The Mechanism of the Ru-Assisted C−C Bond Cleavage of Terminal Alkynes by Water

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Abstract: The hydration of phenylacetylene in the presence of the complex *mer,trans*-(PNP)$RuCl_2(PPh_3)$ in THF at 60 °C leads to the cleavage of the C−C triple bond with formation of the carbonyl complex *fac,cis*-(PNP)$RuCl_2$(CO) and toluene [PNP = $CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$]. A study under different experimental conditions, the use of model and isotope labeling experiments, and the detection of several intermediates, taken altogether, show that the C−C bond cleavage reaction comprises a number of steps, among which the most relevant to the mechanism are 1-alkyne to vinylidene tautomerism, conversion of a vinylidene ligand to hydroxycarbene by intramolecular attack of water, deprotonation of hydroxycarbene to σ-acyl, deinsertion of CO from the acyl ligand, and hydrocarbon elimination by protonation of the metal-alkyl moiety. The following intermediate species have been isolated and characterized: the vinylidene *fac,cis*-(PNP)$RuCl_2${C═C(H)Ph}, the (aquo)(σ-alkynyl) complex *fac*-(PNP)RuCl-(C≡CPh)(OH_2), and the (benzyl)carbonyl *mer*-(PNP)RuCl(η^1-CH_2Ph)(CO). Other intermediates such as the σ-acyl *mer*-(PNP)RuCl(η^1-$COCH_2$Ph)(CO) have been intercepted by addition of appropriate reagents, while the independent synthesis of the aminocarbene complex *fac,cis*-(PNP)$RuCl_2${$C(NC_5H_{10})(CH_2Ph)$} and its reaction with water have provided evidence for the intermediacy of a hydroxycarbene species in the C−C bond cleavage reaction.

Introduction

The hydration of alkynes to give carbonyl compounds is a well-known reaction[1] that can be promoted by either electrophiles (H^+, Hg^{2+})[2] or transition metal complexes.[3] In the peculiar case of terminal alkynes and iron-group metal promoters, the binary combination of the unsaturated hydrocarbon and water may lead to the cleavage of the C−C triple bond with formation of CO and the saturated hydrocarbon with one less carbon atom (generally in the form of carbonyl and alkyl ligands).[4]

Although the first example of ruthenium-assisted C−C triple bond cleavage by water was reported more than ten years ago,[4a] the overall mechanism of this important reaction, which involves two plentiful molecules of nature, is still rather obscure. From the mechanistic viewpoint, all of what is known may be summarized by reporting the following comment from the most recent edition of *Comprehensive Organometallic Chemistry*: "*The hydrolysis of vinylidene ligands typically leads to acyl or alkyl-carbonyl complexes and accordingly vinylidene intermediates, while not isolated, are almost certainly involved in the synthesis of such complexes from terminal alkynes and halide complexes of ruthenium(II)*".[5]

In this article we present a mechanistic study of the reaction between water and the model 1-alkyne, phenylacetylene, in the presence of a Ru(II) promoter. We are confident that the results obtained may constitute the final chapter for the mechanism of the metal-assisted C−C bond cleavage of 1-alkynes by water as well as provide new insight into many other reactions in which C−C bond cleavage is believed to occur *via* metal-hydroxycarbene intermediates (*i.e.*, Fischer−Tropsch chemistry).

Experimental Section

General Procedures. Tetrahydrofuran (THF), chloroform, and dichloromethane were purified by distillation under nitrogen over $LiAlH_4$ and P_2O_5, respectively. Piperidine and triethylamine were purchased from Carlo Erba, dried over KOH and distilled from BaO under an N_2 atmosphere prior to use. Oxygen-18 labeled water (95 atom % ^{18}O) was purchased from Aldrich. All the other reagents and chemicals were reagent grade and, unless otherwise stated, were used as received by commercial suppliers. All reactions and manipulations were routinely performed under a dry nitrogen atmosphere by using standard Schlenk-tube techniques. The solid complexes were collected on sintered glass-frits and washed with light petroleum ether (b.p. 40−60 °C) or *n*-pentane before being dried in a stream of nitrogen. The ligand $CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$ (PNP)[6] and the complexes

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mer,trans-(PNP)$RuCl_2(PPh_3)$ (**1**)[7] and *fac,cis*-(PNP)$RuCl_2${C═C(H)-Ph} (**4**)[8] were prepared as described in the literature. Deuterated solvents for NMR measurements (Merck and Aldrich) were dried over molecular sieves (0.4 nm). ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Varian VXR 300 or Bruker AC200 spectrometer operating at 299.94 or 200.13 MHz (^1H) and 75.42 or 50.32 MHz (^{13}C), respectively. Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (^1H) or the deuterated solvent multiplet (^{13}C). ^{13}C-DEPT experiments were run on the Bruker AC200 spectrometer. $^1H,^{13}C$-2D HETCOR NMR experiments were recorded on either the Bruker AC200 spectrometer using the XHCORR pulse program or a Bruker AVANCE DRX 500 spectrometer equipped with a 5-mm triple resonance probe head for ^1H detection and inverse detection of the heteronucleus (inverse correlation mode, HMQC experiment) with no sample spinning. The $^1H,^1H$-2D COSY NMR experiments were routinely conducted on the Bruker AC200 instrument in the absolute magnitude mode using a 45° or 90° pulse after the incremental delay or were acquired on the AVANCE DRX 500 Bruker spectrometer using the phase-sensitive TPPI mode with double quantum filter. $^{31}P\{^1H\}$ NMR spectra were recorded on either the Varian VXR 300 or Bruker AC200 instruments operating at 121.42 and 81.01 MHz, respectively. Chemical shifts were measured relative to external 85% H_3PO_4 with downfield values taken as positive. The proton NMR spectra with broad-band phosphorus decoupling were recorded on the Bruker AC200 instrument equipped with a 5-mm inverse probe and a BFX-5 amplifier device using the wideband phosphorus decoupling sequence GARP. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 1600 series FT-IR spectrometer between KBr plates. Reactions under controlled pressure were performed with a Parr 4565 reactor equipped with a Parr 4842 temperature and pressure controller. A Shimadzu GC-14A/GCMS-QP2000 instrument was employed for all GC-MS investigations. Elemental analyses (C, H, N) were performed using a Carlo Erba Model 1106 elemental analyzer.

