiv}CSiMe_3$ (**2a**-d_3) revealed that the isomerization between **2a** and **2b** occurred by consecutive α-hydrogen/α-deuterium transfers with a large primary kinetic isotope effect $k_{HH}/k_{DD} = 5.1\ (0.3)$ and $k_{HH}/k_{HD} = 3.0\ (0.2)$ at 100 °C. Crossover experiments indicate that the isomerization is a unimolecular process. These results are discussed in terms of a concerted four-center transition state leading to a bis(alkylidene) activated complex or reactive intermediate. An alternate reaction pathway involving the simultaneous transfer of two α-hydrogen atoms is ruled out by the rule of the geometric mean. The molecular structure of **2a**-d_6 was determined by X-ray crystallography. The molecule has rigorous C_3 symmetry with $W{\equiv}C = 1.739\ (8)$ Å and $W—C_{sp^3} = 2.096\ (5)$ Å. At −169 °C, crystal data are $a = 15.232\ (3)$ Å, $c = 17.140(4)$ Å, $Z = 6$, $d_{calcd} = 1.36$ g cm^{-3}, and space group $R\bar{3}$.

Introduction

The α-hydrogen atoms of so-called β-hydrogen-stabilized alkyl ligands (e.g. CH_2CMe_3 and CH_2SiMe_3) play a pivotal role in the synthesis of high-oxidation-state transition-metal–alkylidene and -alkylidyne complexes.[1,2] Indeed, α-hydrogen abstraction is believed to be one of the primary reactions leading to metal–carbon multiple bonds, as was seen in Schrock's[3] initial synthesis of the η^1-neopentylidene complex, $(Me_3CCH_2)_3Ta{=}CHCMe_3$. Hydridoalkylidenetantalum(V) complexes have been shown to exhibit a hydrogen atom exchange involving the alkylidene α-hydrogen and the hydride ligand: $\mathit{H}Ta{=}CHR \rightleftarrows HTa{=}C\mathit{H}R$.[4] A plausible mechanism for this exchange would involve a Ta(III)–alkyl complex. A similar case was observed wherein hydridoalkylidynetantalum(V) complexes were found to be in equilibrium with alkylidenetantalum(III) complexes: $(H)(RC{\equiv})Ta^V \rightleftarrows RCH{=}Ta^{III}$.[5] Also $Ta(CR_2CMe_3)Cl_4$, where R = H or D, was found to be reduced by Na in the presence of PMe_3 to yield $Ta(R)({=}CRCMe_3)Cl_2(PMe_3)_3$.[6] Alkylidene ligands bonded to highly unsaturated early transition metals have been shown to have weakened C—H bonds as a result of agostic metal α-CH interactions, and this has been the subject of a theoretical study.[7,8]

α-Hydrogen abstraction reactions or isomerizations involving α-CH groups generally involve a formal-oxidation-state change of the metal. α-Hydrogen migrations that occur without a change in oxidation state are less common but have been well documented. Schrock and Fellmann in the study of the formation of $(Me_3CCH_2)_3M{=}CHCMe_3$ (M = Nb, Ta) found that the α-deuterium in $(Me_3CCH_2)_3Ta{=}CDCMe_3$ scrambles among the other α-carbon atoms.[2b] Deuterium-labeling studies involving $(Me_3CCH_2)ClRe(NDCMe_3)(NCMe_3)(CHCMe_3)$ suggest a migration of the neopentylidene α-hydrogen to the imido nitrogen to give the alkylidyne amide complex $(Me_3CCH_2)ClRe(NDCMe_3)(NHCMe_3)({\equiv}CCMe_3)$.[9]

We have initiated a study of the thermal decomposition of group 6 transition-metal complexes containing metal–ligand multiple bonds, e.g. $X_3W{\equiv}Y$ compounds where Y = N or CR, with a view toward their application in metal organic chemical vapor deposition (MOCVD) of thin films. A key question is whether or not the molecular precursor that contains an element-to-tungsten triple bond yields a material wherein that element is selectively retained. During the course of the MOCVD experiments transforming $(Me_3CCH_2)_3W{\equiv}CR$ into WC films, we observed significant quantities of RCH_3 in addition to neopentane and isobutylene in the gas-phase products.[10] This led us to investigate potential molecular-based chemistry that might be responsible for α-hydrogen transfer between the alkylidyne and alkyl ligands. We report the first observations of such α-hydrogen atom transfer in the equilibrium shown in eq 1.

$$\underset{\mathbf{2a}}{(Me_3CCH_2)_3W{\equiv}CSiMe_3} \underset{k'}{\overset{k}{\rightleftarrows}} \underset{\mathbf{2b}}{(Me_3CCH_2)_2(Me_3SiCH_2)W{\equiv}CCMe_3} \quad (1)$$

$$K_{eq} = k/k'$$

---

(1) Reviews: (a) Murdzek, J. S.; Schrock, R. R. In *Carbyne Complexes*; Fischer, H., Hofmann, P., Kreissl, F. R., Schrock, R. R., Schubert, U., Weiss, K., Eds.; VCH: New York, 1988. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988. (c) Aguero, A.; Osborn, J. A. *New. J. Chem.* **1988**, *12*, 111. (d) Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342. (e) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177. (f) Fischer, H. In *Transition Metal Carbene Complexes*; Dötz, K. H., Fischer, H., Hofmann, P., Kreissl, F. R., Schubert, U., Weiss, K., Eds.; VCH: Weinheim, Germany, 1983. (g) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

(2) (a) Huq, F.; Mowat, W.; Skapski, A. C.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1971**, *1477*. (b) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359. (c) Fellmann, J. D.; Rupprecht, G. A.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 5964. (d) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774. (e) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210. (f) Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236. (g) Messerle, L. W.; Jennische, P.; Schrock, R. R.; Stucky, G. *J. Am. Chem. Soc.* **1980**, *102*, 6744. (h) Andersen, R. A.; Chisholm, M. H.; Gibson, J. F.; Reichert, W. W.; Rothwell, I. P.; Wilkinson, G. *Inorg. Chem.* **1981**, *20*, 3934. (i) Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* **1982**, *1*, 1645. (j) Holmes, S. J.; Clark, D. N.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6322. (k) Chamberlain, L. R.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Chem. Soc., Dalton Trans.* **1987**, 155. (l) Liu, A. H.; Murray, R. C.; Dewan, J. C.; Santarsiero, B. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 4282.

(3) Schrock, R. R. *J. Am. Chem. Soc.* **1974**, *96*, 6796.

(4) Turner, H. W.; Schrock, R. R.; Fellmann, J. D.; Holmes, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4942.

(5) Churchill, M. R.; Wasserman, H. J.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 1710.

(6) Fellmann, J. D.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6608.

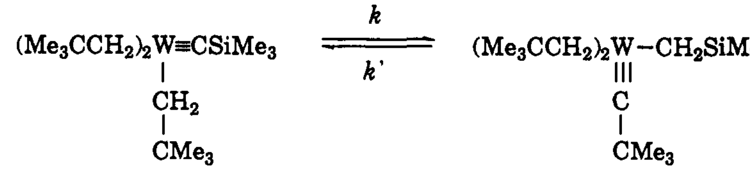
(7) Goddard, R. J.; Hoffmann, R.; Jemmis, E. D. *J. Am. Chem. Soc.* **1980**, *102*, 7667.

(8) Hofmann, P. In *Carbyne Complexes*; Fischer, H.; Hofmann, P., Kreissl, F. R., Schrock, R. R., Schubert, U., Weiss, K., Eds.; VCH: New York, 1988.

(9) Edwards, D. S.; Biondi, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983**, *2*, 1505.

(10) Xue, Z.; Caulton, K. G.; Chisholm, M. H. *Chem. Mater.* **1991**, *3*, 384.

0002-7863/91/1513-6082\$02.50/0



$$(\mathrm{Me_3CCH_2})_2\mathrm{W}(\mathrm{CH_2CMe_3})\equiv\mathrm{CSiMe_3} \underset{k'}{\overset{k}{\rightleftharpoons}} (\mathrm{Me_3CCH_2})_2\mathrm{W}(\mathrm{CH_2SiMe_3})\equiv\mathrm{CCMe_3}$$

