

Isomeric Hydrido/Vinylidene, MH(halide)(C=CH₂)L₂, and Ethylidyne, M(halide)(C–CH₃)L₂ (M = Os, Ru; L = Phosphine), Are Energetically Similar but Not Interconverting

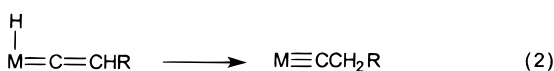
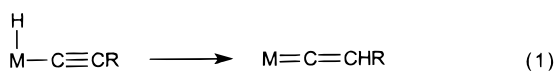
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Received October 30, 1997

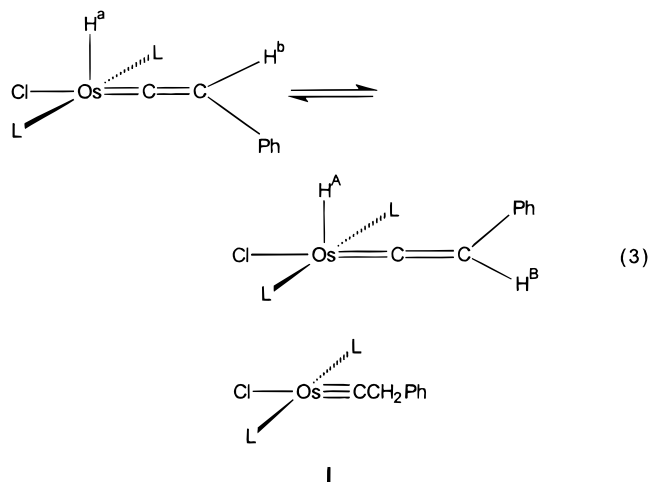
It is shown that there is no deuterium-isotope incorporation in the vinylidene CHPh group of RuDX(CCHPh)(P^tBu₂Me)₂ (X = Cl, I) on the time scale of 24 h at 25 °C, which indicates that the (unobserved) isomeric alkylidyne species RuX(CCHDPh)(P^tBu₂Me)₂ is not readily accessible under these conditions. Ab initio (B3LYP) calculations on the model MHCl(CCH₂)-(PH₃)₂ (M = Os, Ru) show the ethylidyne isomer MCl(CCH₃)(PH₃)₂ to be close in energy (2.5, –1.1 kcal mol^{–1} for Os and Ru, respectively) and effectively inaccessible at 25 °C due to the high energy (54.2, 45.5 kcal mol^{–1} for Os and Ru, respectively) of the transition state for such a 1,3-migration. In contrast, simple rotation of the CCH₂ group of MHCl(CCH₂)-(PH₃)₂ by 180° around the C–C axis is calculated to have a low barrier (8.1, 4.3 kcal mol^{–1} for Os and Ru, respectively), indicating this to be the mechanism for isomerization observed in OsHCl(CCHPh)(PⁱPr₃)₂.

An increasing number of publications postulate a 1,3-hydrogen migration (eq 1) for the conversion of a hydrido/acetylide to a vinylidene complex,¹ and this reaction has recently been treated computationally, considering both intra- and bimolecular mechanisms.² A 1,3-migration, which could also convert a hydrido/vinylidene to a carbyne (eq 2), might have been expected to be difficult in the linear MCC geometry but it has been reported.³



Against this background, the observed isomerization

of the CHPh group in the hydrido/vinylidene complex in eq 3 (L = PⁱPr₃) was suggested⁴ to occur not by simple rotation of the intact CCHPh ligand about its C=C axis, but rather by an intermediate **I**, where rotation is facile around the newly formed C–C single bond. The activa-



tion parameters for the observed fluxional process (i.e., the coalescence of the hydride resonances H^a and H^A of the two isomers in eq 3) are $\Delta H^\ddagger = 11.0 \pm 0.2$ kcal mol^{–1} and $\Delta S^\ddagger = 3.2 \pm 0.6$ cal K^{–1} mol^{–1}.⁴ The rotational barriers of vinylidene ligands have been found experimentally to be in the range from 7 to 12 kcal mol^{–1},⁵ with a few exceptions, like $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)\text{-(CCRR)}]^\ddagger$, where the barrier was found to be around 20 kcal mol^{–1}.⁶

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Given that this 1,3-hydrogen migration process is a potentially general mechanism for the creation of the important carbyne ligand and given our simultaneous but independent study of analogous $\text{RuHX}(\text{CCHR})\text{L}_2$ ($\text{X} = \text{I}, \text{Cl}$) species,⁷ we were attracted to a more comprehensive study of what was a small part of a previous study⁴ of $\text{OsHCl}(\text{CCHPh})\text{L}_2$. We report here the results of synthetic, isotope-labeling, and computational studies which reveal that an equilibrium such as that in eq 3 does not occur by a 1,3-hydrogen migration (i.e., via **I**) but rather by rotation around the $\text{M}=\text{C}=\text{C}$ bond axis ($\text{M} = \text{Os}, \text{Ru}$).

