

Hydride Is Not a Spectator Ligand in the Formation of Hydrido Vinylidene from Terminal Alkyne and Ruthenium and Osmium Hydrides: Mechanistic Differences

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RuHX(H₂)L₂ (L = P^tBu₂Me; X = Cl, I) and OsH₃ClL₂ (L = PⁱPr₃) react (time of mixing) with terminal alkynes in a 1:2 stoichiometry to give MHX(=C=CHR)L₂ and RCH=CH₂. The reactions of RuHX(H₂)L₂ with PhC≡CD lead to RuDX(=C=CHPh)L₂ as the only isotopomers. This result is understood in terms of an insertion of the alkyne in the Ru–H bond to make a vinyl, followed by an α-hydrogen migration, giving the hydrido/vinylidene. This reaction path has been studied by ab initio (B3LYP) calculations with location of the minima and transition states. In agreement with isotopic labeling experiments, it is shown that the path starting with insertion into the Ru–H bond is more favorable than a 1,2-migration within the coordinated alkyne ligand. The favored reaction is calculated to be exothermic from the starting compounds to intermediates and to products with the energies of all transition states well below that of the separated reactants. The mechanism involves the formation of a 14-electron η¹-vinyl intermediate which, after structural changes, gives the 16-electron hydrido/vinylidene product. The same general reaction path is calculated to be preferred for Os, but differences occur between the geometries of the vinyl intermediate (it is η²-vinyl for Os) and in the total number of intermediates involved.

Introduction

Olefin metathesis is a very useful method for C–C bond formation in organic synthesis.¹ Among all of the transition-metal complexes that catalyze this reaction, the ruthenium-based compounds RuCl₂(=CR₂)(PR'₃)₂ represented a breakthrough in the field, due to their wide functional group and protic media tolerance, as well as because of their high stability and easy handling.² While the current methods of preparing such compounds provide a wide array of R groups in the carbene ligand,^{2,3} less attention has been paid to the possibility of introducing different functionalities on the ruthenium center.⁴

On the other hand, and while the subject of transformation of a terminal alkyne into its vinylidene isomer promoted by a metal center has been widely addressed,⁵ the role that polyhydrides play in this transformation has been scarcely investigated.⁶

We find that the complexes RuHX(H₂)L₂ (X = Cl, I) are a convenient source of a 14-e⁻ ruthenium fragment "RuHCIL₂" that by reaction with terminal alkynes lead to the hydrido/vinylidene complexes RuHX(=C=CHR)-L₂, providing a new synthetic approach to the Ru-based carbenoids described above and also achieving the goal of functionalizing the ruthenium center. Similar functionalization can be achieved starting from OsH₃XL₂ (X = Cl). It will be shown by isotope labeling and theoretical studies of the reaction path that the hydride initially on the metal plays not only the role of a spectator ligand but is an active participant in the formation of the vinylidene group. Moreover, this theoretical study

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reveals fundamental structural differences between the Ru and Os intermediates in this reaction.

Experimental Section

General. All reactions and manipulations were conducted using standard Schlenk and glovebox techniques under prepurified argon. Solvents were dried and distilled under nitrogen or 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. T_1 measurements were made at 300 MHz using the inversion-recovery method and standard Varian software. Chemical shifts are referenced to residual solvent peaks (^1H , ^2H , $^{13}\text{C}\{^1\text{H}\}$) or external H_3PO_4 (^{31}P). Complexes $[\text{RuCl}_2(\text{COD})]_n$ ⁷ and $\text{OsH}_3\text{Cl}(\text{P}^i\text{Pr}_3)_2$ ⁸ were synthesized according to published procedures. HCCPh (Aldrich) and HCCSiMe_3 (Oakwood) were distilled and degassed prior to use. 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.

$\text{RuH}_2\text{Cl}_2(\text{P}^i\text{Bu}_2\text{Me})_2$. To a suspension of $[\text{RuCl}_2(\text{COD})]_n$ (750 mg, 2.68 mmol for $n = 1$) in 2-propanol (20 mL), placed in a Fisher-Porter bottle, was added $\text{P}^i\text{Bu}_2\text{Me}$ (1072 μL , 5.35 mmol). The brown suspension was degassed, and the Fisher-Porter bottle was filled with H_2 (2.5 atm) and heated at 85 °C for 4 h. The bottle was then recharged to 2.5 atm of H_2 and stirred at 85 °C for 20 h. After this time, the resulting reddish suspension was transferred to a Schlenk flask and concentrated to ca. 5 mL under reduced pressure. The burgundy solid was filtered, washed with cold diethyl ether, and dried in vacuo. Yield: 980 mg (74%). Anal. Calcd for $\text{C}_{18}\text{H}_{44}\text{Cl}_2\text{P}_2\text{Ru}$: C, 43.72; H, 8.97. Found: C, 43.57; H, 8.28. ^1H NMR (300 MHz, CD_2Cl_2 , 20 °C): -11.31 (t, $J_{\text{P-H}} = 29.8$ Hz, 2H, Ru-H), 1.12 (d, $J_{\text{P-H}} = 10.2$ Hz, 6H, PCH_3), 1.51 (d, $J_{\text{P-H}} = 14.4$ Hz, 36H, $\text{PC}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2 , 20 °C): 99.8 (s). IR (Nujol, cm^{-1}): $\nu(\text{Ru-H})$ 2162 (s).

$\text{RuHCl}(\text{H}_2)(\text{P}^i\text{Bu}_2\text{Me})_2$. To a suspension of $\text{RuH}_2\text{Cl}_2(\text{P}^i\text{Bu}_2\text{Me})_2$ (100 mg, 0.2 mmol) in toluene (10 mL) was added Et_3N (57 μL , 0.4 mmol). After freeze/pump/thaw degassing 3 times, the suspension was warmed to room temperature and H_2 (1 atm) was admitted to the Schlenk flask. In 2 h the reaction mixture changed to a brown-yellowish solution with a whitish precipitate. After the solution was stirred for an additional hour, the toluene solution was filtered through Celite. Removal of the volatiles in vacuo left a brown solid. Yield: 67 mg (72%). Anal. Calcd for $\text{C}_{18}\text{H}_{45}\text{ClP}_2\text{Ru}$: C, 47.00; H, 9.86. Found: C, 46.51; H, 9.40. ^1H NMR (300 MHz, C_6D_6 , 20 °C): -15.78 (br s, 3H, Ru-H), 1.10 (vt, $N = 6.1$ Hz, 36H, $\text{PC}(\text{CH}_3)_3$), 1.32 (vt, $N = 2.2$ Hz, 6H, PCH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6 , 20 °C): 58.7 (s). IR (Nujol, cm^{-1}): $\nu(\text{Ru-H})$ 2125 (m), 2083 (m), 1910 (w).

$\text{RuH}_2\text{I}_2(\text{P}^i\text{Bu}_2\text{Me})_2$. A CH_2Cl_2 (10 mL) solution of $\text{RuH}_2\text{Cl}_2(\text{P}^i\text{Bu}_2\text{Me})_2$ (100 mg, 0.2 mmol) was placed in a Schlenk flask fitted with a rubber septum. To this solution, Me_3SiI (63 μL , 0.44 mmol) was added via syringe at room temperature. Immediately, the dark red solution color changed to deep violet. After 10 min of stirring, the volatiles were removed in vacuo, quantitatively yielding $\text{RuH}_2\text{I}_2(\text{P}^i\text{Bu}_2\text{Me})_2$. Anal. Calcd for $\text{C}_{18}\text{H}_{44}\text{I}_2\text{P}_2\text{Ru}$: C, 32.92; H, 6.55. Found: C, 33.36; H, 7.02. ^1H NMR (300 MHz, CD_2Cl_2 , 20 °C): -8.54 (t, $J_{\text{P-H}} = 26.8$ Hz, 2H, Ru-H), 1.16 (d, $J_{\text{P-H}} = 10.2$ Hz, 6H, PCH_3), 1.51 (d, $J_{\text{P-H}} = 15$ Hz, 36H, $\text{PC}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2 , 20 °C): 90.4 (s). IR (Nujol, cm^{-1}): $\nu(\text{Ru-H})$ 2145 (s).

Spectroscopic Characterization of $\text{RuH}_6(\text{P}^i\text{Bu}_2\text{Me})_2$. In an NMR tube $\text{RuH}_2\text{Cl}_2(\text{P}^i\text{Bu}_2\text{Me})_2$ (10 mg, 0.020 mmol) and NaBH_4 (7.6 mg, 0.20 mmol) were suspended in benzene- d_6 . To that suspension, 5 μL of methanol was added. The NMR tube was kept open until the gas evolution ceased, then the tube was closed and its NMR spectrum was taken. During this time, the color changed from red-burgundy to yellowish. ^1H NMR (300 MHz, C_6D_6 , 20 °C): -7.45 (br t, $J_{\text{P-H}} = 8.1$ Hz, 6H, RuH_6), 1.20 (vt, $N = 6.1$ Hz, 36H, $\text{PC}(\text{CH}_3)_3$), 1.31 (vt, $N = 2.1$ Hz, 6H, PCH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6 , 20 °C): 78.9 (s).

