ORGANOMETALLICS

Volume 16, Number 11, May 27, 1997

## Communications

# New Access to Vinylidenes from Ruthenium Polyhydrides

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*Received February 10, 1997*[⊗]

*Summary: Reaction of the terminal acetylenes RC≡CH (R = Ph and SiMe*$_3$*) with* $RuH_3XL_2$ *(X = Cl, I; L =* $P^tBu_2Me$*) occurs (in the time of mixing) in a 2:1 stoichiometry to release* $RHC{=}CH_2$ *and form the vinylidene complexes RuHX(CCHR)L*$_2$*. Ab initio DFT (B3LYP) calculations show that the vinylidene complex has a Y structure with a Cl at the foot of the Y. No intermediate is seen for this reaction, even at low temperature, or for the analogous reaction of* $OsH_3Cl(P^iPr_3)_2$*. Since PhC≡CD forms only the isotopomer RuDI(CCHPh)L*$_2$ *and PhHC=CHD, a mechanism is proposed where an early event is addition of Ru−H across the C≡C bond. Preliminary computational studies of the reaction path for the formation of the vinylidene complex support this step of insertion of the acetylene into the Ru−H bond.*

Late transition metals carrying carbenoid (including vinylidene) ligands have special utility for stoichiometric or catalytic transformations of olefins (e.g., olefin metathesis) or alkynes.[1,2] Their special advantage, in comparison to early transition metal carbenoids, is their tolerance of polar functional groups or even of water as a solvent.[3] Central issues in expanding the range of late metal carbenoid complexes are the source of the carbenoid and the maintenance of unsaturation in the carbenoid complex, in order to facilitate substrate binding in applications of the resulting complexes. We report here how the complexes $RuH_3XL_2$ serve as a formal source of the fragment "RuHXL$_2$" (by loss of 2H to alkyne substrate), which thus have the characteristic of avoiding the presence of the strong $\pi$-acid ligand CO. This loss of 2H from $RuH_3XL_2$, which is already unsaturated, represents a conceptual advance by providing a 14-electron equivalent, "RuHXL$_2$", for reacting with substrate.

The 16-electron species $RuH_3ClL_2$ (L = $P^tBu_2Me$) is available by hydrogenolysis (<1.5 atm $H_2$) of 1 equiv of $RuH_2Cl_2L_2$[4] (eq 1; 2 h in benzene at 25 °C). The

$$RuH_2Cl_2L_2 + H_2 + NEt_3 \rightarrow RuH_3ClL_2 + [HNEt_3]Cl \quad (1)$$

analogous reaction of $RuH_2I_2L_2$ proceeds much slower (after 113 h, less than 50% of conversion was achieved). Alternatively, $RuH_3IL_2$ was prepared by using Chaudret's procedure.[5] The products each show one hydride resonance and one $^t$Bu virtual triplet by $^1$H NMR at 25 °C in benzene. The $T_1$ value of the hydride signal in the iodide derivative (41 ms at 300 MHz and the lowest

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1997.

(1) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

(2) For a study of syntheses using 18-electron ruthenium vinylidenes, see: Ting, P.; Lin, Y.; Lee, G.; Cheng, M.; Wang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 6433.

(3) (a) Bruce, M. I.; Hall, B. C.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1996**, *522*, 307. (b) Novack, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 960. (c) Novack, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542. (d) Mohr, B.; Lynn, D. M.; Grubbs, R. H. *Organometallics* **1996**, *15*, 4317.

(4) Grünwald, C.; Gevert, O.; Wolf, J.; González-Herrero, P.; Werner, H. *Organometallics* **1996**, *15*, 1960. This synthetic method was employed, but using $P^tBu_2Me$.

(5) Burrow, T.; Sabo-Etienne, S.; Chaudret, B. *Inorg. Chem.* **1995**, *34*, 2470.

S0276-7333(97)00095-2 CCC: $14.00 © 1997 American Chemical Society

available temperature, −90 °C) is short enough to be consistent with a $RuH(H_2)$ structure. Although it is also consistent with a trihydride structure analogous to that of $Os(H)_3X(P^iPr_3)_2$,[6] where H−M−H < 60° (i.e., strongly distorted from octahedral geometry), an X-ray diffraction study of $RuH_3I(PCy_3)_2$[7] has been interpreted in terms of a $RuH(H_2)$ form.