Experimental Section

General. All reactions and manipulations were conducted using standard Schlenk and glovebox techniques under prepurified argon. Solvents were dried and distilled under argon and stored in airtight solvent bulbs with Teflon closures. All NMR solvents were dried, vacuum-transferred, and stored in a glovebox. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and ^{31}P NMR spectra were obtained on a Varian Gemini 300, while ^2H NMR spectra were recorded on a Varian Inova 400 instrument. Chemical shifts are referenced to residual solvent peaks (^1H , ^2H , $^{13}\text{C}\{^1\text{H}\}$) or external H_3PO_4 (^{31}P). The complexes $\text{RuHCl}(\text{C}=\text{CHSiMe}_3)(\text{P}^t\text{-Bu}_2\text{Me})_2$,⁷ $\text{RuHCl}(\text{C}=\text{CHPh})(\text{P}^t\text{-Bu}_2\text{Me})_2$,⁷ $\text{OsHCl}(\text{C}=\text{CHSiMe}_3)(\text{P}^i\text{-Pr}_3)_2$,⁷ $\text{RuH}_3\text{Cl}(\text{P}^i\text{-Pr}_3)_2$,⁸ $\text{RuH}_3\text{Cl}(\text{P}^t\text{-Bu}_2\text{Me})_2$,⁷ and $\text{OsH}_2\text{-Cl}_2(\text{P}^t\text{-Bu}_2\text{Me})_2$ ⁹ were synthesized according to published procedures. $\text{PhC}\equiv\text{CH}$ (Aldrich) and $\text{Me}_3\text{SiC}\equiv\text{CH}$ (Oakwood) were distilled and degassed prior to use. $\text{PhC}\equiv\text{CD}$ (Aldrich) was used as received. Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHNS/O at the Chemistry Department, Indiana University.

$\text{OsH}_2\text{Cl}_2(\text{P}^t\text{-Bu}_2\text{Me})_2$. To a suspension of $\text{OsH}_2\text{Cl}_2(\text{P}^t\text{-Bu}_2\text{Me})_2$ (200 mg, 0.34 mmol) in toluene (10 mL) was added Et_3N (100 μL , 0.72 mmol), followed by freeze-pump-thaw degassing 3 times. The suspension was warmed to room temperature, and H_2 (1 atm) was admitted into the Schlenk flask. In 2 h, the reaction changed to a brown-yellowish solution with a whitish precipitate. After the mixture was stirred for an additional hour, the toluene solution was filtered through Celite. Removal of the volatiles in vacuo left a brown solid. Yield: 141 mg (75%). Anal. Calcd for $\text{C}_{18}\text{H}_{45}\text{Cl}_2\text{O}_2\text{Os}$: C, 39.37; H, 8.26. Found: C, 39.19; H, 8.09. ^1H NMR (300 MHz, C_6D_6): δ -18.93 (br s, 3H, Os-H), 1.16 (vt, $N = 4.6$ Hz, 36H, $\text{PC}(\text{CH}_3)_3$), 1.48 (vt, $N = 2.4$ Hz, 6H, PCH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6): δ 45.2 (s). IR (Nujol, cm^{-1}): $\nu(\text{Os}-\text{H})$ 2143 (m).

$\text{RuHCl}(\text{C}=\text{CHPh})(\text{P}^i\text{-Pr}_3)_2$. To a solution of $\text{RuH}_3\text{Cl}(\text{P}^i\text{-Pr}_3)_2$ (100 mg, 0.22 mmol) in 5 mL of toluene was added $\text{PhC}\equiv\text{CH}$ (48 μL , 0.44 mmol). Immediately, the color of the solution changed from brown-red to dark brown. The solution was concentrated to dryness, pentane was added, and the resulting solution was cooled at -40°C to give an olive green solid; yield 49 mg (40%). Anal. Calcd for $\text{C}_{26}\text{H}_{49}\text{ClP}_2\text{Ru}$: C, 55.74; H, 8.82. Found: C, 55.97; H, 8.38. ^1H NMR (300 MHz,