2a **2b**

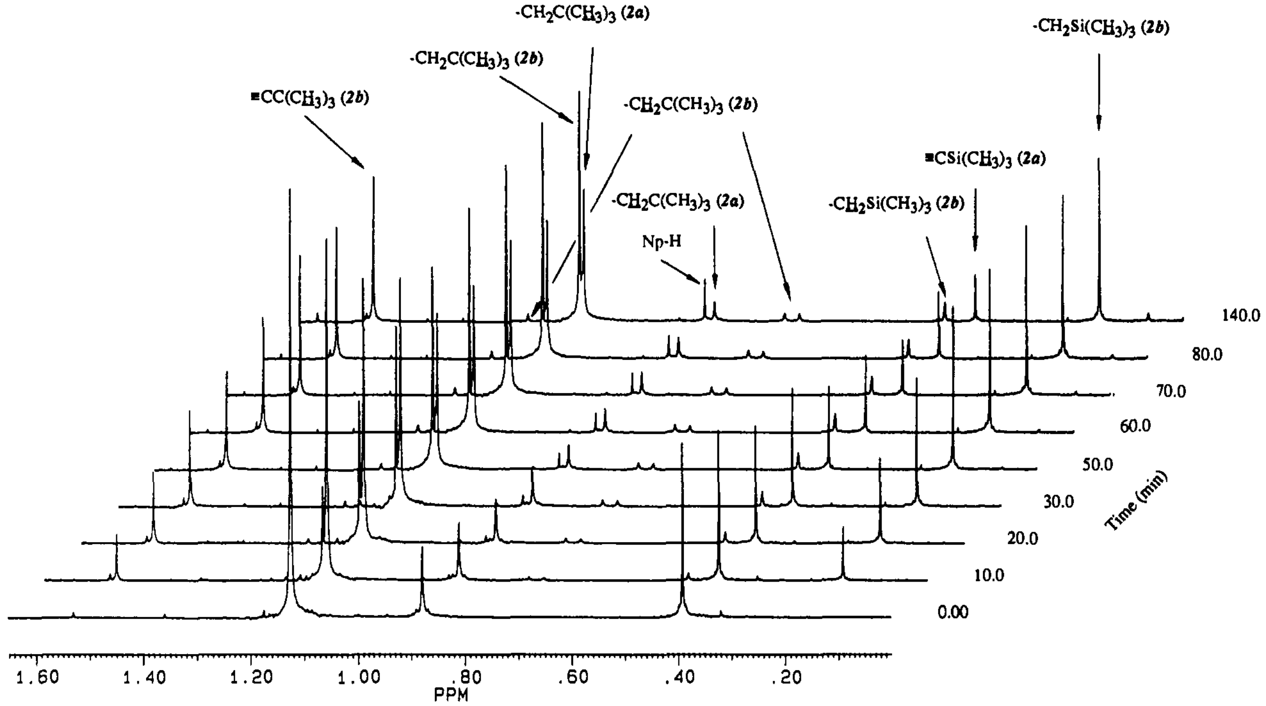


Figure 1. Time-resolved ^{1}H NMR spectra at 23 °C of $(\mathrm{Me_3CCH_2})_3\mathrm{W}\equiv\mathrm{CSiMe_3}$ (**2a**) in *o*-xylene-d_{10} at 109 °C. Isomerization was quenched at the end of each time period to take the spectra.

Experimental Section

All manipulations, unless noted, were conducted under dry nitrogen or helium atmosphere with use of standard Schlenk techniques or in a drybox. Pentane and diethyl ether were distilled from sodium potassium benzophenone ketyl. *N*,*N*-Dimethylformamide (DMF) was dried over KOH, distilled under vacuum, and stored under N_2. *o*-Xylene-d_{10} (Aldrich) packed under nitrogen was stored in a drybox. NMR spectra were recorded at 23 or 70 °C on a Bruker AM-500 Fourier transform spectrometer. $(\mathrm{Me_3CCH_2})_3\mathrm{W}\equiv\mathrm{CCMe_3}$ (**1**) and $(\mathrm{Me_3CCH_2})_3\mathrm{W}\equiv\mathrm{CSiMe_3}$ (**2a**) were synthesized with modified literature procedures[2d,11,12] from $(\mathrm{Me_3CO})_3\mathrm{W}\equiv\mathrm{CCMe_3}$ and $\mathrm{Me_3CCH_2MgCl}$ and from $(\mathrm{Me_3CO})_3\mathrm{W}\equiv\mathrm{CSiMe_3}$[13] and $\mathrm{Me_3CCH_2MgCl}$, respectively.

(1) **Preparation of $(\mathrm{Me_3CCD_2})_3\mathrm{W}\equiv\mathrm{CSiMe_3}$ (2a-d_6).** The deuterium-labeled compounds were prepared as follows: The reduction of 24.47 g (0.203 mol) of trimethylacetyl chloride with 4.97 g of $\mathrm{LiAlD_4}$ (0.118 mol) in diethyl ether at −78 °C and subsequent hydrolysis with 5 mL of 15% aqueous NaOH solution and 5 mL of H_2O gave 15.9 g of $\mathrm{Me_3CCD_2OH}$ from the diethyl ether extract (>98% pure from ^{1}H NMR spectrum, 0.176 mol, 87% yield).[14] $\mathrm{Me_3CCD_2OH}$ (15.7 g) was then allowed to react with $[\mathrm{Me(CH_2)_3}]_3\mathrm{P}$ and $\mathrm{Br_2}$ in DMF.[15] Distillation at 150 °C gave a mixture of $\mathrm{Me_3CCD_2Br}$ and DMF. The latter was washed away with H_2O to give 23.5 g of NMR-pure $\mathrm{Me_3CCD_2Br}$ after drying over anhydrous $\mathrm{CaCl_2}$ (0.154 mol, 88% yield). The neopentyl bromide was then used in a Grignard synthesis in diethyl ether to give $\mathrm{Me_3CCD_2MgBr}$. $(\mathrm{Me_3CCD_2})_3\mathrm{W}\equiv\mathrm{CSiMe_3}$ (**2a**-d_6) was synthesized as described above from $(\mathrm{Me_3CO})_3\mathrm{W}\equiv\mathrm{CSiMe_3}$ and $\mathrm{Me_3CCD_2MgBr}$.

(2) **Preparation of $[\mathrm{Me_3CC(H)D}]_3\mathrm{W}\equiv\mathrm{CSiMe_3}$ (2a-d_3).** $\mathrm{Me_3CC(H)DOH}$ was synthesized as follows: A 17.1-g quantity of trimethylacetaldehyde (0.199 mol) in diethyl ether was added dropwise to 2.35 g of $\mathrm{LiAlD_4}$ (0.224 mol) in $\mathrm{Et_2O}$ at −78 °C. Subsequent hydrolysis with 2.3 mL of 15% aqueous NaOH solution and 2.3 mL of H_2O gave 7.57 g (0.0849 mol, 42.7% yield) of $\mathrm{Me_3CC(H)DOH}$. The latter was transformed to $\mathrm{Me_3CC(H)DBr}$ as described above for $\mathrm{Me_3CCD_2Br}$. The reaction between Mg metal and $\mathrm{Me_3CC(H)DBr}$ gave $\mathrm{Me_3CC(H)DMgBr}$. $[\mathrm{Me_3CC(H)D}]_3\mathrm{W}\equiv\mathrm{CSiMe_3}$ (**2a**-d_3) was similarly synthesized from $(\mathrm{Me_3CO})_3\mathrm{W}\equiv\mathrm{CSiMe_3}$ and $\mathrm{Me_3CC(H)DMgBr}$.

(3) **^{1}H NMR Study of Isomerizations of 2a, 2a-d_6, and 2a-d_3.** Solutions (0.0503 M) of **2a**, **2a**-d_6, and **2a**-d_3 were made by dissolving 10.0 mg of **2a**, 10.1 mg of **2a**-d_6, and 10.1 mg of **2a**-d_3 (20.7 μmol) in 405 (3) mg of *o*-xylene-d_{10} in 5-mm NMR tubes. One solution in an NMR tube was then put into a heated oil bath at a controlled (±0.5 °C) temperature. At the end of each time period, the NMR tube was quickly removed from the oil bath and placed into an ice bath to quench the isomerization.

Samples for crossover experiments were made from 1.0:1.0 mixtures of either **1** and **2a**-d_6 (sample A) or **2a** and **2a**-d_6 (sample B) in *o*-xylene-d_{10}. They were then heated at 100.5 (0.5) °C and treated as mentioned above for ^{1}H NMR measurement.

^{1}H NMR (*o*-xylene-d_{10}, TMS at 0.00 ppm, Figure 1): for **2a**, δ 0.39 (9 H, $\equiv\mathrm{CSi(C}H_3)_3$, 0.88 (s, 6 H, $\mathrm{C}H_2\mathrm{(CH_3)_3}$), 1.12 (s, 27 H, $\mathrm{CH_2(C}H_3)_3$); for **2b**, δ 0.16 (s, 9 H, $\mathrm{CH_2Si(C}H_3)_3$), 0.45 (s, 2 H, $\mathrm{C}H_2\mathrm{Si(CH_3)_3}$), 0.73 and 1.21 (d, 4 H, $\mathrm{C}H_aH_b\mathrm{C(CH_3)_3}$, $J_{H_a-H_b} = 13.7$ Hz), 1.13 (s, 18 H, $\mathrm{CH_2C(C}H_3)_3$), 1.52 (s, 9 H, $\equiv\mathrm{CC(C}H_3)_3$). ^{13}C{^{1}H} NMR (*o*-xylene-d_{10}, TMS at 0.0 ppm): for **2a**, δ 2.0 ($\equiv\mathrm{CSi(}C\mathrm{H_3)_3}$), 33.9 ($\mathrm{CH_2C(}C\mathrm{H_3)_3}$), 34.7 ($\mathrm{CH_2}C\mathrm{(CH_3)_3}$), 105.2 ($C\mathrm{H_2C(CH_3)_3}$), 337.7 ($\equiv C\mathrm{Si(CH_3)_3}$); for **2b**, δ 2.8 ($\mathrm{CH_2Si(}C\mathrm{H_3)_3}$, 32.5 ($\equiv\mathrm{CC(}C\mathrm{H_3)_3}$), 34.2 ($\mathrm{CH_2}C\mathrm{Me_3}$), 34.5 ($\mathrm{CH_2C(}C\mathrm{H_3)_3}$), 52.7 ($\equiv\mathrm{C}C\mathrm{Me_3}$), 70.0 ($C\mathrm{H_2SiMe_3}$), 104.5 ($C\mathrm{H_2CMe_3}$), 317.6 ($\equiv C\mathrm{CMe_3}$).

^{1}H resonances of $\mathrm{CH_3}$– on $\mathrm{(CH_3)_3SiC}\equiv$ at 0.39 ppm (**2a** or **2a**-d_6) and 0.41 ppm (**2a**-d_3) and of $\mathrm{CH_3}$– on $\mathrm{(CH_3)_3SiCR_1R_2}$– at 0.16 ppm ($R_1 = R_2 = H$, **2b** or $R_1 = R_2 = D$, **2b**-d_6) and 0.17 ppm ($R_1 = H$, $R_2 = D$, **2b**-d_3) (Figure 1) were used to calculate [**2b**]/[**2a**], [**2b**-d_6]/[**2a**-d_6], or [**2b**-d_3]/[**2a**-d_3]. The equilibrium constant was obtained when the above

---

(11) Schrock, R. R.; Sancho, J.; Pederson, S. F. *Inorg. Synth.* **1989**, *26*, 44.