Reaction of $RuH_3XL_2$ (X = Cl, I; L = $P^tBu_2Me$) with $RC_2H$ occurs (in the time of mixing) in a 1:2 stoichiometry (eq 2) to give the vinylidene complexes $RuHX(CCHR)L_2$ (R = Ph, $Me_3Si$).[8,9] The second equivalent

$$RuH_3XL_2 + 2RC{\equiv}CH \rightarrow RuHX(C{=}CHR)L_2 + RHC{=}CH_2 \quad (2)$$

of alkyne serves as a hydrogen acceptor to give the corresponding alkene. The metal vinylidene complexes show low-field triplets at about 320 ppm ($J_{PC}$ = 14 Hz) for $C_\alpha$ in the $^{13}C\{^1H\}$ NMR spectra and a hydride triplet (about −12 ppm) in the $^1H$ NMR spectra. The PMe $^1H$ NMR signal is a virtual triplet, consistent with *transoid* phosphines, and the $^tBu$ $^1H$ NMR signals show two virtual triplets, indicating their diastereotopic inequivalence.

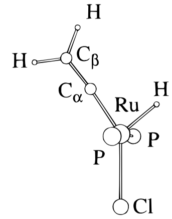
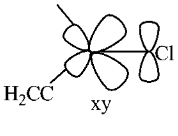
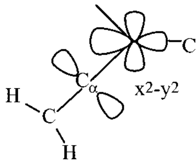


**Figure 1.** Optimized structure (DFT/B3LYP) for $RuHCl(C_2H_2)(PH_3)_2$. Distances in Å and angles in degrees. Ru−H, 1.580; Ru−Cl, 2.432; Ru−$C_\alpha$, 1.820; Ru−P, 2.356; $C_\alpha$−$C_\beta$, 1.317; $C_\alpha$−Ru−H, 84.78; H−Ru−Cl, 128.71; $C_\alpha$−Ru−Cl, 146.52; Ru−$C_\alpha$−$C_\beta$, 174.8; P−Ru−P, 174.75.

The structure of the model $RuHCl(CCH_2)(PH_3)_2$ was optimized in $C_s$ symmetry with *ab initio* DFT (B3LYP) methods using the Gaussian 94 package.[10] A distorted trigonal bipyramid with apical phosphines and inequivalent angles within the Y-shaped equatorial plane was obtained, with H−Ru−Cl = 128.7° and H−Ru−C = 84° (Figure 1). This Y structure is, thus, typical of $d^6$ $ML_5$ species with one $\pi$-donor ligand. The larger angle H−Ru−Cl in the vinylidene complex accounts for the large influence of the halide on the hydride chemical shift.[11] However, unlike all other Y $d^6$ $ML_5$ species,[12] this complex carries a $\pi$-acceptor ligand, which usually favors a square pyramidal geometry (push−pull effect).[13] The preference for a Y structure originates from neutral vinylidene being a potent $\pi$ acceptor in the $CH_2$ plane, but a weak $\pi$ donor in the orthogonal plane. The donating property of $\pi_{CC}$ disfavors a *trans* relationship of Ru−Cl and vinylidene since this maximizes the overlaps between the occupied orbitals of the metal (d) and the two ligands ($\pi_{CC}$ and $p_{Cl}$). Two stabilizing interactions occur when $C_\beta H_2$ lies in the H−Ru−Cl plane. In addition to the usual Ru−Cl $\pi$ bond (**I**) characteristic of all Y-shaped $d^6$ $ML_5$ species, the $x^2-y^2$ orbital is back-bonding into the $p_{C\alpha}$ empty orbital (**II**).