C_6D_6): δ -12.53 (t, $J_{\text{P}-\text{H}} = 17.4$ Hz, 1H, Ru-H), 1.20 (dvt, $J_{\text{H}-\text{H}} = 5.7$ Hz, $N = 13.8$ Hz, 36H, $\text{PCH}(\text{CH}_3)_2$), 2.48 (m, 6H, $\text{PCH}(\text{CH}_3)_2$), 4.35 (t, $J_{\text{P}-\text{H}} = 3.6$ Hz, 1H, CHPh), 6.85-7.20 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ 20.20, 20.42 (both s, $\text{PCH}(\text{CH}_3)_2$), 24.69 (vt, $N = 9.7$ Hz, $\text{PCH}(\text{CH}_3)_2$), 109.67 (t, $J_{\text{P}-\text{C}} = 2.1$ Hz, Ru=C=C), 123.59 (s, Ph), 126.54 (s, Ph), 128.74 (s, Ph), 133.77 (t, $J_{\text{P}-\text{C}} = 2.5$ Hz, C_{ipso} , Ph), 329.24 (t, $J_{\text{P}-\text{C}} = 14$ Hz, Ru=C). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6): δ 51.0 (s). IR (Nujol, cm^{-1}): $\nu(\text{Ru}-\text{H})$ 2071 (m), $\nu(\text{C}=\text{C})$ 1610 (s).

$\text{RuHCl}(\text{C}=\text{CH}_2)(\text{P}^t\text{-Bu}_2\text{Me})_2$. A solution of $\text{RuH}_3\text{Cl}(\text{P}^t\text{-Bu}_2\text{Me})_2$ (100 mg, 0.22 mmol) in toluene (5 mL) was frozen in liquid N_2 , the headspace of the Schlenk flask was evacuated, and excess $\text{HC}\equiv\text{CH}$ was introduced. On warming, a color change from orange to deep brown was observed. Excess $\text{HC}\equiv\text{CH}$ was removed via vacuum. The resulting solution was filtered through Celite, and the volatiles were removed to give a dark brown solid. Yield: 80 mg (76%). Anal. Calcd for $\text{C}_{20}\text{H}_{45}\text{ClP}_2\text{Ru}$: C, 49.63; H, 9.37. Found: C, 49.81; H, 8.39. ^1H NMR (300 MHz, C_6D_6): δ -14.42 (t, $J_{\text{P}-\text{H}} = 18.3$ Hz, 1H, Ru-H), 1.26 (vt, $N = 6.3$ Hz, 18H, $\text{PC}(\text{CH}_3)_3$), 1.35 (vt, $N = 2.7$ Hz, 6H, PCH_3), 1.37 (vt, $N = 6.3$ Hz, 18H, $\text{PC}(\text{CH}_3)_3$), 2.78 (t, $J_{\text{P}-\text{H}} = 3.4$ Hz, 2H, Ru=C=CH₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ 8.56 (vt, $N = 11.6$ Hz, PCH_3), 29.75, 29.88 (both s, $\text{PC}(\text{CH}_3)_3$), 34.91 (vt, $N = 8$ Hz, $\text{PC}(\text{CH}_3)_3$), 36.29 (vt, $N = 7.6$ Hz, $\text{PC}(\text{CH}_3)_3$), 87.34 (t, $J_{\text{P}-\text{C}} = 3.8$ Hz, Ru=C=C), 328.41 (t, $J_{\text{P}-\text{C}} = 14.3$ Hz, Ru=C). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6): δ 41.9 (s). IR (Nujol, cm^{-1}): $\nu(\text{Ru}-\text{H})$ 2056 (w), $\nu(\text{C}=\text{C})$ 1606 (s).