$\text{RuHI}(\text{H}_2)(\text{P}^i\text{Bu}_2\text{Me})_2$. To a suspension of $\text{RuH}_2\text{Cl}_2(\text{P}^i\text{Bu}_2\text{Me})_2$ (300 mg, 0.61 mmol) and NaBH_4 (229 mg, 6.1 mmol) in toluene (8 mL), several drops of methanol were added. After the mixture was stirred for 10 min, it was filtered. To the resulting yellow-greenish solution, CH_3I (38 μL , 0.61 mmol) was added and immediate gas evolution and color change (to brown) was observed. After the mixture was stirred for 1 h, the volatiles were removed under vacuum, obtaining a brown solid. Yield: 230 mg (68%). Anal. Calcd for $\text{C}_{18}\text{H}_{45}\text{IP}_2\text{Ru}$: C, 39.20; H, 8.22. Found: C, 39.37; H, 7.74. ^1H NMR (300 MHz, C_6D_6 , 20 °C): -16.01 (br s, 3H, Ru-H), 1.04 (vt, $N = 6.1$ Hz, 36H, $\text{PC}(\text{CH}_3)_3$), 1.73 (vt, $N = 2.4$ Hz, 6H, PCH_3). ^1H NMR (300 MHz, C_7D_8 , -90 °C): -15.90 (br s, $T_1 = 41$ ms, Ru-H). ^1H NMR (300 MHz, C_7D_8 , -70 °C): -15.90 (t, $J_{\text{P-H}} = 13.8$ Hz, Ru-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6 , 20 °C): 59.1 (s). IR (Nujol, cm^{-1}): $\nu(\text{Ru-H})$ 2112 (m), 2062 (m), 1905 (m).

$\text{RuHCl}(\text{C}=\text{CHPh})(\text{P}^i\text{Bu}_2\text{Me})_2$. To a solution of $\text{RuHCl}(\text{H}_2)(\text{P}^i\text{Bu}_2\text{Me})_2$ (32 mg, 0.069 mmol) in 0.5 mL of benzene- d_6 was added PhCCH (15.5 μL , 0.14 mmol). Immediately, the color of the solution changed from brown-yellowish to brown. The reaction was quantitative by NMR, but the complex could not be isolated as a solid due to its high solubility in all common organic solvents (it could only be isolated as an oil, and this prevented carrying out its elemental analysis). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show the presence of styrene together with $\text{RuHCl}(\text{C}=\text{CHPh})(\text{P}^i\text{Bu}_2\text{Me})_2$. ^1H NMR (300 MHz, C_6D_6 , 20 °C): -12.65 (t, $J_{\text{P-H}} = 17.8$ Hz, 1H, Ru-H), 1.20 (vt, $N = 6.2$ Hz, 18H, $\text{PC}(\text{CH}_3)_3$), 1.24 (vt, $N = 2.7$ Hz, 6H, PCH_3), 1.33 (vt, $N = 6.4$ Hz, 18H, $\text{PC}(\text{CH}_3)_3$), 4.41 (t, $J_{\text{P-H}} = 3.4$ Hz, 1H, CHPh), 6.88-7.24 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, C_6D_6 , 20 °C): 9.06 (vt, $N = 12.2$ Hz, PCH_3), 29.53 (vt, $N = 2.4$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.89 (vt, $N = 2.6$ Hz, $\text{PC}(\text{CH}_3)_3$), 34.47 (vt, $N = 8.2$ Hz, $\text{PC}(\text{CH}_3)_3$), 35.76 (vt, $N = 7.5$ Hz, $\text{PC}(\text{CH}_3)_3$), 109.04 (t, $J_{\text{P-C}} = 4.0$ Hz, $\text{Ru}=\text{C}$), 123.12 (s, Ph), 123.69 (s, Ph), 128.68 (s, Ph), 133.76 (t, $J_{\text{P-C}} = 2.4$ Hz, $\text{C}_{\text{ipso}}\text{Ph}$), 331.86 (t, $J_{\text{P-C}} = 14.9$ Hz, $\text{Ru}=\text{C}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.421 MHz, C_6D_6 , 20 °C): 42.7 (s). IR (C_6D_6 , cm^{-1}): $\nu(\text{Ru-H})$ 2044 (vw), $\nu(\text{C}=\text{C}, \text{phenyl})$ 1587 (s), $\nu(\text{C}=\text{C})$ 1568 (s).

$\text{RuHCl}(\text{C}=\text{CHSiMe}_3)(\text{P}^i\text{Bu}_2\text{Me})_2$. This compound was prepared analogously to the method described for $\text{RuHCl}(\text{C}=\text{CHPh})(\text{P}^i\text{Bu}_2\text{Me})_2$, starting from $\text{RuHCl}(\text{H}_2)(\text{P}^i\text{Bu}_2\text{Me})_2$ (30 mg, 0.065 mmol) and Me_3SiCCH (18.5 μL , 0.13 mmol). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the resulting red solution show the presence of $\text{Me}_3\text{SiCH}=\text{CH}_2$ together with $\text{RuHCl}(\text{C}=\text{CHSiMe}_3)(\text{P}^i\text{Bu}_2\text{Me})_2$. ^1H NMR (300 MHz, C_6D_6 , 20 °C): -14.95 (dt, $J_{\text{P-H}} = 18.3$ Hz, $J_{\text{H-H}} = 1.8$ Hz, 1H, Ru-H), 0.18 (s, 9H, SiMe_3), 1.25 (vt, $N = 6.4$ Hz, 18H, $\text{PC}(\text{CH}_3)_3$), 1.35 (vt, $N = 2.7$ Hz, 6H, PCH_3), 1.42 (vt, $N = 6.4$ Hz, 18H, $\text{PC}(\text{CH}_3)_3$), 2.59 (dt, $J_{\text{P-H}} = 3.6$ Hz, $J_{\text{H-H}} = 1.8$ Hz, 1H, CHSiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, C_6D_6 , 20 °C): 0.18 (s, SiMe_3), 8.51 (vt, $N = 12.0$ Hz, PCH_3), 29.62 (vt, $N = 2.7$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.88 (vt, $N = 2.7$ Hz, $\text{PC}(\text{CH}_3)_3$), 34.41 (vt, $N = 8.3$ Hz, $\text{PC}(\text{CH}_3)_3$), 36.19 (vt, $N = 7.3$ Hz, $\text{PC}(\text{CH}_3)_3$), 88.97 (t, $J_{\text{P-C}} = 2.7$ Hz, $\text{Ru}=\text{C}$), 318.53 (t, $J_{\text{P-C}} = 14.7$ Hz, $\text{Ru}=\text{C}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6 , 20 °C): 40.3 (s). IR (C_6H_6 , cm^{-1}): $\nu(\text{Ru-H})$ 2035 (vw), $\nu(\text{C}=\text{C})$ 1595 (s).

$\text{RuHI}(\text{C}=\text{CHPh})(\text{P}^i\text{Bu}_2\text{Me})_2$. To a solution of $\text{RuHI}(\text{H}_2)(\text{P}^i\text{Bu}_2\text{Me})_2$ (100 mg, 0.18 mmol) in toluene (5 mL) was added PhCCH (40 μL , 0.36 mmol). Immediately, the brown-yellowish solution color changed to dark-brown. The volatiles

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were removed under vacuum, and the residue was dissolved in 2 mL of pentane and cooled to $-78\text{ }^\circ\text{C}$, yielding a brown solid. Yield: 35 mg (29%). The reaction was quantitative by NMR and showed the presence of styrene in a similar amount to that of $\text{RuHI}(\text{C}=\text{CHPh})(\text{P}^i\text{Bu}_2\text{Me})_2$. ^1H NMR (300 MHz, C_6D_6 , $20\text{ }^\circ\text{C}$): -9.80 (t, $J_{\text{P-H}} = 18.3$ Hz, 1H, Ru-H), 1.19 (vt, $N = 4.5$ Hz, 18H, $\text{PC}(\text{CH}_3)_3$), 1.35 (vt, $N = 5.1$ Hz, 18H, $\text{PC}(\text{CH}_3)_3$), 1.44 (vt, $N = 1.8$ Hz, 6H, PCH_3), 4.40 (t, $J_{\text{P-H}} = 2.8$ Hz, 1H, CHPh), $6.85\text{--}7.23$ (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6 , $20\text{ }^\circ\text{C}$): 12.28 (vt, $N = 12.2$ Hz, PCH_3), 30.05 (vt, $N = 2.7$ Hz, $\text{PC}(\text{CH}_3)_3$), 30.34 (vt, $N = 2.7$ Hz, $\text{PC}(\text{CH}_3)_3$), 34.76 (vt, $N = 7.9$ Hz, $\text{PC}(\text{CH}_3)_3$), 36.65 (vt, $N = 8.0$ Hz, $\text{PC}(\text{CH}_3)_3$), 108.68 (t, $J_{\text{P-C}} = 4.1$ Hz, Ru=C=C), 123.66 (s, Ph), 124.00 (s, Ph), 128.60 (s, Ph), 132.71 (t, $J_{\text{P-C}} = 2.7$ Hz, C_{ipso} , Ph), 328.43 (t, $J_{\text{P-C}} = 14.2$ Hz, Ru=C). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6 , $20\text{ }^\circ\text{C}$): 46.2 (s). IR (Nujol, cm^{-1}): $\nu(\text{Ru-H})$ 1923 (w), $\nu(\text{C}=\text{C})$ 1612 (s), $\nu(\text{C}=\text{C}, \text{phenyl})$ 1591 (s).