(12) Chisholm, M. H.; Huffman, J. C.; Klang, J. A. *Polyhedron* **1990**, *9*, 1271.

(13) Listemann, M. L.; Schrock, R. R. *Organometallics* **1985**, *4*, 74.

(14) Nystrom, R. F.; Brown, W. G. *J. Am. Chem. Soc.* **1947**, *69*, 1197.

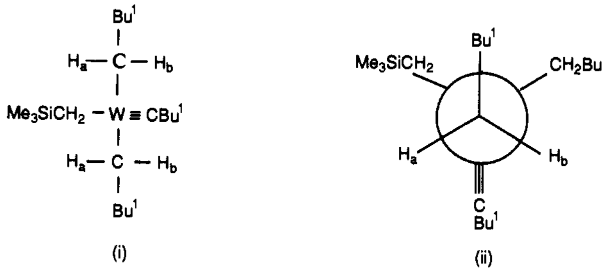
(15) (a) Wiley, G. A.; Hershkowitz, R. L.; Rein, B. M.; Chung, B. C. *J. Am. Chem. Soc.* **1964**, *86*, 964. (b) Hu, B.; Li, T.; Oprescu, C.; Tomescu, M.; Hubca, G.; Dimonie, M. *Bul. Inst. Politeh. Bucuresti, Ser. Chim.* **1987**, *49*, 97.

Table I. Summary of Kinetic and Thermodynamic Data[a]

t, °C	K_{eq}	10^3k_{HH}	$10^3k'_{HH}$	10^3k_{HD}	$10^3k'_{HD}$	10^3k_{DD}	$10^3k'_{DD}$
79	2.16 (12)	1.29 (5)	0.598 (3)				
89	2.41 (13)	4.05 (10)	1.68 (7)				
100	2.67 (15)	12.3 (7)	4.6 (3)	4.16 (9)	1.56 (4)	2.4 (2)	0.91 (1)
109	2.71 (15)	31.6 (20)	11.6 (9)				
120	3.07 (17)						

[a] Unit of rate constants: min^{-1}. k_{HH}, k_{HD}, k_{DD} are for the forward reaction; k'_{HH}, k'_{HD}, k'_{DD} are for the back-reaction. k_{HH}/k_{DD}(100 °C) = 5.1 (3); k_{HH}/k_{HD}(100 °C) = 3.0 (2); k_{HD}/k_{DD} (100 °C) = 1.73 (2).

Chart I[a]



[a] The presence of a prochiral tungsten atom in **2b** (i) results in the nonequivalence of the methylene protons H_a and H_b, as seen in the Newman projection along the C–W bond of a neopentyl group (ii).

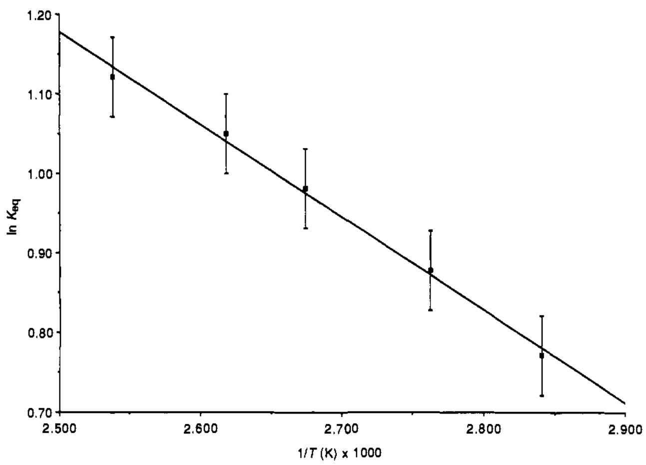


Figure 2. Plot of ln K_{eq} as a function of temperature ($1/T$) for the equilibrium **2a** ⇄ **2b** in *o*-xylene-d_{10}.

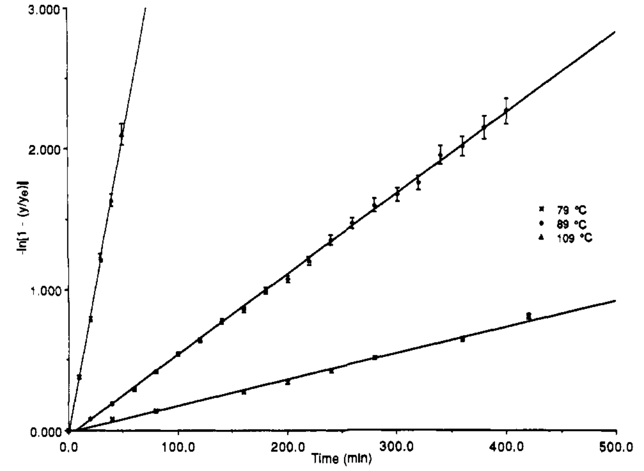


Figure 3. Kinetics plots of the isomerization of $(Me_3CCH_2)_3W{\equiv}CSiMe_3$ (**2a**) at 79, 89, and 109 °C.

ratios showed no change within experimental errors at a given temperature.

(4) **Crystal and Molecular Structure Determination for $(Me_3CCD_2)_3W{\equiv}CSiMe_3$ (2a-d_6).** General procedures and listings of programs have been previously reported.[16]

A crystal of suitable size was mounted under nitrogen atmosphere in a glovebag with the use of silicone grease. It was then transferred to a goniostat where of cooled to −169 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space revealed a rhombohedrally centered hexagonal cell. Following complete intensity data collection and correction for absorption, data processing gave a residual of 0.048 for the averaging of 951 unique intensities that had been measured more than once. Four standards measured every 300 data showed no significant trends. The Laue symmetry was identified as $\bar{3}$, and an initial choice of space group $R\bar{3}$ was proven correct by the successful solution of the structure.

The structure was solved by a combination of direct methods (SHELXS-86) and Fourier techniques. The tungsten, silicon, and most of the carbon positions were located in an initial E map. The remaining atoms, including hydrogens, were obtained from subsequent iterations of least-squares refinement and difference Fourier calculations. There was, of course, no distinction made for the isotopes of hydrogen.

In the final cycles of refinement, the non-hydrogen atoms were varied with anisotropic thermal parameters and the hydrogen atoms were varied with isotropic thermal parameters to a final $R(F)$ = 0.0205. The final difference map was essentially featureless. There were tungsten residuals of 0.5–1.8 e/Å^3. All other residual peaks were less than 0.4 e/Å^3.

The molecule lies on a crystallographic 3-fold axis (containing W–C(1)–Si). Fractional coordinates, anisotropic thermal parameters, and a listing of all bond distances and angles are given in the supplementary material.

Results and Discussion

The Isomerization and Its Thermodynamics. Time-resolved ^{1}H NMR spectra of $(Me_3CCH_2)_3W{\equiv}CSiMe_3$ (**2a**) at 109 °C are shown in Figure 1. The assignment of resonances is based on the known resonances of $(Me_3CCH_2)_3W{\equiv}CCMe_3$ (**1**)[2i,11] and $(Me_3SiCH_2)_3W{\equiv}CCMe_3$.[12] As the intensities of the resonances of **2a** decrease, resonances corresponding to $\equiv C(CH_3)_3$, $-CH_2Si(CH_3)_3$, and $-CH_2Si(CH_3)_3$ of **2b** increase in intensity. The prochiral tungsten atom[17] in **2b** gives rise to nonequivalence of the methylene protons in the neopentyl groups (Chart I). Thus H_a and H_b are diastereotopic with chemical shifts of 0.73 and 1.21 ppm and $J_{H_a-H_b}$ = 13.7 Hz.

Decomposition of **2a** and **2b** to give neopentane (Np–H) or tetramethylsilane (TMS) accompanies the alkyl/alkylidyne isomerization. The percentages of decomposition at equilibrium range from 7% to 12%.[18] We could reasonably assume that the decomposition rate is small compared to the exchange rates between **2a** and **2b**, k and k'. Therefore, once an equilibrium (eq 1) between **2a** and **2b** is established, the decomposition would affect the equilibrium constant, K_{eq}, very little. The calculated equilibrium constants, K_{eq}, are listed in Table I. The plot of ln K_{eq} vs $1/T$ based on $\Delta G° = -RT \ln K_{eq} = \Delta H° - T\Delta S°$,[19] where $\Delta G°$, $\Delta H°$, and $\Delta S°$ are standard Gibbs energy, enthalpy, and entropy changes, respectively, is shown in Figure 2. These plots yield

---

[16] Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

[17] (a) Atta-ur-Rahman. *Nuclear Magnetic Resonance. Basic Principles*; Springer-Verlag: New York, 1986; pp 46–49. (b) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; p 207.

[18] Percentage of decomposition = [Np–H] + [TMS]/([**2a**] + [**2b**]) where [Np–H], [TMS], [**2a**], and [**2b**] are the concentration of each, respectively.

[19] Levine, I. N. *Physical Chemistry*, 3rd ed.; McGraw-Hill: New York, 1988; pp 307–309 (temperature and pressure dependences of the equilibrium constant) and pp 521–522 (reversible first-order reaction).