$\text{OsHCl}(\text{C}=\text{CH}_2)(\text{P}^t\text{-Bu}_2\text{Me})_2$. This compound was prepared using an analogous procedure as described for $\text{RuHCl}(\text{C}=\text{CH}_2)(\text{P}^t\text{-Bu}_2\text{Me})_2$, starting from $\text{OsH}_3\text{Cl}(\text{P}^t\text{-Bu}_2\text{Me})_2$ (50 mg, 0.09 mmol) and $\text{HC}\equiv\text{CH}$. The compound was isolated as a deep brown solid. Yield: 40 mg (76%). Anal. Calcd for $\text{C}_{20}\text{H}_{45}\text{ClO}_2\text{Os}$: C, 41.91; H, 7.91. Found: C, 41.64; H, 7.70. ^1H NMR (300 MHz, C_6D_6): δ -17.41 (t, $J_{\text{P}-\text{H}} = 14.5$ Hz, 1H, Os-H), 0.37 (t, $J_{\text{P}-\text{H}} = 3.4$ Hz, 2H, Os=C=CH₂), 1.24 (vt, $N = 6.1$ Hz, 18H, $\text{PC}(\text{CH}_3)_3$), 1.38 (vt, $N = 6.3$ Hz, 6H, $\text{PC}(\text{CH}_3)_3$), 1.57 (vt, $N = 3$ Hz, 18H, PCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6): δ 9.38 (vt, $N = 15.5$ Hz, PCH_3), 30.01 (vt, $N = 2.1$ Hz, $\text{PC}(\text{CH}_3)_3$), 30.42 (vt, $N = 2.8$ Hz, $\text{PC}(\text{CH}_3)_3$), 36.12 (vt, $N = 11.1$ Hz, $\text{PC}(\text{CH}_3)_3$), 37.95 (vt, $N = 9.6$ Hz, $\text{PC}(\text{CH}_3)_3$), 86.83 (t, $J_{\text{P}-\text{C}} = 3.5$ Hz, Os=C=C), 283.90 (t, $J_{\text{P}-\text{C}} = 9$ Hz, Os=C). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6): δ 26.4 (s). IR (Nujol, cm^{-1}): $\nu(\text{Os}-\text{H})$ 2160 (w), $\nu(\text{C}=\text{C})$ 1612 (s).

Deuterium-Labeling Studies of $\text{RuDCl}(\text{C}=\text{CHPh})(\text{P}^t\text{-Bu}_2\text{Me})_2$. By ^1H NMR Spectroscopy. $\text{RuDCl}(\text{C}=\text{CHPh})(\text{P}^t\text{-Bu}_2\text{Me})_2$ was prepared in an NMR tube by addition of $\text{PhC}\equiv\text{CD}$ (4.8 μL , 0.044 mmol) to a solution of $\text{RuH}_3\text{Cl}(\text{P}^t\text{-Bu}_2\text{Me})_2$ (10 mg, 0.022 mmol) in C_6D_6 (0.5 mL). In the ^1H NMR spectra recorded after 10 min and after 24 h at 25°C , there is no peak assignable to Ru-H (triplet at -12.65 ppm in $\text{RuHCl}(\text{C}=\text{CHPh})(\text{P}^t\text{-Bu}_2\text{Me})_2$).⁷

By ^2H NMR Spectroscopy. In an NMR tube, $\text{RuDCl}(\text{C}=\text{CHPh})(\text{P}^t\text{-Bu}_2\text{Me})_2$ was dissolved in C_6H_6 (0.5 mL). ^2H NMR (61 MHz, 20°C): δ -12.53 (s). After 24 h at 25°C , the ^2H NMR spectrum of the same sample showed only a singlet at δ -12.53.

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(12) $\Delta H^\ddagger = 53.6$ kcal mol⁻¹ for Os, 45.1 kcal mol⁻¹ for Ru.

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Deuterium Labeling Studies of RuDI(=C=CHPh)-(P^tBu₂Me)₂. Similar experiments to those described for the chloride derivative were carried out.

Computational Details. Ab initio calculations were carried out with the Gaussian 94 set of programs within the framework of DFT at the B3LYP level.¹⁰ LANL2DZ effective core potentials (quasi relativistic for the metal centers) were used to replace the 28 innermost electrons of Ru, the 46 innermost electrons of Os, as well as the 10 core electrons of P and Cl. The LANL2DZ basis set was used for all atoms but the H of PH₃, which were represented at the STO-3G level. Polarization functions have been added to all atoms except for the metal and the H of PH₃. Full geometry optimization was performed with no symmetry restriction, and the nature of the optimized structure as a minimum or transition state was assigned by numerical frequency calculations. Enthalpy differences between structures were derived from the frequency calculations. The obtained transition state structures were given small structural perturbations, then further geometrically optimized to ensure that they connect the reactant and product of interest.

Results

Deuterium-Labeling Test of the Mechanism. If **I** is the intermediate in the isomerization of eq 3, this implies a scrambling of the hydride and vinylidene hydrogens. Such scrambling must occur at the same rate as the coalescence of hydrides H^a and H^A (eq 3). At 24 °C, the half-life for the hydride exchange in OsHCl-(CCHPh)₂, observed by ¹H NMR coalescence, is 10⁻⁴ min. We, therefore, synthesized the more kinetically labile RuDX(CCHPh)₂ (X = Cl, I; L = P^tBu₂Me) according to eq 4. These isotopomers show D to remain



on Ru for 24 h at 24 °C in benzene (¹H and ²H NMR evidence). This excludes **I** as an accessible species from the hydrido vinylidene ground state at 24 °C.