RuHI(=C=CHSiMe₃)(PⁱBu₂Me)₂. To a solution of $\text{RuHI}(\text{H}_2)(\text{P}^i\text{Bu}_2\text{Me})_2$ (100 mg, 0.18 mmol) in toluene (5 mL), Me_3SiCCH (51 μL , 0.36 mmol) was added. Immediately, the brown-yellowish solution color changed to dark red. The volatiles were removed under vacuum, and the residue was dissolved in 2 mL of pentane and cooled to $-78\text{ }^\circ\text{C}$, yielding an orange solid. Yield: 38 mg (32%). The reaction was quantitative by NMR spectroscopies and showed the presence of $\text{Me}_3\text{SiCH}=\text{CH}_2$ in a similar amount to that of $\text{RuHI}(\text{C}=\text{CHSiMe}_3)(\text{P}^i\text{Bu}_2\text{Me})_2$. Anal. Calcd for $\text{C}_{23}\text{H}_{53}\text{IP}_2\text{RuSi}$: C, 42.65; H, 8.25. Found: C, 42.89; H, 7.70. ^1H NMR (300 MHz, C_6D_6 , $20\text{ }^\circ\text{C}$): -11.14 (t, $J_{\text{P-H}} = 19.2$ Hz, 1H, Ru-H), 0.15 (s, 9H, SiMe₃), 1.21 (vt, $N = 6.4$ Hz, 18H, $\text{PC}(\text{CH}_3)_3$), 1.40 (vt, $N = 6.4$ Hz, 18H, $\text{PC}(\text{CH}_3)_3$), 1.51 (vt, $N = 2.4$ Hz, 6H, PCH_3), 2.55 (t, $J_{\text{P-H}} = 3.3$ Hz, 1H, CHSiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.429 MHz, C_6D_6 , $20\text{ }^\circ\text{C}$): 0.38 (s, SiMe₃), 11.08 (vt, $N = 11.6$ Hz, PCH_3), 29.65 (vt, $N = 4.1$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.82 (vt, $N = 2.7$ Hz, $\text{PC}(\text{CH}_3)_3$), 34.26 (vt, $N = 8.2$ Hz, $\text{PC}(\text{CH}_3)_3$), 36.75 (vt, $N = 7.5$ Hz, $\text{PC}(\text{CH}_3)_3$), 88.69 (t, $J_{\text{P-C}} = 2.7$ Hz, Ru=C=C), 314.80 (t, $J_{\text{P-C}} = 13.7$ Hz, Ru=C). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.421 MHz, C_6D_6 , $20\text{ }^\circ\text{C}$): 44.1 (s). IR (Nujol, cm^{-1}): $\nu(\text{Ru-H})$ 2019 (m), $\nu(\text{C}=\text{C})$ 1593 (s).

OsHCl(=C=CSiMe₃)(PⁱPr₃)₂. This compound was prepared analogously to the method described for $\text{RuHI}(\text{C}=\text{CHSiMe}_3)(\text{P}^i\text{Bu}_2\text{Me})_2$, starting from $\text{OsH}_3\text{Cl}(\text{P}^i\text{Pr}_3)_2$ (30 mg, 0.054 mmol) and Me_3SiCCH (15.5 μL , 0.109 mmol). ^1H NMR (300 MHz, C_6D_6 , $20\text{ }^\circ\text{C}$): -19.37 (t, $J_{\text{P-H}} = 13.9$ Hz, 1H, Os-H), -0.09 (t, $J_{\text{P-H}} = 2.5$ Hz, 1H, CHSiMe_3), 0.16 (s, 9H, SiMe₃), 1.27 (dvt, $J_{\text{H-H}} = 7.5$ Hz, $N = 14.4$ Hz, 36H, $\text{PCH}(\text{CH}_3)_2$), 2.80 (m, 6H, $\text{PCH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.429 MHz, C_6D_6 , $20\text{ }^\circ\text{C}$): 1.31 (s, SiMe₃), 20.14 (s, $\text{PCH}(\text{CH}_3)_2$), 20.31 (s, $\text{PCH}(\text{CH}_3)_2$), 25.30 (vt, $N = 12.1$ Hz, $\text{PCH}(\text{CH}_3)_2$), 86.36 (t, $J_{\text{P-C}} = 2.5$ Hz, Os=C=C), 275.00 (t, $J_{\text{P-C}} = 9.0$ Hz, Os=C=C). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.421 MHz, C_6D_6 , $20\text{ }^\circ\text{C}$): 36.9 (s). IR (C_6H_6 , cm^{-1}): $\nu(\text{Os-H})$ 2040 (vw), $\nu(\text{C}=\text{C})$ 1591 (s).

RuDI(=C=CHPh)(PⁱBu₂Me)₂. To a solution of $\text{RuHI}(\text{H}_2)(\text{P}^i\text{Bu}_2\text{Me})_2$ (10 mg, 0.018 mmol) in 0.5 mL of benzene was added PhCCD (4 μL , 0.36 mmol). Immediately, the brown-yellowish solution color changed to dark-brown. ^2H NMR (61.421 MHz, C_6H_6 , $20\text{ }^\circ\text{C}$): -9.72 (s, Ru-D), 5.6 (s, *cis*- $\text{PhCH}=\text{CHD}$).

RuDCl(=C=CHPh)(PⁱBu₂Me)₂. This compound was prepared similarly to the method described for $\text{RuDI}(\text{C}=\text{CHPh})(\text{P}^i\text{Bu}_2\text{Me})_2$, starting from $\text{RuHCl}(\text{H}_2)(\text{P}^i\text{Bu}_2\text{Me})_2$ (10 mg, 0.022 mmol) and PhCCD (4.8 μL , 0.044 mmol). ^2H NMR (61.421 MHz, C_6H_6 , $20\text{ }^\circ\text{C}$): -12.53 (s, Ru-D).

[Ru{(E)-CH=CHSiMe₃}(CNMe)₃(PⁱBu₂Me)₂] \cdot I. To a solution of $\text{RuHI}(\text{C}=\text{CHSiMe}_3)(\text{P}^i\text{Bu}_2\text{Me})_2$ (50 mg, 0.077 mmol) in toluene (5 mL) was added MeNC (17 μL , 0.31 mmol). Immediately, the color of the solution changed from red to colorless. After 30 min, the solvent was removed and pentane was added to give a pale yellow solid. Yield: 32 mg (53%). Anal. Calcd for $\text{C}_{29}\text{H}_{62}\text{IN}_3\text{P}_2\text{RuSi}$: C, 45.18; H, 7.98; N, 5.45. Found: C, 44.77; H, 7.6; N, 5.17. ^1H NMR (300 MHz, CDCl_3 ,

$20\text{ }^\circ\text{C}$): -0.06 (s, 9H, SiMe₃), 1.28 (vt, $N = 6.3$ Hz, 36H, $\text{PC}(\text{CH}_3)_3$), 1.33 (vt, $N = 3$ Hz, 6H, PCH_3), 3.57 (s, 3H, MeNC), 3.59 (t, $J_{\text{P-H}} = 1$ Hz, 6H, MeNC), 6.11 (dt, $J_{\text{H-H}} = 21$ Hz, $J_{\text{P-H}} = 2.1$ Hz, Ru-CH=CH), 8.14 (dt, $J_{\text{H-H}} = 21$ Hz, $J_{\text{P-H}} = 1.6$ Hz, Ru-CH=CH). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_3 , $20\text{ }^\circ\text{C}$): 43.7 (s). IR (CDCl_3 , cm^{-1}): $\nu(\text{NC})$ 2148 (vs).

Reaction of OsHCl(=C=CHSiMe₃)(PⁱPr₃)₂ with CO. A solution of $\text{OsHCl}(\text{C}=\text{CHSiMe}_3)(\text{P}^i\text{Pr}_3)_2$ (10 mg, 0.015 mmol) in benzene-*d*₆ (0.5 mL) was placed in an NMR tube with a Teflon closure. The solution was frozen in liquid N₂, and the headspace of the tube was evacuated and filled with CO (1 atm). Upon warming, an immediate color change from red to very pale yellow was observed. ^1H and ^{31}P NMR spectroscopies show clean conversion to $\text{Os}\{(\text{E})\text{-CH}=\text{CHSiMe}_3\}\text{Cl}(\text{CO})_2(\text{P}^i\text{Pr}_3)_2$. ^1H NMR (300 MHz, C_6D_6 , $20\text{ }^\circ\text{C}$): 0.21 (s, 9H, SiMe₃), 1.09 (dvt, $J_{\text{P-H}} = 6.6$ Hz, $N = 12.9$ Hz, 18H, $\text{PCH}(\text{CH}_3)_2$), 1.29 (dvt, $J_{\text{P-H}} = 6.6$ Hz, $N = 13.8$ Hz, 18H, $\text{PCH}(\text{CH}_3)_2$), 2.85 (m, 6H, $\text{PCH}(\text{CH}_3)_2$), 6.98 (dt, $J_{\text{H-H}} = 21.3$ Hz, $J_{\text{P-H}} = 2.2$ Hz, 1H, Os-CH=CH), 8.98 (d, $J_{\text{H-H}} = 21.3$ Hz, 1H, Os-CH=CH). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6 , $20\text{ }^\circ\text{C}$): 4.6 (s). IR (C_6D_6 , cm^{-1}): 1996, 1923 $\nu(\text{CO})$.

Reaction of OsHCl(=C=CHSiMe₃)(PⁱPr₃)₂ with CNMe. To a solution of $\text{OsHCl}(\text{C}=\text{CHSiMe}_3)(\text{P}^i\text{Pr}_3)_2$ (10 mg, 0.015 mmol) in benzene-*d*₆ (0.5 mL) placed in an NMR tube, MeNC (1.7 μL , 0.031 mmol) was added via syringe, and an immediate color change from red to pale yellow was observed. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopies show quantitative conversion to $\text{Os}\{(\text{E})\text{-CH}=\text{CHSiMe}_3\}\text{Cl}(\text{CNMe})_2(\text{P}^i\text{Pr}_3)_2$. ^1H NMR (300 MHz, C_6D_6 , $20\text{ }^\circ\text{C}$): 0.35 (s, 9H, SiMe₃), 1.32 (dvt, $J_{\text{H-H}} = 6.9$ Hz, $N = 12.3$ Hz, 18H, $\text{PCH}(\text{CH}_3)_2$), 1.39 (dvt, $J_{\text{H-H}} = 6.6$ Hz, $N = 12.9$ Hz, 18H, $\text{PCH}(\text{CH}_3)_2$), 2.53 (s, 3H, MeNC), 2.81 (s, 3H, MeNC), 2.84 (m, 6H, $\text{PCH}(\text{CH}_3)_2$), 6.78 (dt, $J_{\text{H-H}} = 21.3$ Hz, $J_{\text{P-H}} = 2.7$ Hz, 1H, Os-CH=CH), 9.74 (d, $J_{\text{H-H}} = 21.3$ Hz, 1H, Os-CH=CH). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6 , $20\text{ }^\circ\text{C}$): -1.4 (s).