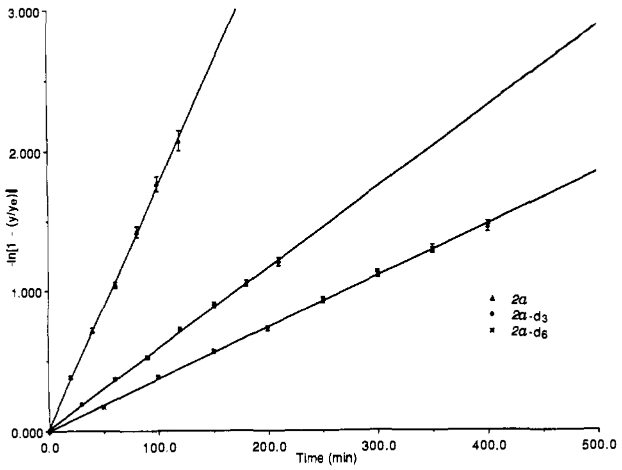


Figure 4. Kinetics plots of the isomerization of $(Me_3CCR_1R_2)_3W\equiv CSiMe_3$ (R_1 and R_2 = H (**2a**); R_1 = H and R_2 = D (**2a**-d_3); R_1 and R_2 = D (**2a**-d_6)) at 100 °C.

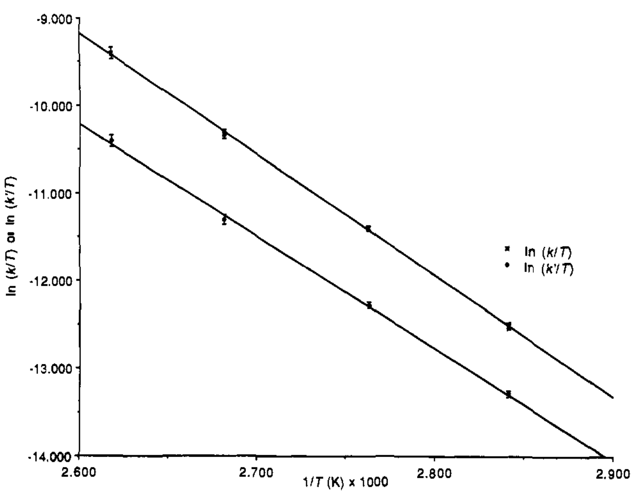


Figure 5. Eyring plot of the isomerization reaction **2a** ⇄ **2b**.

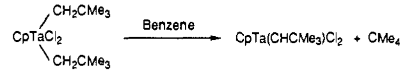
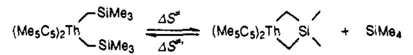
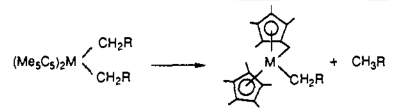
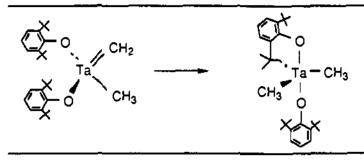
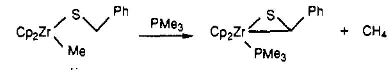
$\Delta H°$ = 2.3 (0.5) kcal/mol and $\Delta S°$ = 8.1 (1.3) eu.

The equilibrium constants, K_{eq}, measured for the isomerization (eq 1) range from 2.16 (0.12) at 79 °C to 3.07 (0.17) at 120 °C (Table I), indicating **2b** is favored in this equilibrium; k and k' are the rate constants for **2a** → **2b** and **2b** → **2a**, respectively (eq 1). Process **2a** → **2b** is endothermic with $\Delta H°$ = 2.3 (0.5) kcal/mol. The entropy change $\Delta S°$ = 8.1 (1.3) eu (resulting from the descent in symmetry from the C_{3v} point group in **2a** to the C_s point group in **2b**) clearly outweighs the enthalpy change in the present system to give $\Delta G°$ from −0.54 (0.04) kcal/mol at 79 °C to −0.88 (0.04) kcal/mol at 120 °C in favor of **2b**.

Reaction Kinetics. An overall reversible first-order reaction[19] is observed for the migration of two hydrogens in eq 1. If y and y_e are the percentages of **2b** in **2a** + **2b** at time t and at equilibrium, respectively, then $-\ln [1 - (y/y_e)] = (k + k')t$. The plots $-\ln [1 - (y/y_e)]$ vs t at 79, 89, and 109 °C are shown in Figure 3 and at 100 °C in Figure 4. From the slope = $k + k'$ (Table I), the rate constants at these temperatures were calculated and are listed in Table I.

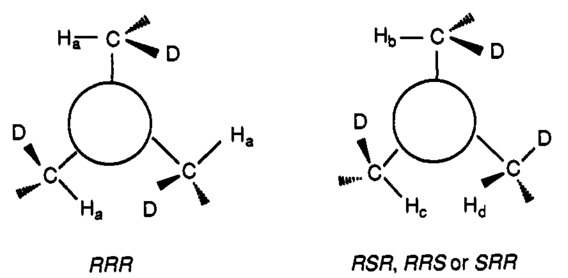
Eyring plots of ln (k/T) vs $1/T$ and ln (k'/T) vs $1/T$ are shown in Figure 5. Activation parameters thus derived are $\Delta H^{\ddagger}$ = 27.5 (0.6) kcal/mol and $\Delta S^{\ddagger}$ = −2.0 (1.7) eu for the forward isomerization **2a** → **2b** and $\Delta H^{\ddagger\prime}$ = 25.4 (0.8) kcal/mol and $\Delta S^{\ddagger\prime}$ = −9.5 (1.9) eu for the reverse isomerization **2b** → **2a**. Negative values for $\Delta S^{\ddagger}$ and $\Delta S^{\ddagger\prime}$ indicate forward and reverse transition states where the rotations of single bonds are restricted and the symmetries of molecules descend. The larger negative value of $\Delta S^{\ddagger\prime}$ presumably reflects the reduced availability of methylene protons. In the reaction **2b** → **2a** only the methylene protons of the Me_3SiCH_2 ligand are available whereas in the reaction **2a** → **2b** any pair of the three neopentyl methylene protons can react. The statistical factor is 3:1 for **2a** → **2b** relative to **2b** → **2a**.

Table II. Entropy Changes ($\Delta S^{\ddagger}$) in Reactions through Cyclometalation Transition States

Reactions	$\Delta S^{\ddagger}$ (eu)
	$\Delta S^{\ddagger}$ = -4 ± 10 [a]
	$\Delta S^{\ddagger}$ = -17.6 ± 0.5 $\Delta S^{\ddagger\prime}$ = -34.2 ± 0.5 [b]
	M = Ti; R = H, $\Delta S^{\ddagger}$ = -2.9 ± 0.7 [c] M = Hf; R = C_6H_5, $\Delta S^{\ddagger}$ = 1 ± 3 [d]
	-31 ± 6 [e]
	-20.6 ± 0.4 [f]

[a] Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210. [b] Smith, G. M.; Carpenter, J. D.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 6805. [c] McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629. [d] Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219. [e] Rothwell, I. P. *Acc. Chem. Res.* **1988**, *21*, 153. [f] Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1988**, *110*, 3171.

Chart II. Newman Projection Analysis of the Inequivalent Hydrogen Atoms in $[Me_3CC(H)D]_3W\equiv CSiMe_3$ (**2a**-d_3)[a]



RRR *RSR*, *RRS* or *SRR*

[a] Me_3C– groups are omitted for clarity. Three chiral α-carbon atoms lead to 2^3 = 8 *potential* isomers of four pairs of *potential* enantiomers. [(*RRR*,*SSS*), (*RSS*,*SRR*), (*RSR*,*SRS*), and (*SSR*,*RRS*)]. *RSS*, *SRS*, and *SSR* (or *SRR*, *RSR*, and *RRS*) are equivalent due to the presence of a pseudo-C_3 axis. Therefore there are only *two* pairs of enantiomers in **2a**-d_3.

Concerted four-center transition states, especially those involving cyclometalation, have been proposed for C–H bond activation processes where $\Delta S^{\ddagger}$ is negative. Pertinent $\Delta S^{\ddagger}$ values for various C–H activation procsses are given in Table II. The $\Delta S^{\ddagger}$ values observed in the present study are small in magnitude and comparable to those observed by Bercaw and co-workers in the alkane-elimination reactions involving $Cp^*_2M(CH_2R)_2$ compounds. This suggests there is little required ordering of the ligands between two adjacent α-carbon atoms.

Deuterium-Labeling Studies. A labeling study was conducted by employing $(Me_3CCD_2)_3W\equiv CSiMe_3$ (**2a**-d_6) and $(Me_3CCHD)_3W\equiv CSiMe_3$ (**2a**-d_3). Before the specific experiments are described, it is worth commenting on the NMR spectra of the labeled compounds. First, in compound **2a**-d_6 and its isomer **2b**-d_6 (to be described in detail later) there are small isotope chemical shifts. The signals arising from the neopentyl methyl protons are shifted upfield (0.003–0.004 ppm) relative to its protio isotopomer. See Figure 6. Second, for compound **2a**-d_3 the presence of three $Me_3CC(H)D$ groups attached to a pseudotetrahedral tungsten center introduces the complication of diastereomers and enantiomers. With three optically active centers, there are 2^3 = 8 potential isomers, as shown in Chart II. By NMR spectroscopy, we can expect to see only two sets of enan-