Theoretical Studies. Calculations have been carried out for Os and Ru, and the results are similar for both metal centers. As a consequence, numerical values will refer only to Os, unless comparison is necessary for the sake of discussion. Figures are drawn for the Os complex, and equivalent figures for Ru are given in the Supporting Information.

a. Hydride Migration Process. The hydrido/vinylidene MHCl(CCH₂)(PH₃)₂, **1^{Os}** and **1^{Ru}**, and the related ethylidene complexes **2^{Os}** and **2^{Ru}** are both minima on the potential energy surface, and **1^{Os}** and **2^{Os}** are shown in Figure 1. The two minima are close in energy: **1^{Os}** is more stable than **2^{Os}** by 2.5 kcal mol⁻¹ ($\Delta H^\circ = 4.8$ kcal mol⁻¹) (Figure 2), and **1^{Ru}** is less stable than **2^{Ru}** according to the difference in electronic energies by 1.1 kcal mol⁻¹ but *more* stable according to the differences in enthalpies ($\Delta H^\circ = 1.9$ kcal mol⁻¹). Note that both **1** and **2** have the same valence electron count. The complex **1^{Os}** has a distorted trigonal-bipyramidal geometry with a small Cl–Os–H(3) angle (86.7°) and a short Os–Cl bond (2.436 Å), indicating the presence of an Os–Cl π bond. This structure, which is characteristic of a 16-electron, five-coordinate complex with a π -donor ligand, has been called “Y” in earlier work.¹¹ It is favored over the square-pyramidal structure by the presence of a π donor, which makes a π bond between

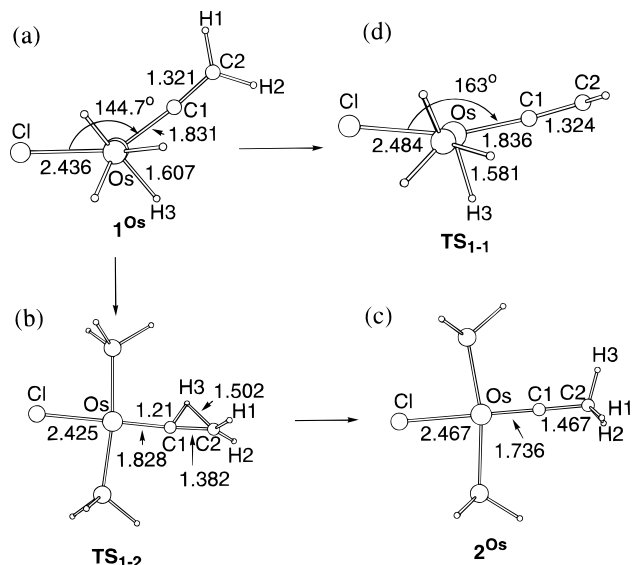


Figure 1. Optimized structural parameters for (a) OsHCl-(CCH₂)(PH₃)₂, **1^{Os}**, (b) transition state **TS₁₋₂** for H(3) migration from Os to C(2), (c) OsCl(CCH₃)(PH₃)₂, **2^{Os}**, and (d) transition state **TS₁₋₁** for rotation of the vinylidene.

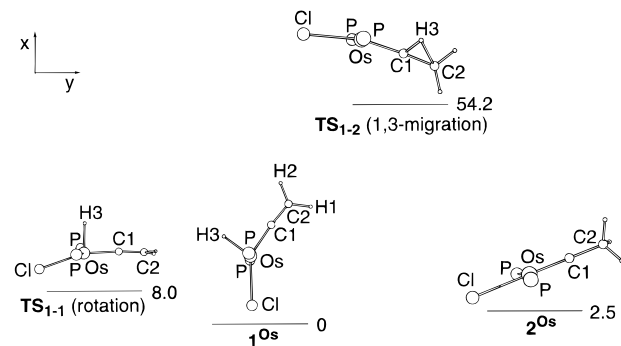
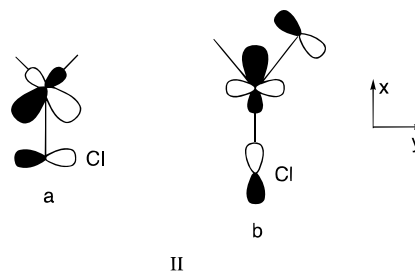


Figure 2. Relative energies (kcal mol⁻¹) for OsHCl(CCH₂)(PH₃)₂, **1^{Os}**, OsCl(CCH₃)(PH₃)₂, **2^{Os}**, and the transition states **TS₁₋₁** (rotation of the vinylidene) and **TS₁₋₂** (1,3-hydrogen migration). Hydrogens on the phosphines have been omitted for clarity.

one of the lone pairs of Cl and the empty *xy* metal orbital (**IIa**). The vinylidene CH₂ group lies in the Cl–Os–



H(3) mirror plane. This conformation has the empty orbital of C(1) in the mirror plane, which stabilizes the *x*² – *y*² orbital through back-donation (**IIb**) and leads to a short Os–C(1) bond (1.831 Å).