Computational Details. Ab initio calculations were carried out with the Gaussian 94 set of programs^{9a} within the framework of DFT at the B3LYP level.^{9b} LANL2DZ effective core potentials (quasi-relativistic for the metal centers) were used to replace the 28 innermost electrons of Ru, the 60 innermost electrons of Os, as well as the 10 core electrons of P and Cl.^{9c} The associated double ζ basis set^{9c} augmented by a d function was used for Cl and P.¹⁰ The other atoms were represented by a 6-31G(d,p) basis set.¹¹ The H atoms of PH_3 were represented at the STO-3G level.¹² 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. Differences in enthalpies were evaluated from the frequency calculations. The transition-state structures were given small structural perturbations, then further geometrically optimized to ensure that they connect the reactant and product of interest. Since, with one exception, the enthalpy differences are, in general, close to the electronic energy difference (discrepancy of less than 1 kcal mol⁻¹), mention of enthalpy differences will be given only when needed.

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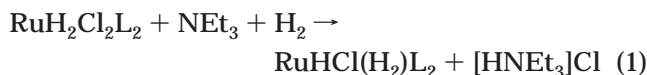
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Results

Synthesis of Complexes $\text{RuHX}(\text{H}_2)(\text{P}^t\text{Bu}_2\text{Me})_2$.

The recent synthesis of the compound $\text{RuH}_2\text{Cl}_2\text{L}_2$ ($\text{L} = \text{P}^i\text{Pr}_3$) in Werner's group^{3h} has opened the door to an easy and very convenient route for the synthesis of the known compounds $\text{RuHX}(\text{H}_2)\text{L}_2$ that otherwise had to be prepared by using Chaudret's procedure,¹³ which is less convenient, mainly for the irksome synthesis and low yields of the starting material, $\text{Ru}(\text{COD})(\text{COT})$. Hydrogenolysis (<1.5 atm of H_2) of $\text{RuH}_2\text{Cl}_2\text{L}_2$ ($\text{L} = \text{P}^t\text{Bu}_2\text{Me}$) (eq 1) in the presence of stoichiometric base leads (within 2 h at room temperature) to $\text{RuHCl}(\text{H}_2)(\text{P}^t\text{Bu}_2\text{Me})_2$ in 72% isolated yield.

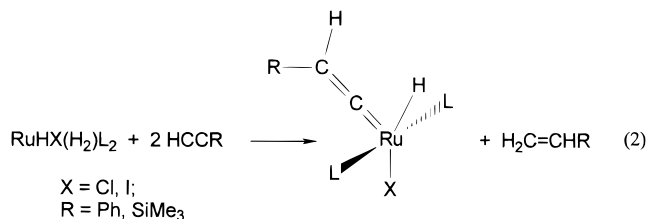


A similar method for preparing $\text{RuHCl}(\text{H}_2)(\text{PCy}_3)_2$ has been reported very recently.^{3d} However, this procedure (analogous to eq 1) fails with $\text{RuH}_2\text{I}_2\text{L}_2$ ($\text{L} = \text{P}^t\text{Bu}_2\text{Me}$), where after 113 h of reaction, only 50% conversion was achieved. This could be understood in light of the thermodynamic parameters obtained for the analogous $\text{OsH}_2\text{X}_2(\text{P}^i\text{Pr}_3)_2$ system, where the heavier halide favors H_2 coordination enthalpically but disfavors it entropically.¹⁴ Alternatively, $\text{RuHI}(\text{H}_2)\text{L}_2$ was prepared by treatment of a solution of RuH_6L_2 with CH_3I in about 60% yield.

RuH_6L_2 ($\text{L} = \text{P}^t\text{Bu}_2\text{Me}$) was prepared in situ by reaction of $\text{RuH}_2\text{Cl}_2\text{L}_2$ with excess of NaBH_4 . The ^1H NMR spectrum shows a triplet at -7.45 ppm, with a $J_{\text{P-H}}$ coupling constant of 8.1 Hz. This chemical shift agrees very well with the ones for related RuH_6L_2 ($\text{L} = \text{PCy}_3$, P^iPr_3) reported previously in the literature.^{13,15} This compound, analogously to the one with P^iPr_3 , is highly unstable under vacuum,¹³ preventing its isolation.

The $\text{RuHX}(\text{H}_2)(\text{P}^t\text{Bu}_2\text{Me})_2$ complexes show one upfield resonance due to all three H atoms on Ru and one ^tBu virtual triplet by ^1H NMR at 25 °C in benzene- d_6 . The T_1 value of the hydride signal in the iodide derivative (41 ms at 300 MHz and the lowest available temperature, -90 °C) is short enough to be consistent with a $\text{RuH}(\text{H}_2)$ structure.

Synthesis and Structure of Complexes $\text{RuHX}(\text{H}_2)(\text{P}^t\text{Bu}_2\text{Me})_2$. Reaction of $\text{RuHX}(\text{H}_2)\text{L}_2$ ($\text{L} = \text{P}^t\text{Bu}_2\text{Me}$; $\text{X} = \text{Cl}, \text{I}$) with terminal alkynes in a 1:2 molar ratio affords (time of mixing in benzene) the unsaturated hydrido/vinylidene compounds $\text{RuHX}(\text{H}_2)(\text{P}^t\text{Bu}_2\text{Me})_2$ ($\text{R} = \text{Ph}, \text{SiMe}_3$) and the corresponding alkene as the only organic product (eq 2). The most characteristic features in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are the low-field triplets at about 320 ($J_{\text{P-C}} = 14$ Hz) and 99 ppm ($J_{\text{P-C}} = 3.5$ Hz), which by comparison are assigned to C_α and C_β vinylidene carbon atoms. The PMe ^1H NMR signal appears as a triplet, consistent with transoid phosphines, while the ^tBu ^1H NMR signals show two virtual



triplets, indicating diastereotopic inequivalence. Since the molecules of the type $\text{MHX}(\text{CO})\text{L}_2$ ($\text{L} =$ tertiary phosphine) adopt a square-based pyramidal geometry with the hydride occupying the axial position and the π -donor and π -acceptor ligands occupying trans basal positions,¹⁶ one might propose that the compounds $\text{RuHX}(\text{H}_2)(\text{P}^t\text{Bu}_2\text{Me})_2$, which also carry a π -donor (X^-) and π -acceptor ligand (vinylidene), adopt a similar geometry. However, a closer look at their ^1H NMR spectra reveals the weakness of this proposal: (i) if the hydride in the compounds $\text{RuHX}(\text{H}_2)(\text{P}^t\text{Bu}_2\text{Me})_2$ is in the apical position (i.e., trans to the empty site), we will expect its ^1H NMR chemical shift to be similar to those reported for $\text{RuHX}(\text{CO})\text{L}_2$ (around -24 ppm).^{16a} Contrary to this expectation, there is a difference of more than 10 ppm. (ii) In the series of compounds $\text{RuHX}(\text{H}_2)(\text{P}^t\text{Bu}_2\text{Me})_2$, the difference in hydride chemical shifts between the chloride and iodide derivatives is only 0.8 ppm, while in the complexes $\text{RuHX}(\text{H}_2)(\text{P}^t\text{Bu}_2\text{Me})_2$ it is 2.8 ppm when $\text{R} = \text{Ph}$ and 3.8 ppm when $\text{R} = \text{SiMe}_3$, indicating a greater influence of the halide on the hydride chemical shift. These observations are easily explained in light of the results of an ab initio (B3LYP) calculation study on the model molecule $\text{RuHCl}(\text{H}_2)(\text{P}^t\text{Bu}_2\text{Me})_2$ (Figure 1, structure **5^{Ru}**) whose geometry has been discussed previously.¹⁷ Briefly, the H-Ru-Cl angle, 129.6° , is large enough that the hydride chemical shift should be significantly influenced by halide identity.

Similar to the ruthenium complexes, the osmium trihydride $\text{OsH}_3\text{Cl}(\text{P}^i\text{Pr}_3)_2$ reacts with Me_3SiCCH to give $\text{OsHCl}(\text{H}_2)(\text{P}^i\text{Pr}_3)_2$ and $(\text{Me}_3\text{Si})\text{HC}=\text{CH}_2$ in the time of mixing in benzene.

Mechanistic Studies. Attempts to search for intermediates of the reaction at low temperature failed. When the reactants were combined at -78 °C in an NMR tube and then the tube inserted in a precooled NMR probe (-80 °C), no intermediate could be detected, observing only starting material and the final vinylidene on warming. As an alternative method, we decided to perform a labeling experiment: the reactions of $\text{RuHX}(\text{H}_2)(\text{P}^t\text{Bu}_2\text{Me})_2$ ($\text{X} = \text{Cl}, \text{I}$) with phenylacetylene- d_1 , PhCCD , were carried out. The ^1H NMR spectra of the resulting products show no resonance assignable to Ru-H . The presence of deuterium attached to the Ru center was confirmed by ^2H NMR spectroscopy, which shows singlets at -9.72 ($\text{X} = \text{I}$) and -12.53 ppm ($\text{X} = \text{Cl}$). In general, formation of a vinylidene ligand from a terminal alkyne has been speculated to start with η^2 -coordination of the alkyne to the metal center, followed by (i) hydride migration to the β -carbon (1,2-hydrogen