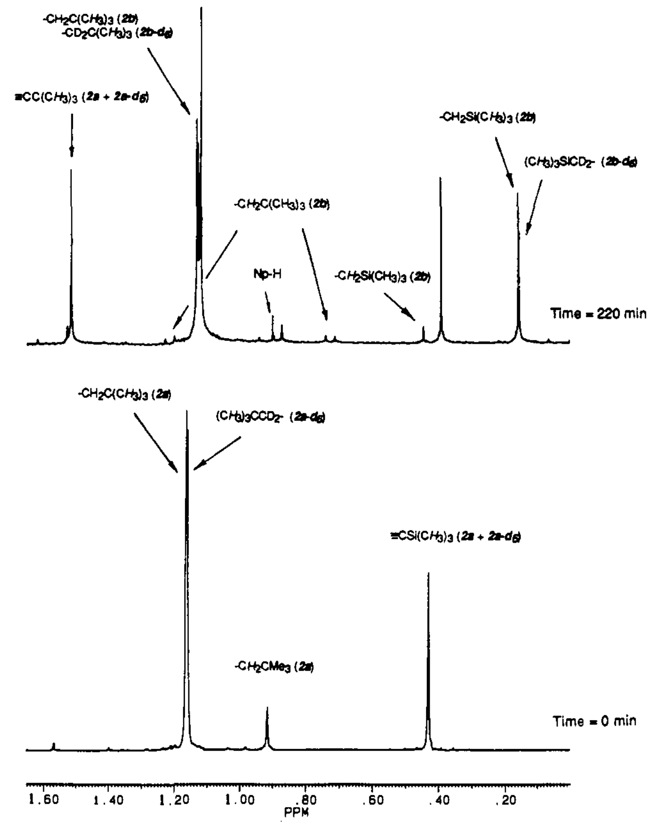


Figure 6. ^{1}H NMR spectra (500.136 MHz, 23 °C) of a 1:1 mixture of $(Me_3CCH_2)_3W{\equiv}CSiMe_3$ (**2a**) and $(Me_3CCD_2)_3W{\equiv}CSiMe_3$ (**2a**-d_6). Lower scan: spectrum before heating at 100 °C. Isotope chemical shift difference (0.003–0.004 ppm) for Me_3C–groups is observed. Upper scan: spectrum after heating at 100 °C for 200 min. There is *no* resonance of $Me_3SiC(H)D$–buried in the resonance of $\equiv CSi(CH_3)_3$. See the upper insert of Figure 10 for the 0.28–0.46 ppm region of the spectrum at 70 °C where overlapping $Me_3SiC(H)D$– and $\equiv CSi(CH_3)_3$ resonances would be resolved.

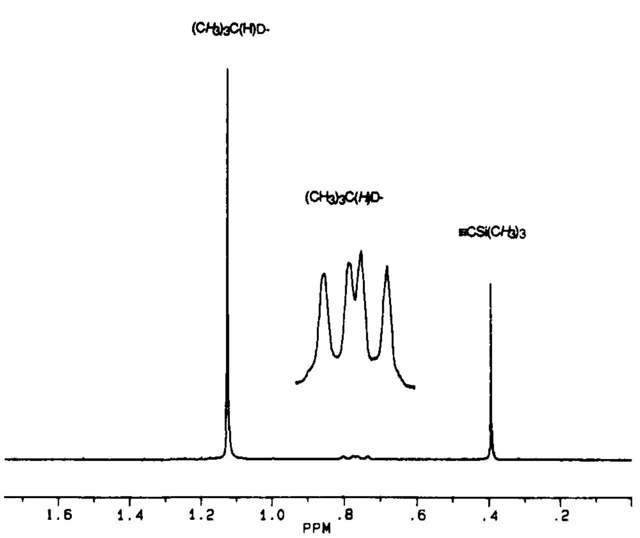


Figure 7. ^{1}H NMR spectrum (500.136 MHz, 23 °C) of $[Me_3CC(H)D]_3W{\equiv}CSiMe_3$ (**2a**-d_3). See Chart II for the analysis of the inequivalent α-H atoms.

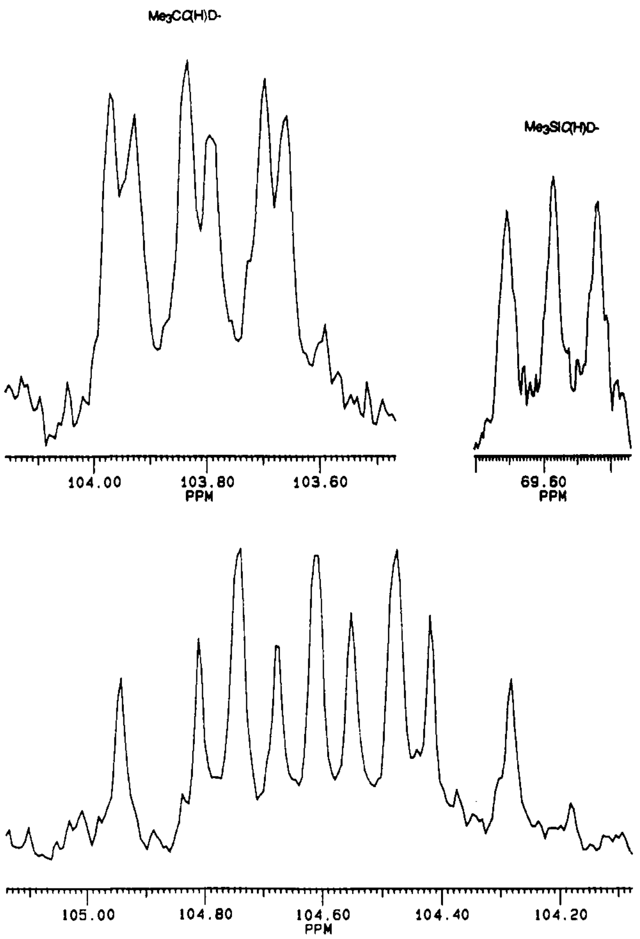
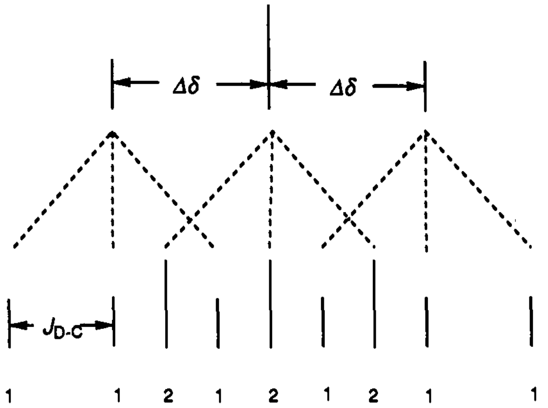


Figure 8. α-Carbon resonances in $^{13}C\{^1H\}$ NMR spectra (125.760 MHz, 23 °C). Lower scan: $[Me_3CC(H)D]_3W{\equiv}CSiMe_3$ (**2a**-d_3). See Chart III for the calculation of the resonance. Upper scan: $[Me_3CC(H)D]_2[(Me_3SiC(H)D)]W{\equiv}CCMe_3$ (**2b**-d_3). Accidental degeneracies result in two sets of signals for the two $Me_3CC(H)D$– groups ($J_{^{13}C-^2H}$ = 17 Hz) and one set of signals for the $Me_3SiC(H)D$– groups ($J_{^{13}C-^2H}$ = 16 Hz).

Chart III. Calculation of the Observed ^{13}C Signals for Four -*C*HD– Groups[a]



[a] To first-order approximation, (1) two ^{13}C NMR resonances are accidently degenerate, (2) chemical shift differences ($\Delta\delta$) between the three signals are equal, (3) J_{D-C} coupling constants are equal for the three signals, and (4) $\Delta\delta \approx {}^3/_2 J_{D-C}$ at 125 MHz.

tiomers in a nonchiral solvent. In fact, in the ^{1}H NMR spectrum of **2a**-d_3, we observe four signals of roughly equal intensity due to the presence of the four different hydrogen atoms arising from two different pairs of enantiomers [(*RRR,SSS*) and (*RSS,SRR*)]. Under pseudo-C_3 symmetry, *RSS*, *SRS*, and *SSR* are equivalent as are their enantiomers *SRR*, *RSR*, and *RRS*, as shown in Chart II. The fact that *gem* $^1H-^2H$ coupling is small causes line broadening, as shown in Figure 7. The appearance of a roughly 1:1:1:1 signal for the CHD protons in **2a**-d_3 indicates no preference in the synthesis employed here: the population of enantiomers is statistical. In the $^{13}C\{^1H\}$ spectrum of **2a**-d_3, we observe a complex signal for the methylene carbon atoms, as shown in Figure 8. Because of the enantiomers previously described, we have in theory the expectation of four inequivalent α-carbon atoms for the methylene CHD groups. This, together with $^{13}C-^2H$ coupling,

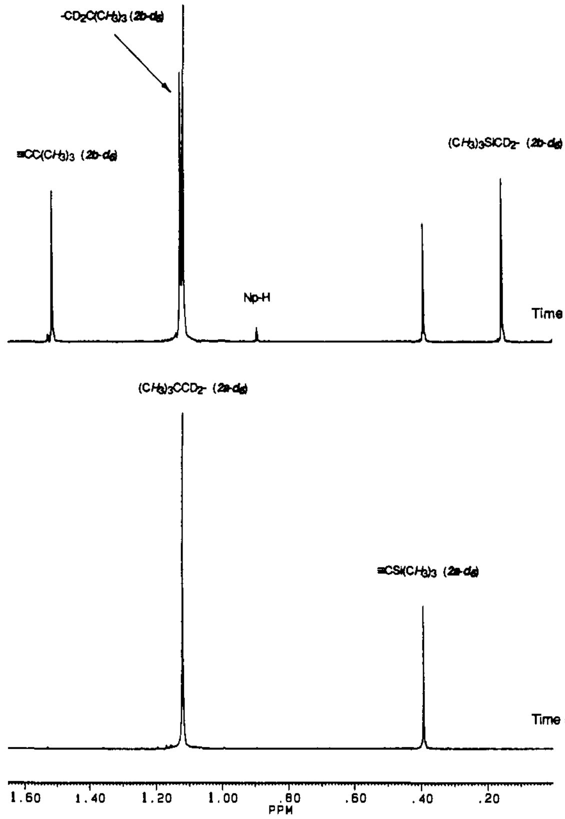


Figure 9. ^{1}H NMR spectra (500.136 MHz, 23 °C) of $(Me_3CCD_2)_3W{\equiv}CSiMe_3$ (**2a**-d_6) before heating (lower scan) and after 400 min at 100 °C (upper scan). No resonance attributable to Me_3SiCH_2– (0.44 ppm) is observed, indicating α-H atom transfer in the isomerization.

would lead to four sets of 1:1:1 triplets. As shown in Chart III, the observed spectrum can be anticipated by a fortuitous ^{13}C–^2H coupling and chemical separation with two signals being degenerate.