The carbyne **2** is a square-planar complex with trans phosphines. The metal *xy* and *yz* orbitals are involved in π bonding with the carbon *p_x* and *p_z* orbitals, which stabilizes the formal Os(IV) oxidation state, shortens the Os–C(1) bond (1.736 Å), and causes the phosphines to bend slightly away from the carbyne (P–Os–P = 168.3°) to enhance Os–C(1) multiple bonding.

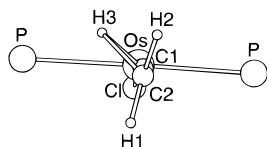


Figure 3. View of TS_{1-2} down the $\text{C}(2)\text{--C}(1)$ vector.

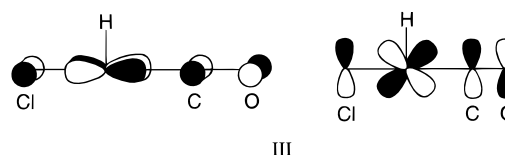
The transition state (TS_{1-2}) has been located (Figures 1 and 3) at a very high energy (54.5 kcal mol⁻¹ for Os, 45.5 kcal mol⁻¹ for Ru)¹² (Figure 1). The ligand atoms form a square-planar geometry around the metal very similar to that in the carbyne complex $\mathbf{2}^{\text{Os}}$. The transfer of H(3) to the terminal CH_2 group requires a significant displacement of H(3) out of the original mirror plane to reach the available p orbital of C(2). To retain maximum bonding with other atoms along such a path, H(3) can take advantage of the *two* available p orbitals of C(1). At TS_{1-2} , the $\text{C}(1)\text{--H}(1)$ partially formed bond is oriented in a plane which is intermediate between the original plane ($\text{H}(2)\text{--C}(2)\text{--C}(1)\text{--H}(3) = 0^\circ$) and the final plane ($\text{H}(2)\text{--C}(2)\text{--C}(1)\text{--H}(3) = 120^\circ$), since $\text{H}(2)\text{--C}(2)\text{--C}(1)\text{--H}(3)$ is equal to 68° (Figure 3). This situation allows H(3) to start bonding with C(2), although the $\text{C}(1)\text{--H}(3)$ bond remains shorter (1.210 Å) than $\text{C}(2)\text{--H}(3)$ (1.502 Å). At the same time, $\text{C}(1)\text{--C}(2)$ is considerably lengthened (1.382 Å), showing the loss of π character as C(1) and C(2) rehybridize. The metal is in a conventional coordination geometry, so that it appears that the extreme distortion within the carbon ligand is the main cause for the high energy of the transition state.

b. Vinylidene Rotation. A rotation of the vinylidene by 180° about the $\text{Os}\text{--C}(1)\text{--C}(2)$ axis is the alternative mechanism for eq 3. The transition state TS_{1-1} is calculated to be only 8.1 kcal mol⁻¹ ($\Delta H^\ddagger = 7.4$ kcal mol⁻¹) for Os and 4.3 kcal mol⁻¹ ($\Delta H^\ddagger = 3.9$ kcal mol⁻¹) for Ru above the vinylidene structure. This is clearly the preferred path for interconverting H(1) and H(2) (Figure 1); the real rotational barrier should be larger, with introduction of steric bulk on phosphorus as well as phenyl at C(2), closer to ΔH^\ddagger observed (11 kcal mol⁻¹) for $\text{OsHCl}(\text{CCHPh})(\text{P}^i\text{Pr}_3)_2$.

The structure of TS_{1-1} , a vinylidene complex, presents some significant structural changes around the metal with respect to the ground-state vinylidene complex. The overall structure is a distorted square-based pyramid, with apical hydride and basal chloride, vinylidene ($\text{Cl}\text{--Os}\text{--C}(1) = 163^\circ$), and phosphine ligands. Since the $\text{C}(1)\text{--Os}\text{--H}(3)$ angle has remained approximately constant, it appears that the rotation of the vinylidene has, thus, been accompanied by a sliding motion of the chloride within the mirror plane of the complex. In addition, the $\text{Os}\text{--Cl}$ bond has been significantly stretched (2.484 vs 2.436 Å in $\mathbf{1}^{\text{Os}}$) as a consequence of being trans to a ligand and losing its π character to the metal. Conversely, the $\text{Os}\text{--H}(3)$ bond has contracted, as expected, from the absence of any trans ligand.