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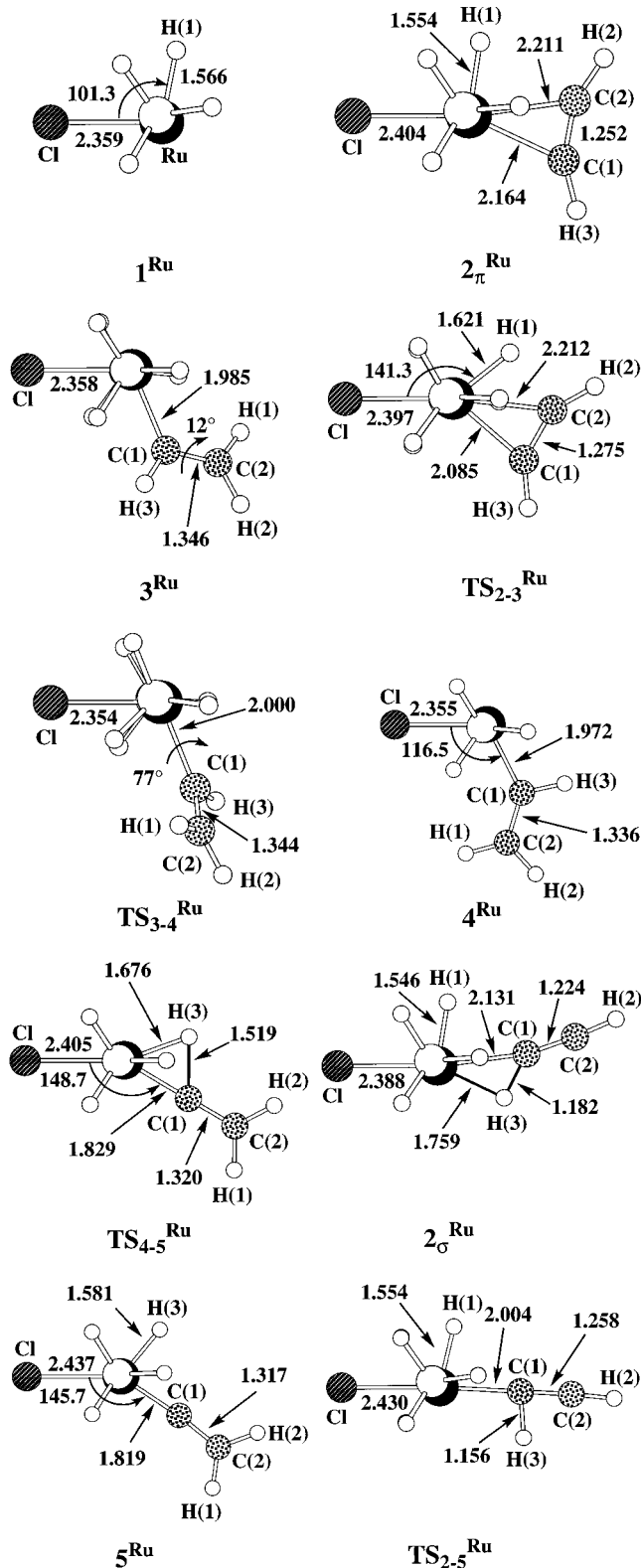


Figure 1. Optimized ab initio (B3LYP) structures (Å, deg) of reactants, intermediates, products, and transition states for the formation of $\text{RuHCl}(\text{C}=\text{CH}_2)(\text{PH}_3)_2$ from $\text{RuHCl}(\text{PH}_3)_2$ and C_2H_2 .

shift) or (ii) insertion of the metal into the H–C bond to give a hydrido alkynyl that rearranges to the vinylidene (1,3-hydrogen shift).^{5a} In our case, the presence of H, and not D, on the β -carbon atom of the vinylidene excludes the possibility of a 1,2-hydrogen

shift mechanism. On the other hand, the 1,3-hydrogen shift is ruled out because the oxidative addition of the alkyne would give a Ru(IV) alkynyl–dihydride intermediate, which would thus lead to a mixture of $\text{RuDX}(\text{C}=\text{CHPh})\text{L}_2$ and $\text{RuHX}(\text{C}=\text{CDPh})\text{L}_2$. This disagrees with our experimental observation.

The isotopic labeling is consistent with a path which starts with the insertion of an alkyne into the Ru–H bond, to make a vinyl complex, followed by the selective migration of the α -hydrogen of the vinyl to the metal. In this manner, the hydrogen that was originally bonded to the ruthenium ends up at the β -carbon atom of the vinylidene in a selective fashion.

In the 1:2 reaction of MH_3CIL_2 ($\text{M} = \text{Ru}$ and Os) with terminal alkynes, the function of the first alkyne is to abstract two H atoms from M. This reaction occurs with the usual syn addition of two H's to the triple bond, and the mechanistic focus of our computational study of the reaction mechanism, therefore, became the second stage of the reaction: combination of acetylene with the fragment $\text{MHCl}(\text{PH}_3)_2$. How does it form the vinylidene complex $\text{MHCl}(\text{CCH}_2)(\text{PH}_3)_2$? We have answered this question by a full study of the reaction path from reactants to products. This path raises several questions. One starts with 14- e^- RuHClL_2 and a ligand that probably coordinates to the metal prior to insertion to make a 16- e^- complex. What is the driving force to form a vinyl ligand which is again a 14- e^- species? The next step involves an α -hydrogen migration (from C to Ru) transforming vinyl to hydrido vinylidene. This migration has been observed in a number of cases.^{18,19} To better understand this pathway, we have used ab initio (B3LYP) calculations and the model systems $\text{MHCl}(\text{PH}_3)_2$ ($\text{M} = \text{Ru}, \text{Os}$) and C_2H_2 .

Theoretical Study

The geometries of all structures that have been optimized as minima or transition states are collected in Figure 1, and the energy scheme for the reaction paths is shown in Figure 2 for Ru. The corresponding results for Os are shown in Figures 3 (geometries) and 4 (energy diagram).

(A) Reaction Path for Ru. The four-coordinate model complex $\text{RuHCl}(\text{PH}_3)_2$, **1^{Ru}**, is not planar but has a saw-horse geometry with trans phosphines and H–Ru–Cl = 101.3° (Figure 1). This angle, marginally larger than H–Ir–H in $\text{IrH}_2(\text{PH}_3)_2^+$ (88.9°),²⁰ H–Ru–C in $\text{RuH}(\text{CO})(\text{PH}_3)_2^+$ (87.0°),²¹ and C–Ru–C in $\text{Ru}(\text{Ph})(\text{CO})(\text{PH}_3)_2^+$ (97.4°),²² illustrates that a d^6 tetracoordinated complex prefers to be a fragment of an octahedron with

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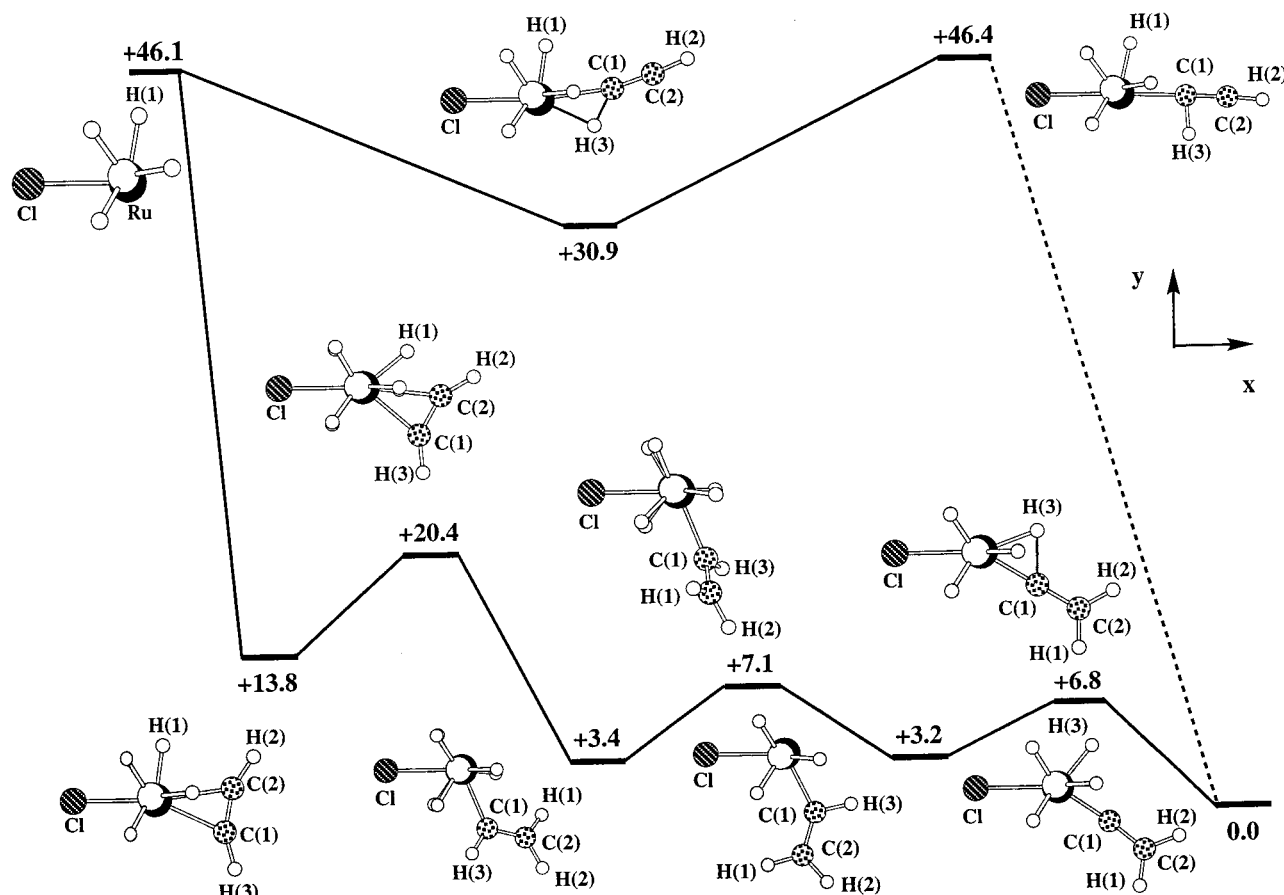


Figure 2. Energy diagram (kcal mol⁻¹) for the formation of RuHCl(C=CH₂)(PH₃)₂ from RuHCl(PH₃)₂ and C₂H₂. (a) In the lower path, the reaction is initiated by an insertion of the alkyne into the Ru–H(1) bond. Two transition states have been located for the **3** to **4** transformation (see text). The higher one TS_{3-4(inv)}, 21.7 kcal mol⁻¹ above **3**, is not shown. (b) In the upper path, a 1,2-migration occurs within the coordinated alkyne. This path gives **5**^{Ru} with the H(1) and H(3) labels reversed.

two empty coordination sites in order to keep the six electrons of the metal in nonbonding orbitals (*t*_{2g}-like occupied d orbitals of an octahedron).