With the labeled compounds at hand, the isomerizations involving **2a**-d_6 and **2a**-d_3 were studied and found to obey first-order reversible kinetics, giving **2b**-d_6 and **2a**-d_3, respectively. The plots of $-\ln [1 - (y/y_e)]$ vs t are shown in Figure 4 for isomerizations carried out at 100 °C. From the comparative rate data at 100 °C, we obtain the ratios $k_{HH}/k_{DD} = 5.1$ (0.3) and $k_{HH}/k_{HD} = 3.0$ (0.2). Before turning our attention to the significance of these ratios, it is worthwhile to note that the isomerization of **2a**-d_6 yields $(Me_3SiCD_2)(Me_3CCD_2)_2W{\equiv}CCMe_3$ exclusively, thus ruling out a γ-CH/γ-CD exchange process. Furthermore, the isomerization of **2a**-d_3 gives exclusively $(Me_3SiCHD)(Me_3CCHD)_2W{\equiv}CCMe_3$, as can be seen in Figures 9 and 10. The formation of isotopomers with CH_2 or CD_2 methylene groups is estimated to reflect approximately the isotope purity of the starting materials. Thus the alkyl–alkylidyne isomerization involves the transfer of both α-hydrogens from one carbon atom. The significance of this will be discussed later.

The methylene protons signals of **2b**-d_3 also warrant some comment. For the neopentyl groups ($CHDCMe_3$), we observe four resonances, two at ca. 1.1 ppm and two at ca. 0.6 ppm. We expect four pairs of enantiomers for **2b**-d_3 namely *R*RR* and *S*SS*, *R*SS* and *S*RR*, *R*RS* and *S*SR*, and *R*SR* and *S*RS* where the asterisk represents the chirality of the Me_3SiCHD ligand. The two hydrogen atoms of each enantiomeric pair are inequivalent, and thus by ^{1}H NMR spectroscopy, eight neopentyl methylene signals are possible. See Chart IV. That only four signals are seen is probably due to the fact that the neopentyl methylene protons are not sensitive to the absolute stereochemistry of the (trimethylsilyl)methyl ligand.

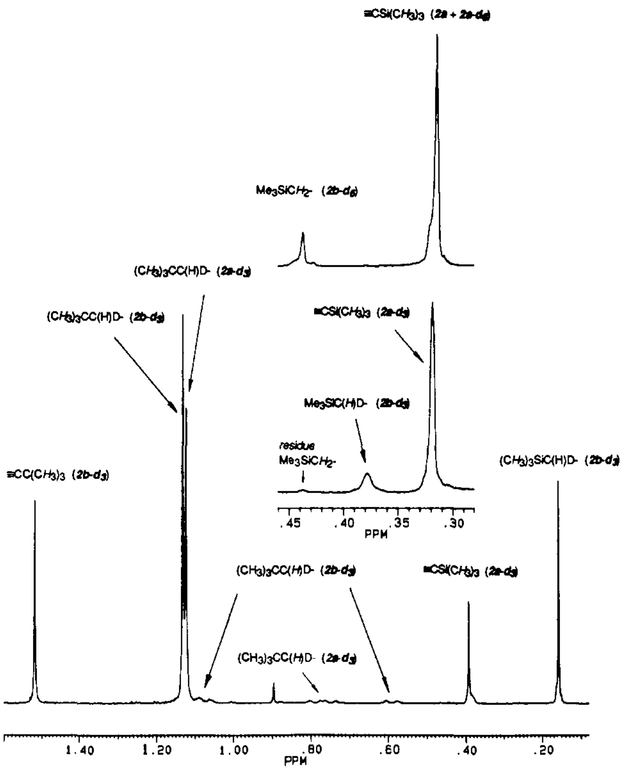
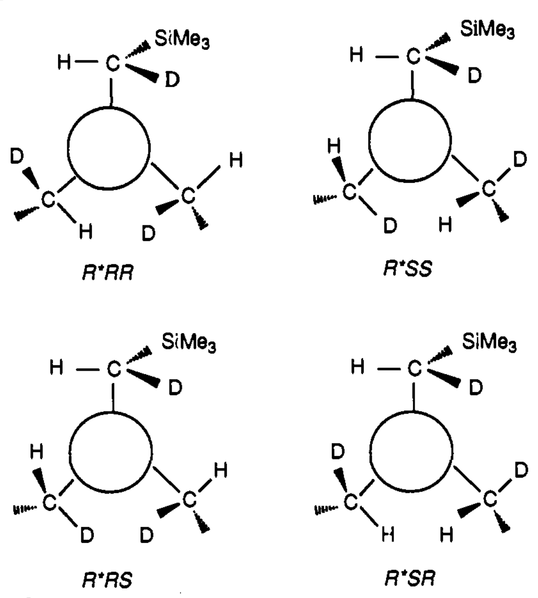


Figure 10. ^{1}H NMR spectrum (500.136 MHz, 23 °C) of **2a**-d_3 and **2b**-d_3 after being heated for 400 min at 100 °C. Lower insert: 0.28–0.46 ppm region of the spectrum (500.136 MHz, 70 °C) of **2a**-$d_3 \rightleftarrows$ **2b**-d_3. The $Me_3SiC(H)D$– resonance (0.38 ppm) indicates over 96% (deuterium-isotope purity >98%) of isomerization proceeds through transfer of *two* hydrogen atoms from the *same* α-carbon atom. Upper insert: 0.28–0.46 ppm region of the spectrum (500.136 MHz, 70 °C) of a 1:1 mixture of **2a** $\rightleftarrows$ **2b** and **2a**-$d_6 \rightleftarrows$ **2b**-d_6 after being heated at 100 °C for 200 min. No resonance attributable to $Me_3SiC(H)D$– (0.38 ppm) is observed, indicating *intramolecular* α-H atom transfer in the isomerization.

Chart IV. Newman Projection Analysis of the Inequivalent Hydrogen Atoms in $[Me_3CC(H)D]_2[Me_3SiC(H)D]W{\equiv}CCMe_3$ (**2b**-d_3)^a



^{a} Me_3C– groups are omitted for clarity. Two hydrogen atoms in each isomer are diastereotopic, resulting in 2 × 4 = 8 inequivalent hydrogen atoms

Two crossover experiments were carried out in order to determine whether or not intermolecular processes involving H or alkyl group exchange were operative. In one experiment, $(Me_3CCH_2)W{\equiv}CCMe_3$ (**1**) and $(Me_3CCD_2)_3W{\equiv}CSiMe_3$ (**2a**-d_6) were mixed in a 1:1 ratio and heated to 100 °C for 240 min (Figure 11). After this time, **1**, **2a**-d_6, and **2b**-d_6 exist in the approximate ratio 1:0.5:0.5, respectively. The significant obser-

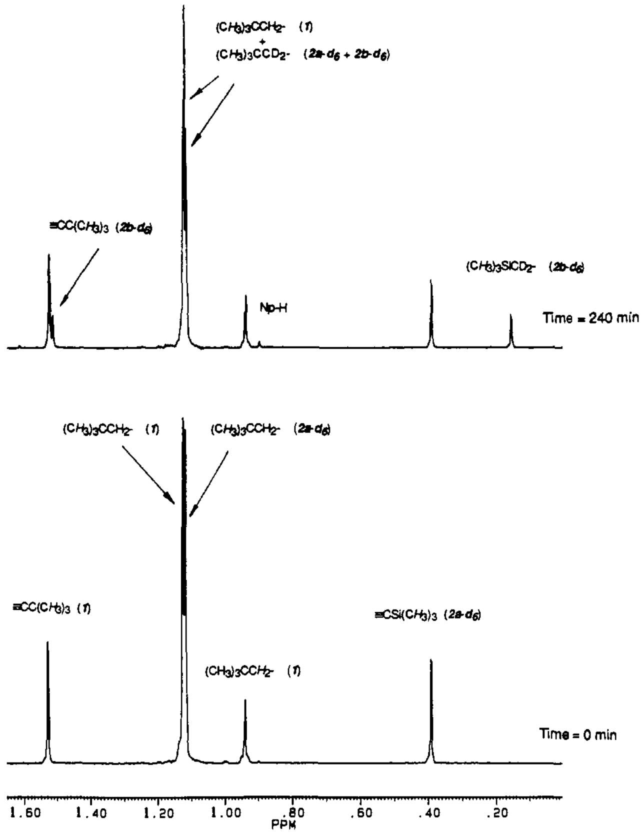


Figure 11. ^{1}H NMR spectra (500.136 MHz, 23 °C) of a 1:1 mixture of $(Me_3CCH_2)_3W{\equiv}CCMe_3$ (**1**) and $(Me_3CCD_2)_3W{\equiv}CSiMe_3$ (**2a**-d_6) after 240 min at 100 °C. No resonance attributable to Me_3SiCH_2- (0.44 ppm) is observed, indicating *intramolecular* α-H atom transfer in the isomerization.

vation here was that there was no evidence for Me_3SiCH_2 protons in **2b**-d_6. Thus an intermolecular alkyl group exchange involving **1** and **2a**-d_6 must be slower than the α-C–H atom transfer, if indeed it occurs. The second experiment involved a 1:1 mixture of **2a** and **2a**-d_6 dissolved in *o*-xylene-d_{10} and maintained at 100 °C for 200 min (Figure 6 and upper scan of Figure 10). Here the significant observation was that after the isomerizations **2a** ⇄ **2b** and **2a**-d_6 ⇄ **2b**-d_6 there was no evidence for the presence of CHD methylene groups in the (trimethylsilyl)methyl ligands. The latter is understandable on the basis of (a) the lack of intermolecular alkyl group exchange and (b) the transfer of both α-methylene protons between the alkyl and alkylidyne groups. Taken together, these crossover experiments confirm that the hydrogen atom transfer is a unimolecular process, as was inferred by the kinetic order of the reaction.