**I**



**II**

Rotating $CH_2$ by 90° costs 4.6 kcal/mol in the absence of any steric effect. This structure contrasts with that found for the carbene complexes $Ru(CR_2)CL_2L_2$, in which the carbene ligand occupies the apical position of the square pyramid.[14]

When the reaction with $RuH_3IL_2$ is repeated using PhCCD, the products are exclusively *cis* PhHC=CDH and $RuDI(CCHPh)L_2$. This result excludes any "direct" 1,2-hydrogen migration for converting an intact alkyne to a vinylidene (eq 3) and also any 1,3-hydrogen migration within a C−H oxidative addition primary product (eq 4), since intermediate **A** would scramble H from the metal and D from the alkyne (yielding a mixture of RuH(CCDPh) and RuD(CCHPh) products). In contrast,

$$HC{\equiv}CPh \xrightarrow{\text{“Ru”}} Ru{=}C{=}CHPh \quad (3)$$

$$\text{“RuH”} + HC{\equiv}CPh \rightarrow \underset{\mathbf{A}}{H_2RuC{\equiv}CPh} \rightarrow HRu{=}C{=}CHPh \quad (4)$$

Esteruelas *et al.* have found that the reaction of $OsDCl(CO)(P^iPr_3)_2$ with HC≡CCy gives a mixture of $OsHCl(=C=CDCy)(CO)(P^iPr_3)_2$ and $OsDCl(=C=CHCy)$-

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[6] Gusev, D. G.; Kuhlman, R.; Sini, G.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 2685.

[7] Chaudret, B.; Chung, G.; Eisenstein, O.; Jackson, S. A.; Lahoz, F. J.; López, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 2314.

[8] Reaction in a 1:1 stoichiometry gives only the vinylidene and unreacted $RuH_3XL_2$.

[9] $RuHI(=C=CHSiMe_3)(P^tBu_2Me)_2$. To a solution of $RuH_3I(P^tBu_2Me)_2$ (100 mg, 0.18 mmol) in toluene (5 mL) $Me_3SiC{\equiv}CH$ (51 $\mu$L, 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 °C, yielding an orange solid. Yield: 38 mg (32%). The reaction was quantitative by NMR spectroscopies and showed the presence of $Me_3SiCH{=}CH_2$ in a similar amount to that of $RuHI(=C=CHSiMe_3)(P^tBu_2Me)_2$. Anal. Calcd for $C_{23}H_{53}IP_2RuSi$: C, 42.65; H, 8.25. Found: C, 42.89; H, 7.70. $^1H$ NMR (300 MHz, $C_6D_6$): $\delta$ −11.14 (t, $J_{P-H}$ = 19.2 Hz, 1H, Ru−H), 0.15 (s, 9H, $SiMe_3$), 1.21 (vt, $N$ = 6.4 Hz, 18H, $PC(CH_3)_3$), 1.40 (vt, $N$ = 6.4 Hz, 18H, $PC(CH_3)_3$), 1.51 (vt, $N$ = 2.4 Hz, 6H, $PCH_3$), 2.55 (t, $J_{P-H}$ = 3.3 Hz, 1H, $CHSiMe_3$). $^{13}C\{^1H\}$ NMR (75.429 MHz, $C_6D_6$): $\delta$ 0.38 (s, $SiMe_3$), 11.08 (vt, $N$ = 11.6 Hz, $PCH_3$), 29.65 (vt, $N$ = 4.1 Hz, $PC(\mathit{C}H_3)_3$), 29.82 (vt, $N$ = 2.7 Hz, $PC(\mathit{C}H_3)_3$), 34.26 (vt, $N$ = 8.2 Hz, $P\mathit{C}(CH_3)_3$), 36.75 (vt, $N$ = 7.5 Hz, $P\mathit{C}(CH_3)_3$), 88.69 (t, $J_{P-C}$ = 2.7 Hz, $Ru{=}C{=}\mathit{C}$), 314.80 (t, $J_{P-C}$ =13.7 Hz, $Ru{=}\mathit{C}$). $^{31}P\{^1H\}$ NMR (121.421 MHz, $C_6D_6$): $\delta$ 44.1 (s). IR (Nujol, $cm^{-1}$): $\nu$(Ru−H) 2019 (m), $\nu$(C=C) 1593 (s).

[10] The calculations were performed with the Gaussian 94 package. The pseudopotential and basis sets for Ru, P, Cl, C, and H are those of $LANL_2DZ$. Polarization functions were added to P, C, and the hydrides. The hydrogens of $PH_3$ are calculated with a minimal basis set. Optimization was carried out at the DFT (B3LYP) level. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision D.I.; Gaussian, Inc.: Pittsburgh, PA 1995.

[11] $\delta$(Ru−H, ppm): $RuHX(CCHPh)L_2$ X = Cl, −12.65; X = I, −9.80. $RuHX(CCHSiMe_3)L_2$: X = Cl, −14.95; X = I, −11.14.