The presence of two empty coordination sites makes **1**^{Ru} a strong Lewis acid and the coordination of the alkyne exothermic. If the C–C bond serves as an electron donor, an alkyne complex **2**_π^{Ru} is formed, while if the C–H bond serves as an electron donor, a σ C–H bond complex **2**_σ^{Ru} is formed. As expected, the formation of **2**_π^{Ru} is more exothermic (32.3 kcal mol⁻¹) than that of **2**_σ^{Ru} (15.2 kcal mol⁻¹). For both complexes, the coordination sphere around the metal is square-pyramidal with an apical hydride. This geometry minimizes the trans influence within the complex since the strongest σ-donor ligand (H(1)) is trans to the empty site. It also maximizes the back-donation from the metal d orbital destabilized by one Cl lone pair into the empty orbitals of the alkyne (π*_{CC} or σ*_{CH}). As it will appear in the following, these two different coordination modes are initial structures for different mechanisms for formation of the hydrido vinylidene complex. The insertion of the alkyne into the Ru–H bond is initiated from **2**_π^{Ru}, while the 1,2-migration is initiated from **2**_σ^{Ru} (Figure 2). It should be kept in mind that isotopic labeling is only consistent with the first mechanism.

(i) Formation of the Hydrido/Vinylidene via Insertion into the Ru–H Bond. In the alkyne complex **2**_π^{Ru}, the two Ru–C bonds have similar lengths, indicating a true η²-coordination. From the moderate

elongation of the C–C bond (1.252 vs 1.205 Å in free H–CC–H), the alkyne behaves like a two-electron donor to form a 16-electron complex. The insertion of the alkyne requires a small activation energy (6.6 kcal mol⁻¹ above **2**_π^{Ru}) and gives a new 14-electron vinyl complex **3**^{Ru}, 10.4 kcal mol⁻¹ more stable than **2**_π^{Ru}. The structure of the transition state TS₂₋₃^{Ru} resembles **2**_π^{Ru} with a Ru–H(1) bond (1.621 Å) that is still a typical length and a C–C bond that is hardly elongated (1.275 Å). The hydride H(1) has moved significantly toward the alkyne, which is now less symmetrically bonded to Ru (Ru–C(1) = 2.085 Å; Ru–C(2) = 2.212 Å). During this insertion process, the carbon which will remain bonded to the metal (C(1)) moves very little. Thus, the insertion reaction is better viewed as H(1) moving toward C(2) while the Ru–C(1) bond is being established. Similar results have been observed in other insertion reactions.²³ The migration of H(1) occurs with the alkyne and Ru–H(1) bond being coplanar. This step results in the formation of a vinyl intermediate **3**^{Ru} where the C(1)–H(3) bond of the vinyl group is directed toward the chloride and not toward the empty metal site. The saw-horse structure of **3**^{Ru} is similar to that of **1**^{Ru} (Cl–Ru–C(1) = 112°), but the vinyl ligand is not

(23) See, for instance: Han, Y.; Deng, L.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 5939. Deng, L.; Woo, T. K.; Cavallo, L.; Maryil, P. M.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 6177. Musaev, D. G.; Froese, R. D.; Svensson, M.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 367. Froese, R. D. J.; Musaev, D. G.; Matsubara, T.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 7190.

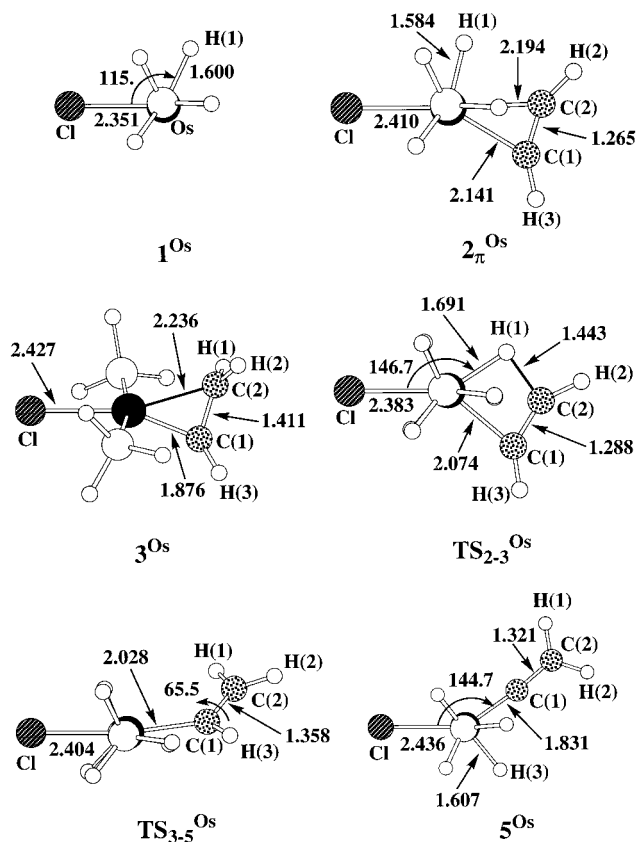


Figure 3. Optimized ab initio (B3LYP) structures (Å, deg) of reactants, intermediates, products, and transition states for the formation of $\text{OsHCl}(\text{C}=\text{CH}_2)(\text{PH}_3)_2$ from $\text{OsHCl}(\text{PH}_3)_2$ and C_2H_2 .

coplanar with the Ru–Cl bond ($\text{Cl}-\text{Ru}-\text{C}(1)-\text{C}(2)$ dihedral angle = 12°) to avoid close contacts between Cl and H(3). The structure of $\mathbf{3}^{\text{Ru}}$ is not suited for an α -hydride migration since the $\text{C}(1)-\text{H}(3)$ bond is not directed toward the empty site of the metal. To achieve that geometry, the whole vinyl group can either rotate around the Ru–C(1) bond or the metal can invert. The transition state for rotation of the vinyl group $\text{TS}_{3-4}^{\text{Ru}}$ has been located $3.7 \text{ kcal mol}^{-1}$ above $\mathbf{3}^{\text{Ru}}$. It has the same saw-horse structure as $\mathbf{3}^{\text{Ru}}$ and an essentially identical geometry except for the conformation of the vinyl ($\text{Cl}-\text{Ru}-\text{C}(1)-\text{C}(2) = 77^\circ$). This rotation brings the closest H of the vinyl within 2.1 \AA of the H of PH_3 . The calculated value is thus a lower limit to the real rotational barrier with more bulky phosphines. Since it is difficult to estimate if the bulk of the phosphine could prevent the transformation, we searched for another path that did not involve the full rotation of the phosphine but instead the inversion at the metal center. The transition state $\text{TS}_{3-4(\text{inv})}^{\text{Ru}}$ for this step was located at a rather high energy ($21.7 \text{ kcal mol}^{-1}$ above $\mathbf{3}^{\text{Ru}}$). In this structure, the vinyl group has continued its rotation away from the $\text{Cl}-\text{Ru}-\text{C}(1)$ plane ($\text{Cl}-\text{Ru}-\text{C}(1)-\text{C}(2)$ dihedral angle = 67°). The $\text{Cl}-\text{Ru}-\text{C}(1)$ angle has drastically increased (172.3°), and the coordination around the metal is almost square planar. Analysis of the transition vector at $\text{TS}_{3-4(\text{inv})}^{\text{Ru}}$ shows that the $\mathbf{3}^{\text{Ru}}$ to $\mathbf{4}^{\text{Ru}}$ transformation is an inversion at the metal center occurring with a very heavily twisted vinyl group. As soon as C(1) has crossed over the Ru–Cl axis, the vinyl group falls back into $\text{Cl}-\text{Ru}-\text{C}(1)$

plane while having never undergone a full rotation. Comparing $\text{TS}_{3-4}^{\text{Ru}}$ and $\text{TS}_{3-4(\text{inv})}^{\text{Ru}}$ clearly reveals the difficulty to reach a planar structure for d^6 Ru and the strong preference for a saw-horse structure. The heavy twist of the vinyl could certainly be diminished in the case of bulky phosphines, so that this transition state may apply for very large phosphine ligands with approximately the same energy cost as in the PH_3 model system. Structure $\mathbf{4}^{\text{Ru}}$ is another 14-electron tetracoordinated vinyl complex which resembles $\mathbf{3}^{\text{Ru}}$ but with a different conformation of the vinyl group. In $\mathbf{4}^{\text{Ru}}$, the vinyl group is coplanar with Ru–Cl since no short contacts between Cl and the vinyl group prevent planarity. Any agostic $\text{C}(1)-\text{H}(3)$ bond in $\mathbf{4}^{\text{Ru}}$ is doubtful since the stretch (1.114 \AA) of $\text{C}(1)-\text{H}(3)$ from its value (1.094 \AA) in $\mathbf{3}^{\text{Ru}}$ is not associated with any significant stabilization ($\mathbf{4}^{\text{Ru}}$ is more stable than $\mathbf{3}^{\text{Ru}}$ by only $0.2 \text{ kcal mol}^{-1}$). The vinyl complex $\mathbf{4}^{\text{Ru}}$ has the proper geometry to undergo an α -hydride migration, which does indeed occur easily since the associated transition state $\text{TS}_{4-5}^{\text{Ru}}$ is $3.6 \text{ kcal mol}^{-1}$ (and only $0.4 \text{ kcal mol}^{-1}$ for the enthalpy difference) above $\mathbf{4}^{\text{Ru}}$. To reach this transition state, the $\text{Cl}-\text{Ru}-\text{C}(1)$ angle has opened drastically from 116.5° in $\mathbf{4}^{\text{Ru}}$ to 148.7° in $\text{TS}_{4-5}^{\text{Ru}}$, which brings H(3) to the empty site of the metal. The $\text{C}(1)-\text{H}(3)$ bond has stretched considerably (1.519 \AA), while the Ru–H(3) bond is already significantly formed (1.676 \AA); that is, H(3) truly bridges Ru and C(1) in the transition state. The angle $\text{Ru}-\text{C}(1)-\text{C}(2)$ is essentially 180° , as it is in product $\mathbf{5}^{\text{Ru}}$.