Comments on the Kinetic Isotope Effects (KIE's). With the labeling studies outlined above and the observed rate differences, we can address the question of how the latter should be interpreted. The ratio $k_{HH}/k_{DD} = 5.1$ (0.3) at 100 °C is suggestive of a symmetrical (linear) transition state for the transfer of hydrogen between the carbon atoms.[20] However, there are a number of issues that arise in interpreting the data and we must make some assumptions: We propose (1) to ignore secondary isotope effects, which in general are within error limits of normal rate measurements,[20] and (2) to ignore metal–hydride intermediates since tungsten is in the formal oxidation state +6 in **1**, **2a**, and **2b**. We consider two possible models for the transfer of hydrogen atoms. In both, the metal must assist in orbital steering, since this is formally a sigmatropic 1,3-hydrogen shift which is thermally forbidden by orbital symmetry in organic chemistry.[21] In the first model, two hydrogen atoms are transferred in a concerted one-step process as shown in I.

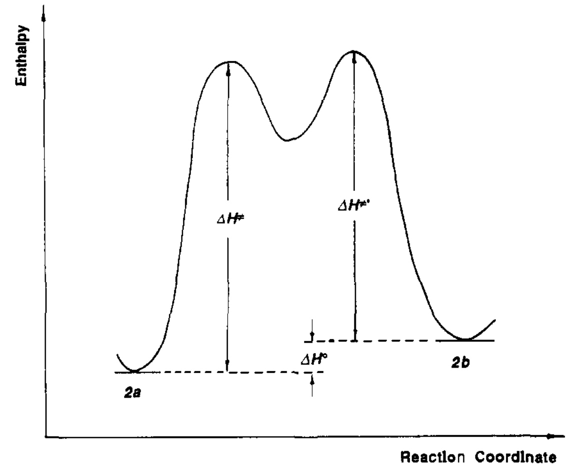
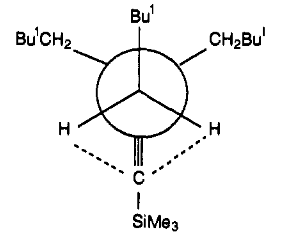
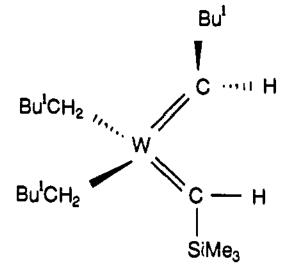


Figure 12. Energy profile for the isomerization **2a** ⇄ **2b**. Scales are arbitrary.



I

In the second model, there is a stepwise transfer of hydrogen atoms via a bis(alkylidene) reactive intermediate, II.[22]



II

The problem of how to differentiate between the concerted and stepwise process described above has an analogy with the Diels–Alder reaction, which has received considerable attention.[23] If in the transition state two bonds are being made and two are broken in a symmetrical and concerted manner, then the rule of the geometric mean (RGM) will apply.[23a] In our system, the ratio $k_{HH}/k_{HD} = (k_{HH}/k_{DD} \times k_{HH}/k_{HH})^{1/2} = (k_{HH}/k_{DD} \times 1)^{1/2}$ leads to a value of 2.25. The observed value for k_{HH}/k_{HD} (= 3.0 (0.22)) is, within experimental error, that predicted by the arithmetic mean:[23a]

$$k_{HH}/k_{HD} = \tfrac{1}{2}(k_{HH}/k_{DD} + k_{HH}/k_{HH}) = \tfrac{1}{2}(k_{HH}/k_{DD} + 1) = 3.05$$

Thus the ratio of the KIE's argues against the symmetrical concerted transfer of two hydrogen atoms in a single step. The proposed reaction profile and mechanism are shown in Figure 12 and Scheme I.

---

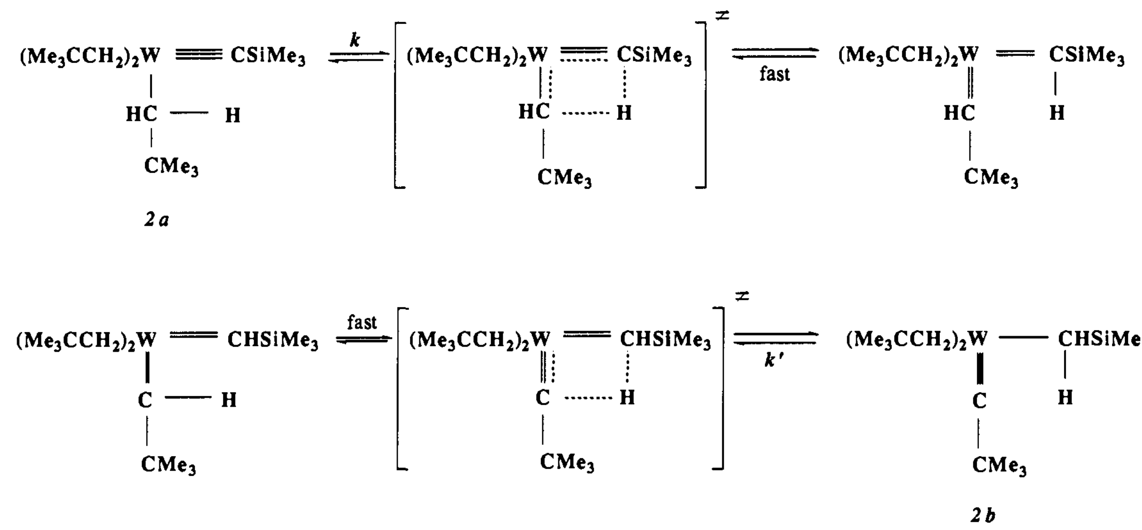
[20] Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980; p 171.

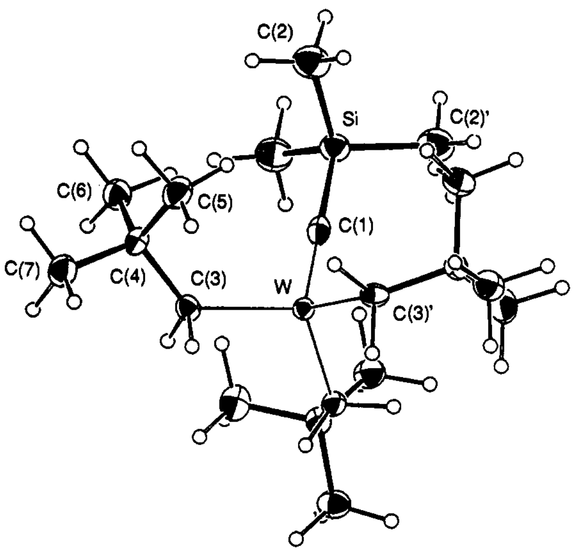
[21] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987; p 946.

[22] Bis(neopentylidene) complexes of niobium and tantalum are known: Reference 2c. Fellmann, J. D.; Schrock, R. R.; Rupprecht, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 5752.

[23] (a) Taagepera, M.; Thornton, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 1168. (b) Gajewski, J. J.; Peterson, K. B.; Kagel, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 5545 and references therein.

Scheme I. Proposed Mechanism for the Hydrogen Transfers between Alkyl and Alkylidyne Ligands





Selected Bond Distances (Å)		Selected Bond Angles (deg)	
W - C(1)	1.739 (8)	W - C(1) - Si	179.97
W - C(3)	2.096 (5)	C(1) - W - C(3)	106.59 (13)
Si - C(1)	1.856 (8)	C(3) - W - C(3)'	112.19 (12)
Si - C(2)	1.840 (6)	C(1) - Si - C(2)	109.20 (22)

Figure 13. ORTEP drawing of $(Me_3CCD_2)_3W\equiv CSiMe_3$ (**2a**-d_6) showing the atom-numbering scheme.

Crystal and Molecular Structure of 2a-d_6. During the course of this work, we have considered bimolecular reaction pathways by which ligands are scrambled and possibly C–H bonds activated. Furthermore, it is known that the compounds of formula $X(Me_3SiCH_2)_2W\equiv CSiMe_3$ where X = Cl and Br are dimeric in the solid state, having a pair of μ-$CSiMe_3$ bridges.[24] The compounds of formula $(RCH_2)_3W\equiv CR'$ where R = R' = CMe_3 and R = CMe_3, R' = $CSiMe_3$ are waxy hydrocarbon-soluble solids or liquids (R = $SiMe_3$, R' = CMe_3) at room temperature. However, during preparation of $(Me_3CCD_2)_3W\equiv CSiMe_3$ (**2a**-d_6), crystals suitable for an X-ray structure determination were obtained by vacuum sublimation.

In the space group $R\bar{3}$, there is one unique molecule in the unit cell with crystallographically imposed C_3 symmetry. An ORTEP view of the molecule is given in Figure 13, as well as selected bond distances and angles. A summary of crystal data is given in Table III.