The factors that are responsible for the coordination geometry change are worth discussing, since a correlation between the rotation of a ligand and the coordination geometry at the metal is rare. The most related case is that of $d^8 \text{ML}_4$ (olefin) complexes where rotation of the olefin and pseudorotation at the metal are intimately mixed.¹³

The geometry of $d^6 \text{ML}_5$ has been found to be highly sensitive to the nature of the ligand.¹¹ In the presence of a π donor (Cl), the passage from Y to square pyramidal (T) has been shown to be facile.¹¹ In the present case, where the rotation and the sliding motions are coupled, the change in geometry remains energetically accessible. In fact, the square-pyramidal structure of $\text{OsHCl}(\text{CCH}_2)(\text{PH}_3)_2$ with an apical H is not surprising, since it is also the structure for $\text{MHCl}(\text{CO})\text{L}_2$ ($\text{M} = \text{Os},^{14} \text{Ru}^{14,15}$). A point of discussion is why two different conformations of the same single-face π -acceptor vinylidene favor two different geometries around the metal. In the square-based pyramidal structure such as in $\text{MHCl}(\text{CO})\text{L}_2$, the favorable factors are (i) a strong σ -donor ligand like H which can be trans to the empty site and (ii) the alignment of the π -donor Cl ligand and π -acceptor ligand, which relieves the four-electron interaction between the lone pair of the π -donor ligand and π -acceptor trans ligand (**III**). This last interaction



would be operative for the π -acceptor orbital in the mirror plane or perpendicular to it. If, however, the $\text{C}(1)$ empty p orbital lies in the mirror plane, the Y geometry permits a more potent back-donation than the T structure through $x^2 - y^2$, which is destabilized by its interaction with the Cl p_x orbital (**IIb**). Simultaneously, as mentioned earlier, the π interaction between the empty metal xy orbital and Cl p_y occupied orbital is also favorable to the Y structure.

In summary, both $\text{MHCl}(\text{CCH}_2)(\text{PH}_3)_2$ and $\text{MCl}(\text{CCH}_3)(\text{PH}_3)_2$ gave optimized geometries which were identified as minima on the potential energy surface. Although the energy difference between the ground state (hydride/vinylidene) and the four-coordinate ethylidyne (planar OsClCP_2 coordination geometry) is not so large as to exclude **I** as an intermediate in the NMR coalescence process observed for $\text{OsHCl}(\text{CCHPh})\text{L}_2$, the high energy of the transition state to get to this carbyne makes this species kinetically inaccessible.

Concerning the Existence of the Isomers in Eq 3. We were initially puzzled as to why $\text{OsHCl}(\text{CCHPh})(\text{P}^i\text{Pr}_3)_2$ shows detectable populations of the syn and anti isomers shown in eq 3 while $\text{RuHCl}[\text{CC}(\text{H})\text{SiMe}_3](\text{P}^i\text{Bu}_2\text{Me})_2$ (**3**) shows only one isomer by ^1H and ^{31}P NMR. Since calculations showed the rotational barrier to be higher for Os than for Ru (8.1 vs 4.3 kcal mol⁻¹), we considered that our ^1H and ^{31}P NMR observations on $\text{RuHCl}[\text{CC}(\text{H})\text{SiMe}_3](\text{P}^i\text{Bu}_2\text{Me})_2$ were above the coalescence temperature, thus, failing to detect isomers. We, therefore, did a variable-temperature study of this ruthenium complex and (to test the metal, vinylidene, and phosphine steric and electronic effects) the following five analogous compounds: $\text{RuHCl}(\text{C}=\text{CHPh})(\text{P}^i\text{Pr}_3)_2$ (**4**), $\text{RuHCl}(\text{C}=\text{CHPh})(\text{P}^i\text{Bu}_2\text{Me})_2$ (**5**), $\text{RuHCl}(\text{C}=\text{CH}_2)(\text{P}^i\text{Bu}_2\text{Me})_2$ (**6**), $\text{OsHCl}(\text{C}=\text{CH}_2)(\text{P}^i\text{Bu}_2\text{Me})_2$ (**7**), $\text{OsHCl}(\text{C}=\text{CHSiMe}_3)(\text{P}^i\text{Pr}_3)_2$ (**8**).