The hydrido/vinylidene $\mathbf{5}^{\text{Ru}}$ is only $3.2 \text{ kcal mol}^{-1}$ below the most stable vinyl intermediate $\mathbf{4}^{\text{Ru}}$. The coordination at the metal is that of a distorted trigonal bipyramid (Y geometry) with a small $\text{C}(1)-\text{Ru}-\text{H}(3)$ angle (84.8°), and the vinylidene group lies in the $\text{C}(1)-\text{Ru}-\text{H}(3)$ plane. This geometry has been extensively discussed previously.^{17,24} It is favored by the presence of a π -donor ligand Cl which forms a Ru–Cl multiple bond and a potent back-donation from the occupied $d_{x^2-y^2}$ into the empty p orbital on C(1), which accounts for the short Ru–C(1) distance (1.819 \AA).

(ii) Formation of the Hydrido/Vinylidene via 1,2-Migration Within the Coordinated Acetylene Ligand. As mentioned earlier, coordination of the C–H bond is a less favorable alternative to coordination of the π system to the empty site of $\mathbf{1}^{\text{Ru}}$. This starting geometry $\mathbf{2}_\sigma^{\text{Ru}}$ leads to a transition state which describes the 1,2-migration of the hydrogen from C(1) to C(2). This transition state $\text{TS}_{2-5}^{\text{Ru}}$ leads to the final hydrido/vinylidene in only one step, but the energy of $\text{TS}_{2-5}^{\text{Ru}}$ is much higher than any stationary point of the previous path ($26.0 \text{ kcal mol}^{-1}$ above $\text{TS}_{2-3}^{\text{Ru}}$) and is even marginally higher ($0.3 \text{ kcal mol}^{-1}$) than the separated reactants $\mathbf{1}^{\text{Ru}}$ and H–CC–H. It is, thus, much more unfavorable than the multistep reaction initiated by the insertion into Ru–H(1). The geometry of the transition state $\text{TS}_{2-5}^{\text{Ru}}$ is that of a square pyramid with an apical hydride, an angle $\text{Cl}-\text{Ru}-\text{C}(1)$ equal to 176.8° , and the migrating H not yet bridging the $\text{C}(1)-\text{C}(2)$ bond ($\text{C}(2)-\text{C}(1)-\text{H}(1) = 83.1^\circ$).

(iii) Formation of the Hydrido/Vinylidene through a Ru(IV) Intermediate. The last mecha-

(24) Jean, Y.; Eisenstein, O. *Polyhedron* **1988**, *7*, 405. Rachidi, I. E.-I.; Eisenstein, O.; Jean, Y. *New J. Chem.* **1990**, *14*, 671. Riehl, J.-F.; Jean, Y.; Eisenstein, O. *Péllissier, M. Organometallics* **1992**, *11*, 729.

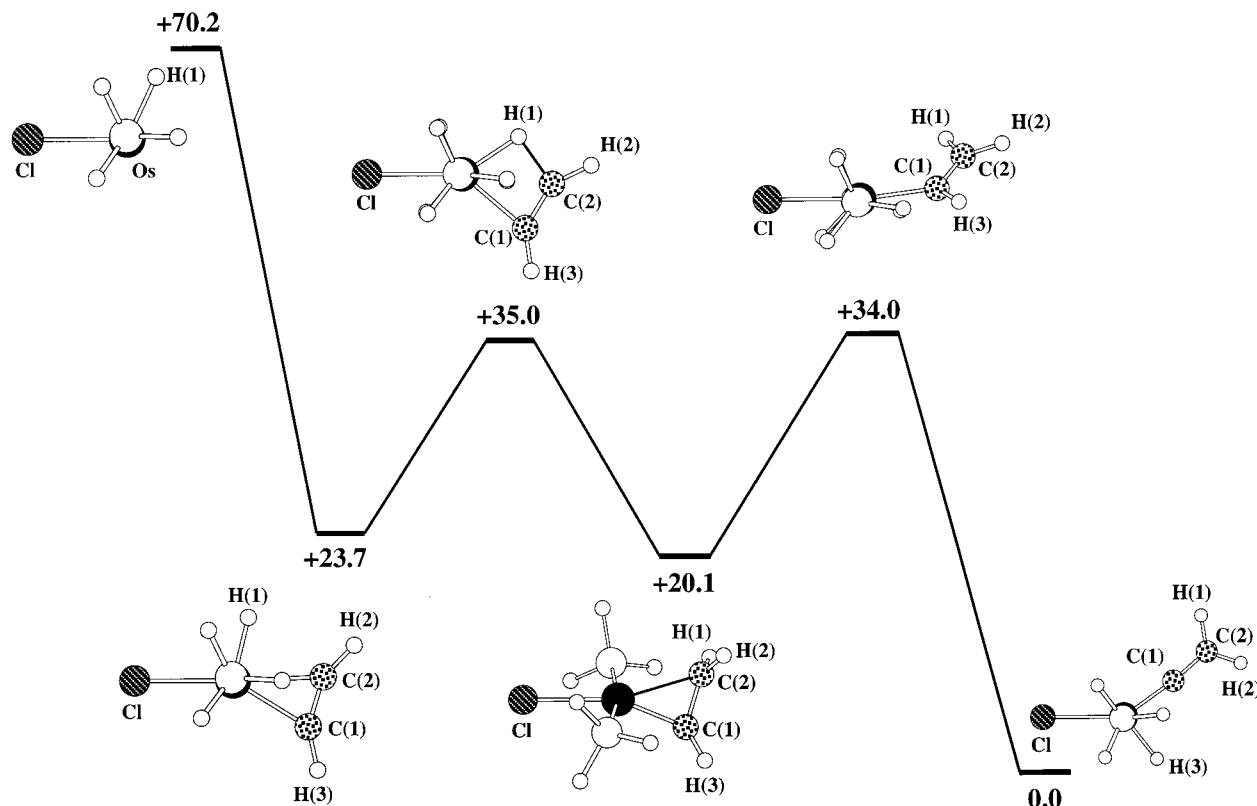
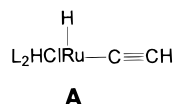


Figure 4. Energy diagram (kcal mol⁻¹) for the formation of OsHCl(C=CH₂)(PH₃)₂ from OsHCl(PH₃)₂ and C₂H₂.

nism which could be suggested for the formation of the vinyl complex is through a Ru(IV) dihydrido complex **A**. It is remarkable that the η^1 -vinyl species **4**^{Ru} is



preferable to structure **A**. In fact, no such dihydrido complex with either trans or cis hydrides has been found to be a minimum on the potential energy surface. Calculations of a trans dihydrido complex enforcing C_{2v} symmetry gives a structure 44.3 kcal mol⁻¹ above the 14-electron vinyl species, excluding that any such Ru(IV) species could be on the path to the hydrido/vinylidene from the acetylene complex.

(iv) Discussion of the Paths for Formation of **5**^{Ru}.

The preferred path is, thus, the one initiated by insertion of the alkyne into the Ru–H bond, in full agreement with the isotopic labeling studies. The insertion of the alkyne into the Ru–H bond is followed by a structural transformation that leads to a 14-electron intermediate, which permits the α migration of H to Ru. Two pathways for this transformation have been found. In the most energetically facile path, the vinyl rotates without changing the coordination geometry of the metal. In a significantly energetically more demanding path, an inversion occurs at the metal. However, the associated transition state has an energy well below that of the reactants, which should make this step feasible. Formation of successive intermediates is thermodynamically favored. It is remarkable that the 14-electron structures are so competitive with respect to the initial 16-electron coordinated alkyne. In the experimental species, where agostic interactions from

phosphine substituents can provide additional stabilization,^{20–22} going through 14-electron complexes should be even easier.

(B) The Os Analogues. We calculated the path in the case of Os with the goal of examining the similarities and differences between the two paths. This was prompted by our recent findings that Ru and Os can lead to significant differences in the geometries of intermediate and transition states.²⁵ The initial reactive metal fragment is considered to be OsHClL₂, and the only alkyne complex that was located on the potential energy path was **2** _{π} ^{Os}. The results are presented in Figures 3 (geometries) and 4 (energy diagram).

The stabilization upon coordination of the alkyne is considerably more exothermic (46.5 kcal mol⁻¹) than for Ru, indicating a strong Os–ligand interaction. The structure of **2** _{π} ^{Os} is very similar to that of **2** _{π} ^{Ru}. The C–C bond length is almost identical in the structures. The energy required to reach **TS**_{2–3}^{Os} for insertion into Os–H is 11.3 kcal mol⁻¹, compared to 6.6 kcal mol⁻¹ for Ru; the geometries of the transition states are similar. In the case of Os, the two metal–C distances are more strongly differentiated (Os–C(1) 2.074 Å, Os–C(2) 2.258 Å; Ru–C(1) 2.085 Å, Ru–C(2) 2.212 Å) while C(2)–H(1) bond formation is more advanced (1.443 Å for Os and 1.581 Å for Ru). A major difference between the two metals is the structure of the intermediate **3**^{Os}. It is an η^2 -vinyl complex with the C–C bond coplanar with Os–Cl. The C–C bond is long (1.411 Å) and the Os–C(1) bond very short (1.876 Å), while Os–C(2) is rather long (2.236 Å) but well within the Os–C bonding

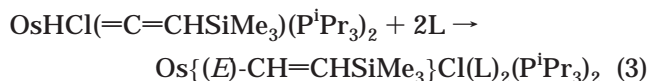
(25) (a) Spivak, G. J.; Coalter, J. N.; Oliván, M.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 999. (b) Huang, D.; Oliván, M.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *Organometallics*, submitted for publication.

interaction. It should be noted that no σ -bonded vinyl structure could be found on the potential energy surface for Os, while no η^2 -vinyl complex was obtained as a stable minimum for Ru.