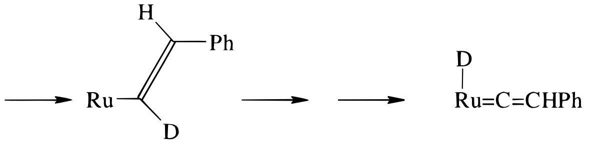
[12] Rachidi, I. E.-I.; Eisenstein, O.; Jean, Y. *New J. Chem.* **1990**, *14*, 671. Riehl, J.-F.; Jean, Y.; Eisenstein, O.; Pélissier, M. *Organometallics* **1992**, *11*, 729.

[13] Caulton, K. G. *New J. Chem.* **1994**, *18*, 25.

[14] Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.

$(CO)(P^iPr_3)_2$, implicating an intermediate analogous to **A**.[15] Thus, here the faster reaction is H−C(sp) oxidative addition. This reagent and ours differ primarily in the presence of a CO ligand and in the reagent electron count. Certainly, it seems nonintuitive that the presence of a CO ligand accelerates oxidative addition; perhaps, instead, it slows the addition of the Os−D bond across the C≡C bond.

The crucial feature of the mechanism is to "store" or retain one hydride originally from the ruthenium reagent for the final vinylidene group, even while accomplishing hydrogenation of one molecule of alkyne to olefin. We suggest this occurs at the $\beta$ carbon by preliminary (i.e., fastest) addition of a Ru−H bond[16] across the triple bond to give **B**, which later undergoes α-D migration to give the observed isotopomer.[17,18] This migration, which increases the metal valence electron count, occurs because the species employed here are operationally unsaturated; most vinylidene complexes to date have been formed from saturated intermediates. Our attempts to substantiate this proposed vinyl intermediate failed, since no intermediates are detected upon combining the reagents in toluene at −80 °C; upon warming, only reactants and product are observed. Similarly, combining $OsH_3Cl(P^iPr_3)_2$ and $Me_3SiCCH$ at −80 °C in toluene-$d_8$ shows no intermediates but forms $OsHCl[CCH(SiMe_3)](P^iPr_3)_2$.[19]



**B**

Calculations (assuming that the first step in the reaction is the hydrogenation of one of the two alkyne molecules and it has already taken place) show that the reaction path is exothermic going along the $\pi$-acetylene complex $RuHCl(HC_2H)(PH_3)_2$, to the product of insertion in the Ru−H bond, $RuCl(CH{=}CH_2)(PH_3)_2$ (−10.2 kcal/mol), and finally, α-elimination to give the vinylidene $RuHCl(CCH_2)(PH_3)_2$ (−13.6 kcal/mol), while a Ru(IV) dihydride intermediate ($RuH_2Cl(C_2H)(PH_3)_2$) is considerably higher in energy (22.9 kcal/mol). This accounts for the observed ease of reaction and supports the mechanism deduced from the deuterium labeling study.

The molecules $RuHX(CCHR)L_2$ are operationally unsaturated species incorporating *two* functionalities: vinylidene and hydride. We have sought to exploit this reactive potential and seek evidence for selectivity between these two functionalities. Reaction of $RuHI(CCHSiMe_3)L_2$ with excess MeNC at 25 °C causes immediate (in the time of mixing) insertion giving $[Ru(E\text{-}CH{=}CHSiMe_3)(CNMe)_3L_2]I$, which has *trans* phosphines and *mer*-MeNC ligands.[20,21] This reaction, thus, reverses the α-H migration which initially forms the vinylidene ligand.[22]

**Acknowledgment.** This work was supported by the U.S. National Science Foundation, by an international NSF/CNRS (PICS) grant (KGC/OE), and by material support from Johnson-Matthey/Aesar. M.O. thanks the Spanish Ministerio de Educación y Ciencia for a postdoctoral Fellowship. O.E. thanks E. R. Davidson for a generous donation of computational time.

**Supporting Information Available:** Text of the complete synthetic and characterization details and NMR spectra for all new compounds (17 pages). Ordering information is given on any current masthead page.

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(15) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1995**, *14*, 3596.