Table III. Summary of Crystal Data for $(Me_3CCD_2)_3W\equiv CSiMe_3$ (**2a**-d_6)

empirical formula	$C_{19}H_{36}D_6SiW$
color of crystal	yellow
cryst dimns, mm	0.08 × 0.16 × 0.24
space group	$R\bar{3}$
temp, °C	−169
a, Å	15.232 (3)
b, Å	17.140 (4)
Z, molecules/cell	6
V, Å^3	3443.94
calcd density, g/cm^3	1.361
wavelength, Å	0.71069
mol wt	488.43
linear abs coeff, cm^{-1}	51.385
detector to sample dist, cm	22.5
sample to source dist, cm	23.5
av ω scan width at half-height, deg	0.25
scan speed, deg/min	8.0
scan width, deg + dispersion	1.8
individual bkgd, s	4
aperture size, mm	3.0 × 4.0
2θ range, deg	6–45
tot. no. of reflns collected	2281
no. of unique intensities	1011
no. with $F > 0.0$	995
no. with $F > 3.0\sigma(F)$	968
$R(F)$	0.0205
$R_w(F)$	0.0212
goodness of fit for the last cycle	0.761
max Δ/σ for last cycle	0.69

The W–C alkylidyne distance of 1.74 Å is typical of that for a W≡C bond; c.f W≡C bonds in $(t\text{-}BuO)_3W\equiv CPh$,[25] $(PhCH_2)_3W\equiv CPh(py)$,[12] and $W(\equiv CCMe_3)(CHCMe_3)(CH_2CMe_3)(dmpe)$.[26] The W–C(alkyl) bonds (2.10 Å) are quite short in comparison to those found in alkyl-W_2^{6+}-containing compounds where C_{sp^3}—W≡X groups are also present but similar to the C_{sp^3}-W distances of 2.06 Å (average) in the $X(Me_3SiCH_2)_2W\equiv CSiMe_3$ dimers.[24] There is no evidence for agostic CD–W interactions in the solid-state structure of **2a**-d_6.

Concluding Remarks. The presence of the trimethylsilyl group in **2a** effectively provides a label for the observation of a degenerate reaction for **1**, namely the interconversion of alkyl and alkylidyne ligands at a W(6+) center. All the available evidence points to a unimolecular process involving the stepwise transfer of hydrogen atoms via a reactive bis(alkylidene) intermediate. A seemingly analogous organic reaction would involve alkyne isomerization via an allene intermediate: $R'C\equiv CCH_2R \rightleftarrows R'CH_2C\equiv CR$.[27]

---

[24] Chisholm, M. H.; Heppert, J. A.; Huffman, J. C.; Thornton, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1466.

[25] Cotton, F. A.; Schwotzer, W.; Shamshoum, E. S. *Organometallics* **1984**, *3*, 1770.

[26] Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 2454.

Propyne isomerization, where R′ = D and R = H, has indeed been observed, but only in the gas phase at high temperatures, 500–700 °C.[27] Moreover, in this study the isomerization was shown to occur via a cyclopropene intermediate. Allene, $CH_2{=}C{=}CHD$, was only formed as a byproduct. Thus the organometallic and organic analogues appear to differ mechanistically and energetically.

---

(27) Hopf, H.; Priebe, H.; Walsh, R. *J. Am. Chem. Soc.* **1980**, *102*, 1210.

Acknowledgment. We thank Professor J. J. Gajewski for assistance in interpreting KIE's and the National Science Foundation for financial support.

Supplementary Material Available: Tables of fractional coordinates, anisotropic thermal parameters, and bond distances and angles (2 pages). Ordering information is given on any current masthead page.

Dynamics of Reaction of [*meso*-Tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphinato]iron(III) Hydrate with Various Alkyl Hydroperoxides in Aqueous Solution. 4. Comparison of Kinetic Parameters and D_2O Solvent Isotope Effects

Enona Gopinath and Thomas C. Bruice*

Contribution from the Department of Chemistry, University of California at Santa Barbara, Santa Barbara, California 93106. *Received December 20, 1990*

Abstract: The second-order rate constants (k_{1y}) for the reactions of the alkyl hydroperoxides $(Ph)_2(MeOCO)COOH$ and $(Ph)(Me)_2COOH$ with [*meso*-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphinato]iron(III) hydrate [$(\mathbf{1})Fe^{III}(X)_2$ ($X = H_2O$ or OH^-)] have been determined in water over the pH range 1–13 by using the one-electron oxidizable trapping agent 2,2′-azinobis(3-ethylbenzthiazolinesulfonate) (ABTS). The complex pH dependencies of k_{1y} reflect the pH dependency of the structure of reactants and intermediates as shown in Scheme II. Plots of log k_{1y} vs pH were fitted by a steady-state kinetic expression (eq 1) shown previously to describe the pH dependence of the reaction of $(CH_3)_3COOH$ with $(\mathbf{1})Fe^{III}(X)_2$. The dependencies of the rate constants for O–O bond cleavage (k_2 and k_4, Scheme II) of the ligated hydroperoxides YOOH to the pK_a of the leaving group YOH ($\delta(\log k_2)/\delta pK_{aYOH}$ and $\delta(\log k_4)/\delta pK_{aYOH}$) can be isolated from the pH dependencies of the k_{1y} values and are determined to be −0.22 and −0.13, respectively. Thus, the sensitivity of rate constants for the cleavage of the O–O bond of ligated hydroperoxide to its polarity is small. Kinetic deuterium solvent isotope effects for reaction of $(Ph)_2(MeOCO)COOH$ with $(\mathbf{1})Fe^{III}X_2$ have been found to be in accord with those determined previously for $(CH_3)_3COOH$.

Introduction

Acyl and alkyl hydroperoxides are substrates for several important classes of metalloporphyrin-containing enzymes. These include peroxidases, catalases, and the cytochrome P-450 enzymes. The mechanism of oxygen transfer from these hydroperoxides to iron(III) porphyrins is a subject of intense scrutiny. Whereas the consensus of opinion is that oxygen transfer from acyl hydroperoxides to iron(III) porphyrins occurs through heterolytic cleavage of the O–O bond of the hydroperoxide, to yield an iron(IV) porphyrin π-cation radical species and carboxylic acid as products, the primary products of alkyl hydroperoxide reduction have been a subject of much debate.[1–3]

This study is a continuation of an ongoing investigation into the reactions of water-soluble, non-μ-oxo dimer-forming tetraphenyliron(III) porphyrins with alkyl and acyl hydroperoxides in aqueous solution. Previous investigations have shown that the second-order rate constants (k_{1y}) for the reactions of [*meso*-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphinato]iron(III) hydrate [$(\mathbf{1})Fe^{III}(X)_2$ ($X = H_2O$ or OH^-)] with acyl or alkyl hydroperoxides, YOOH, exhibit different dependence upon the acidity of the YOH leaving group.[1,4] Plots of log k_{1y} vs the pK_a of YOH exhibit a definitive break at pK_a of about 11, so that k_{1y} values for the acyl hydroperoxides $m\text{-}ClC_6H_4CO_3H$, $p\text{-}O_2NC_6H_4CO_3H$, $PhCH_2CO_3H$, and $n\text{-}C_5H_{11}CO_3H$ and the alkyl hydroperoxide $Ph_2(CN)COOH$ fall on lines with slopes (β_{lg}) of −0.63, and −0.36 at pH 2.2 and 6.7, respectively, whereas k_{1y} values for the hydroperoxides $(Ph)_2(MeOCO)COOH$, $(Ph)(Me)_2COOH$, HOOH, and $(Me)_3COOH$ fall on separate lines with slopes (β_{lg}) of −0.18 and −0.11 at pH 2.2 and 6.7, respectively.[4] Since heterolytic O–O bond breaking has been established for the reactions of acyl hydroperoxides,[2,5,6] it was proposed that the break in the linear-free energy plot involves a change in mechanism to homolytic O–O bond cleavage with alkyl hydroperoxides. This conclusion is supported by product studies,[6,7] and particularly the stoichiometry of these reactions.[8] That the acyl hydroperoxides and the more acidic alkyl hydroperoxides exhibit a different mechanism than less acidic alkyl hydroperoxides is further supported by results from kinetic studies of the pH dependence of the reactions. Studies of the dynamics of reactions of [$(\mathbf{1})Fe^{III}X_2$, $X = OH^-$ or H_2O] with acyl hydroperoxides reveal no pH dependence of these reactions[4] in the pH range 2.2–6.7, whereas the kinetics of the reactions of HOOH and $(Me)_3COOH$ with the water-soluble

---

(1) Bruice, T. C. In *Mechanistic Principles of Enzyme activity* ed. Lieman, J. F., Greenburg, A., VCH Publishers: New York, 1988; p 227.

(2) (a) Labeque, R.; Marnett, L. J. *J. Am. Chem. Soc.* **1989**, *111*, 6621. (b) Arasasingham, R. D.; Cornman, C. R.; Balch, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 7800. (c) Mansuy, D.; Bartoli, J. F.; Momenteau, M. *Tetrahedron Lett.* **1982**, *23*, 2781.

(3) (a) Traylor, T. G.; Xu, F. *J. Am. Chem. Soc.* **1990**, *112*, 178. (b) Traylor, T. G.; Ciccone, J. P. *J. Am. Chem. Soc.* **1989**, *111*, 8413. (c) Traylor, T. G.; Fann, W-. P.; Bandhopadhyay, D. *J. Am. Chem. Soc.* **1989**, *111*, 8009.

(4) (a) Bruice, T. C.; Balasubramaninan, P. N.; Lee, R. W.; Lindsay-Smith, J. R. *J. Am. Chem. Soc.* **1988**, *110*, 7890. (b) Balasubramaninan, P. N.; Lee, R. W.; Bruice, T. C. *J. Am. Chem. Soc.* **1989**, *111*, 8714.

(5) Lindsay-Smith, J. R.; Balasubramanian, P. N.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7411.

(6) Balasubramanian, P. N.; Lindsay-Smith, J. R.; Davies, M. J.; Kaaret, T. W.; Bruice, T. C. *J. Am. Chem. Soc.* **1989**, *111*, 1477.

(7) Murata, K.; Panicucci, R.; Gopinath, E.; Bruice, T. C. *J. Am. Chem. Soc.* **1990**, *112*, 6072.

(8) Gopinath, E.; Bruice, T. C. *J. Am. Chem. Soc.* **1991**, *113*, 4657.