This η^2 -vinyl complex undergoes an α -hydrogen migration to directly give the hydrido/vinylidene complex in one step less than for Ru (i.e., 4^{Os} is not a stationary point). The transition state TS_{3-5}^{Os} is 13.9 kcal mol⁻¹ above 3^{Os} , indicating an easy reaction. The transition state has a very open Cl–Os–C(1) angle (171.9°) and a dihedral Cl–Os–C(1)–C(2) angle of 65.5°. The final hydrido/vinylidene 5^{Os} is wholly analogous to its Ru analogue. Its formation is strongly exothermic, and in particular, the difference in energy between 3^{Os} and 5^{Os} is 20.1 kcal mol⁻¹ while it was only 3.2 kcal mol⁻¹ between 4^{Ru} and 5^{Ru} .

As in the case of Ru, the 1,2-migration is found to be unlikely since the transition state is 22.2 kcal mol⁻¹ above the highest transition state of the other path.

Reactivity of $MHX(=C=CHR)L_2$ toward Nucleophiles. Addition of nucleophiles (CO, CNMe) to the complexes $MHX(=C=CHR)L_2$ induces migration of the hydride back to the α -carbon atom of the vinylidene, yielding vinyl derivatives. $OsHCl(=C=CHSiMe_3)(P^iPr_3)_2$ reacts with nucleophiles (L = CO, CNMe) in the time of mixing to give $Os\{(E)-CH=CHSiMe_3\}Cl(L)_2(P^iPr_3)_2$ (eq 3).



The IR spectrum in C₆D₆ of $Os\{(E)-CH=CHSiMe_3\}Cl(CO)_2(P^iPr_3)_2$ shows two $\nu(CO)$ bands of similar intensity at 1996 and 1923 cm⁻¹, indicating a cis disposition of these ligands. In the ¹H NMR spectra, there are two peaks in the vinylic region, the one at higher field shows up as a doublet ($J_{H-H} = 21.3$ Hz) of triplets (by coupling with both phosphines) and the one at lower field is a doublet ($J_{H-H} = 21.3$ Hz). The J_{H-H} coupling constant is clearly in the expected range for a trans disposition of both hydrogens.

$RuHI(=C=CHSiMe_3)(P^tBu_2Me)_2$ reacts with excess MeNC, giving $[Ru\{(E)-CH=CHSiMe_3\}(MeNC)_3(P^tBu_2Me)_2]I$, which has trans phosphines and *mer*-MeNC ligands. Addition of $NaBar'_4$ (Ar' = 3,5-bis(trifluoromethyl)phenyl) to a solution of $[Ru\{(E)-CH=CHSiMe_3\}(MeNC)_3(P^tBu_2Me)_2]I$ leaves the NMR signature of the cation unchanged, proving that the iodide is not coordinated.

It is known that $OsHCl(=C=CHCy)(CO)(P^iPr_3)_2$ rearranges to $Os\{(E)-CH=CHCy\}Cl(CO)(P^iPr_3)_2$ in solution after 3 days.^{5b} The reactions described here probably go via a similar mechanism upon coordination of one nucleophile and are extremely accelerated by the presence of an excess of nucleophile.

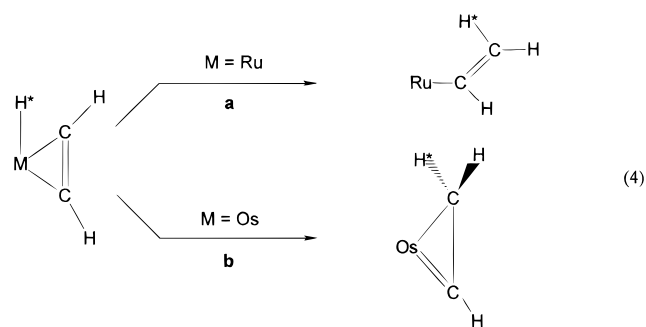
These reactions formally reverse the formation of the vinylidene from a vinyl intermediate.

Discussion

The reaction path suggested by the isotopic labeling is shown to be energetically favorable from the calculations. The paths calculated for Ru and Os are exothermic from reactants to the final product (Figures 2 and

4). The reaction path has several interesting features: while coordination of the alkyne to the 14-electron $RuHCIL_2$ species is thermodynamically highly favorable, returning to the 14-electron vinyl is surprisingly also slightly exothermic, which could be associated with the poor electron-donating ability (i.e., π -basicity) of this Ru. It should be kept in mind that all 14-electron species are probably further stabilized by two agostic interactions, as has been seen in $Ru(Ph)(CO)L_2^+$ ²² and $IrH_2L_2^+$.²⁰ However, the hydrido/vinylidene is overall the most stable of all isomers on the path due in part to the very potent π -accepting ability of the vinylidene ligand.

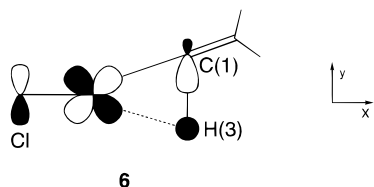
The initial step of the reaction for both metals is the insertion into the metal–H bond. The associated transition states have similar geometries and not too different energies with respect to the alkyne complexes. However, these transition states lead to strikingly different intermediates. In the case of Os, the vinyl complex is found to be η^2 -coordinated, while in the case of Ru, the same ligand is σ -bonded (i.e., η^1) to the metal. Recent related examples show that Ru and Os may favor different isomeric forms of the same compound. Thus, everything else being equal, a carbene complex has been isolated in the case Ru while an hydrido/carbyne has been isolated for Os.^{25a} Similarly, a vinyl/vinylidene complex for Os is isolated while a butadienyl ligand resulting from the formal coupling of the vinyl and vinylidene ligands has been characterized for Ru.^{25b} While more studies are needed for a deeper understanding of the reasons behind these differences, a pattern already emerges: among several isomeric forms, Ru favors the structure with the maximum number of C–C and C–H bonds within the ligands while Os favors the isomer with the maximum number of bonds (Os–C, Os–H) to the metal. The two vinyl isomers calculated in this work fit this pattern well: the C–C π bond is maintained in the four-coordinated η^1 -vinyl Ru complex while it is destroyed in the case of Os in favor of an additional Os–C bond. That is (eq 4), the H* migration destroys a Ru–C bond in **a** but destroys a C=C bond and forms an Os–C π bond in **b**. This pattern is



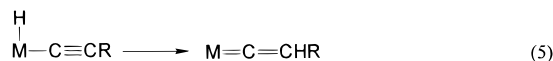
relevant to a deeper understanding of catalysis, where Ru plays a larger role than Os, by favoring new bonds within ligands (e.g., polymerization).⁴

We show here an example of a low-barrier α -migration of H from C(1) to the metal in the transformation of a vinyl into a hydrido vinylidene. The facile migration could be due to the fact that the two orbitals that interchange electron occupancy in the transformation of 4^{Ru} to 5^{Ru} are d_{xy} and $d_{x^2-y^2}$ (occupied in 4^{Ru} and 5^{Ru} , respectively). These two orbitals are of the same a'

symmetry (C_s point group), making the transformation feasible. Noteworthy is the fact that d_{xy} , which will be emptied on going to 5^{Ru} as the C(1)–H(3) bond is cleaved, is destabilized by the p_x lone pair of Cl and is, thus, a powerful electron donor into σ^*_{CH} , as shown in **6**.

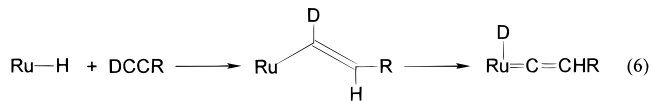


There are experimental indications¹⁸ and increasingly frequent proposals that this α -H migration could be facile.¹⁹ This is true although hydrido/vinylidene and η^1 -vinyl have a different valence electron count. However, it was shown earlier that (1,3-) migration of H in a hydrido acetylide complex (eq 5), to make a vinylidene, has a high (33.5 kcal/mol) barrier; the same is true of TS_{2-5}^{Ru} here (Figure 2). In the facile reaction of $RuHClL_2$ with alkynes, this high barrier is avoided by first forming a vinyl complex (addition of Ru–H across the $C\equiv C$ bond), followed by facile α -H migration from the vinyl C_α to Ru. No 1,3-H migration of eq 5 is required since the oxidative addition of the C–H bond of the primary alkyne to $RuHClL_2$ is not energetically feasible. The facile route, eq 6, through a vinyl complex



is thus preferred. As noted in a theoretical study, the

observed facile conversions of eq 5 may occur preferably via a bimolecular, not unimolecular, path.²⁶



The title and conclusions of this paper apply equally well to the reactions^{3d} of $RuHCl(H_2)(PCy_3)_2$ with vinyl chlorides and propargyl halides: addition of the Ru–H bond across the C/C unsaturation is the fastest reaction; that is, C–halide cleavage occurs later.

Conclusions

This work proposes a new route for the formation of a hydrido/vinylidene going through transformation of a vinyl into a hydrido/vinylidene. The route is supported by isotopic labeling and theoretical studies of several competing routes. It is also shown that although Ru and Os have a similar energetic ability to form the hydrido/vinylidene product, the nature of the intermediates on the path may be different. These differences are consistent with related recent observations for Ru and Os.

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.

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