(16) Generally, the reaction of primary alkynes with transition metal hydride complexes lead to vinyl derivatives: Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(17) While it has been shown previously that a terminal alkyne forms a vinylidene from a *non-hydride* metal complex by the intermediacy of C−H oxidative addition, the mechanistic path in the case of a hydride metal complex has not been established. See: Garcia Alonso, F. J. G.; Höhn, A.; Wolf, J.; Otto, H.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 406. Lass, R. W.; Steinert, P.; Wolf, J.; Werner, H. *Chem. Eur. J.* **1996**, *2*, 19. Werner, H.; Baum, M.; Schneider, D.; Windmüller, B. *Organometallics* **1994**, *13*, 1089. What we show here is that the vinyl species forms prior to (i.e., faster than) H−C(sp) oxidative addition.

(18) For a previous example of such α-H migration from a vinyl complex, see: van Asselt, A.; Burger, B. J.; Gibson, V. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347.

(19) $OsHCl({=}C{=}CSiMe_3)(P^iPr_3)_2$. This compound was prepared analogously, as described for $RuHI({=}C{=}CHSiMe_3)(P^tBu_2Me)_2$, starting from $OsH_3Cl(P^iPr_3)_2$ (30 mg, 0.054 mmol) and $Me_3SiC{\equiv}CH$ (15.5 $\mu$L, 0.109 mmol). $^1H$ NMR (300 MHz, $C_6D_6$): $\delta$ −19.37 (t, $J_{P-H} = 13.9$ Hz, 1H, Os−H), −0.09 (t, $J_{P-H} = 2.5$ Hz, 1H, $CHSiMe_3$), 0.16 (s, 9H, $SiMe_3$), 1.27 (dvt, $J_{H-H} = 7.5$ Hz, $N = 14.4$ Hz, 36H, $PCH(CH_3)_2$), 2.80 (m, 6H, $PCH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75.429 MHz, $C_6D_6$): $\delta$ 1.31 (s, $SiMe_3$), 20.14 (s, $PCH(CH_3)_2$), 20.31 (s, $PCH(CH_3)_2$), 25.30 (vt, $N = 12.1$ Hz, $PCH(CH_3)_2$), 86.36 (t, $J_{P-C} = 2.5$ Hz, Os=C=*C*), 275.00 (t, $J_{P-C} = 9.0$ Hz, Os=*C*=C). $^{31}P\{^1H\}$ NMR (121.421 MHz, $C_6D_6$): $\delta$ 36.9 (s). IR ($C_6H_6$, $cm^{-1}$): $\nu$(Os−H) 2040 (vw), $\nu$(C=C) 1591 (s).

(20) $[Ru(E{-}CH{=}CHSiMe_3)(CNMe)_3(P^tBu_2Me)_2]I$. To a solution of $RuHI({=}C{=}CHSiMe_3)(P^tBu_2Me)_2$ (50 mg, 0.077 mmol) in toluene (5 mL) was added MeNC (17 $\mu$L, 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 $C_{29}H_{62}IN_3P_2RuSi$: C, 45.18; H, 7.98; N, 5.45. Found: C, 44.77; H, 7.6; N, 5.17. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ −0.06 (s, 9H, $SiMe_3$), 1.28 (vt, $N = 6.3$ Hz, 36H, $PC(CH_3)_3$), 1.33 (vt, $N = 3$ Hz, 6H, $PCH_3$), 3.57 (s, 3H, MeNC), 3.59 (t, $J_{P-H} = 1$ Hz, 6H, MeNC), 6.11 (dt, $J_{H-H} = 21$ Hz, $J_{P-H} = 2.1$ Hz, Ru−CH=C*H*), 8.14 (dt, $J_{H-H} = 21$ Hz, $J_{P-H} = 1.6$ Hz, Ru−C*H*=CH). $^{31}P\{^1H\}$ NMR (121.421 MHz,-$CDCl_3$): $\delta$ 43.7 (s). IR ($CDCl_3$, $cm^{-1}$): $\nu$(NC) 2148 (vs).

(21) Anion exchange with $NaBArF_4$ (ArF = 3,5-bis(trifluoromethyl)phenyl) leaves the NMR signature of the cation unchanged, proving that iodide is not coordinated.

(22) After submission of this work, vinylidene osmium analogs were reported. See: Bourgault, M.; Castillo, A.; Esteruelas, M. A.; Oñate, E.; Ruiz, N. *Organometallics* **1997**, *16*, 636.