(14) Esteruelas, M. A.; Werner, H. J. *Organomet. Chem.* **1986**, *303*, 221.

For compounds **3** and **4**, there was no evidence for coexistence of two isomers or NMR decoalescence down to $-90\text{ }^{\circ}\text{C}$ in toluene- d_8 by ^1H and ^{31}P NMR. Compounds **6** and **7** show an unusual temperature dependence of the hydride proton chemical shifts (in **6** it moves 0.66 ppm upfield between 20 and $-90\text{ }^{\circ}\text{C}$, while in compound **7** it moves 0.77 ppm downfield between 20 and $-90\text{ }^{\circ}\text{C}$) but no decoalescence down to $-90\text{ }^{\circ}\text{C}$. Compound **8** shows an unusual temperature dependence of the hydride chemical shift; it moves 1.63 ppm upfield between 20 and $-90\text{ }^{\circ}\text{C}$ and broadens by $0\text{ }^{\circ}\text{C}$ but never decoalesces. For complex **5**, in the ^1H NMR spectrum at $-90\text{ }^{\circ}\text{C}$, two overlapping triplets (at -12.1 and -12.24 ppm; relative intensities 1:4) were observed. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at the same temperature shows two peaks (relative intensities 1:4). However, our experience with many $\text{M}(\text{X})(\text{Y})(\text{Z})\text{L}_2$ species with bulky L shows that *conformers* (i.e., phosphine rotamers) can be decoalesced below ca. $-60\text{ }^{\circ}\text{C}$,¹⁶ and this is *sufficient* to account for the NMR changes in compounds **5–8**. Thus, any evidence for decoalescence of isomers of **3–8** analogous to those in eq 3 is weak to nonexistent. The existence of isomers (eq 3) and the energy of isomerization between these is unaccountably larger for $\text{OsHCl}(\text{CCHPh})(\text{P}^i\text{Pr}_3)_2$ than for any of the analogues **3–8**. A referee has suggested that two vinylidene rotational isomers, separated by a larger ΔG° for all pairs except $\text{OsHCl}(\text{CCHPh})(\text{P}^i\text{Pr}_3)_2$, could lead to negligible population of one species by the time decoalescence is achieved. Temperature-dependent populations would then account for the temperature-dependent chemical shift of the *averaged* signal we observe.

Conclusions

While a 1,3-migration that interconverts hydrido–vinylidene and alkylidyne complexes has been proposed

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(16) Notheis, J. U.; Heyn, R. H.; Caulton, K. G. *Inorg. Chim. Acta* **1995**, *229*, 187.

in some cases,³ such facile intramolecular isomerization is not supported by the studies reported here. A bimolecular mechanism for eq 2 (compare ref 2) is ruled out by the near-zero ΔS^{\ddagger} value.⁴

The low rotational barrier of the vinylidene ligand in the complexes $\text{MHX}(\text{CCHR})(\text{PR}'_3)_2$ is supported by the experimental data on compounds **3–8**, as well as by the theoretical studies. It remains unclear why the barrier is higher in $\text{OsHCl}(\text{C}=\text{CHR})(\text{P}^i\text{Pr}_3)_2$ where $\text{R} = \text{Ph}$ than when $\text{R} = \text{SiMe}_3$.

The change of coordination mode associated with the rotation of the vinylidene is a rather rare feature of transition-metal complexes and plays some role in this complex. If the hydrido/vinylidene complex had been a square pyramid, as is the case when the metal is bonded simultaneously to a π donor X and a π acceptor like CO, the rotation of the vinylidene would have been almost entirely determined by the steric factors and not by the electronic factors. This is because in a square pyramid the two d orbitals that can back-donate electrons into a π -acceptor ligand at the basal site are approximately degenerate in energy (**III**). In the present case, the back-donation is stronger in the Y geometry of the ground state than in the T geometry of the transition state. Thus, there is a nonnegligible electronic barrier associated with the *two* structural changes (rotation accompanied by a sliding motion in the molecular plane). This result illustrates that metal coordination geometry can be modified not only by changes in the nature of the ligand, but also by their orientation in the coordination sphere.

Acknowledgment. This work was supported by the U.S. National Science Foundation and by the French CNRS, in part by an international NSF/CNRS(PICS) grant. M.O. thanks the Spanish Ministerio de Educación y Cultura for a postdoctoral fellowship. We also thank Johnson Matthey/Aesar for material support.

Supporting Information Available: Computed structures and energies for Ru vinylidenes and carbynes (2 pages). Ordering information is given on any current masthead page.

OM9709493