Reaction of *mer,trans*-(PNP)$RuCl_2(PPh_3)$ (1) with Phenylacetylene and Water (*in situ* NMR Experiment). Neat phenylacetylene (28 μL, 0.25 mmol) and water (4.50 μL, 0.25 mmol) were added via syringe to a solution of **1** (23 mg, 0.025 mmol) in a $CDCl_3$/THF-d_8 mixture (1.0 mL 4:1 v/v) in a 5-mm NMR tube. The tube was flame-sealed under nitrogen and then placed into the probe of a NMR spectrometer preheated at 60 °C. The reaction was followed at this temperature by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy over a period of 14 h. Already after the acquisition of the first spectrum, **1** had partially converted to two species, namely the known carbonyl complex *fac,cis*-(PNP)$RuCl_2$(CO) (**2**)[8] and the new complex *mer*-(PNP)RuCl-(η^1-CH_2Ph)(CO) (**3**) (see below) with formation of free PPh_3 (^{31}P NMR: singlet at −4.57 ppm). As an example, 82% of **1** transformed into a 63:19 mixture of **2** and **3** in 4 h. After 7 h, all **1** was converted into a 84:16 mixture of **2** and **3**; further heating for *ca.* 2 h transformed completely **3** into **2** that is thermally stable in these reaction conditions. ^1H NMR and GC-MS analysis showed increasing formation of toluene with the disappearance of **3**. After total disappearance of **3**, a careful NMR integration of the toluene singlet (δ 2.33) with respect to the *n*-propyl CH_3 resonance of the PNP ligand in complex **2** (δ 0.96), confirmed the formation of about 1 equiv of toluene.

Reaction of *mer,trans*-(PNP)$RuCl_2(PPh_3)$ (1) with Phenylacetylene and Water (Parr Reactor Experiment). A solution of **1** (0.60 g, 0.65 mmol) and a tenfold excess of both phenylacetylene (0.75 mL, 6.70 mmol) and water (0.12 mL, 6.66 mmol) in a $CHCl_3$/THF mixture (40 mL 4:1 v/v) was placed into the Parr reactor and pressurized with nitrogen (1 atm). After 9 h at 60 °C, the reactor was cooled to room temperature. The contents of the reactor were transferred into a Schlenk flask and a sample of the solution, analyzed by GC-MS, showed the formation of toluene. The remaining solution was concentrated to dryness in vacuo to give a yellow powder which was analyzed by ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy, which showed the quantitative transformation of **1** into **2**.

Synthesis of *mer*-(PNP)RuCl(η^1-CH_2Ph)(CO) (3) (Open Reactor). Neat phenylacetylene (0.50 mL, 4.50 mmol) was pipetted into a well stirred THF slurry (50 mL) of **1** (0.40 g, 0.44 mmol) containing 80 μL (4.44 mmol) of distilled water and the mixture was refluxed under a stream of nitrogen for 5 h with stirring. During this time, all **1** dissolved to give a pale yellow solution which, after cooling to room temperature separated pale yellow crystals of **3** by addition of ethanol (50 mL) and slow concentration under nitrogen. Yield 93%. Anal. Calcd for $C_{39}H_{42}NClOP_2Ru$: C, 63.37; H, 5.73; N, 1.89. Found: C, 63.29; H, 5.65; N, 1.76. IR: ν(C≡O) 1899 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (21 °C, CD_2Cl_2, 121.42 MHz) 30.64 (s); ^1H NMR (21 °C, CD_2Cl_2, 200.15 MHz): δ_{CH2Ph} 3.00 (t, $^3J_{HP}$ 4.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (21 °C, CD_2Cl_2, 50.32 MHz): $\delta_{C\equiv O}$ 204.50 (t, $^2J_{CP}$ 14.1 Hz), $\delta_{Ipso\text{-}CH2Ph}$ 159.20 (t, $^3J_{CP}$ 2.9 Hz), $\delta_{CH3CH2CH2N}$ 58.71 (s), $\delta_{NCH2CH2P}$ 52.17 (s), $\delta_{NCH2CH2P}$ 33.48 [vt, N = $J_{CP} + J_{CP'}$ = 12.0 Hz], $\delta_{CH3CH2CH2N}$ 13.96 (s), $\delta_{CH3CH2CH2N}$ 11.95 (s), δ_{CH2Ph} 11.04 (t, $^3J_{CP}$ 6.2 Hz).

In a separate experiment, the outlet of the Schlenk flask was connected to another flask containing a solution of NEt_3 in diethyl ether. As the gases coming from the reactor bubbled into the latter solution, precipitation of $[NEt_3H]Cl$ occurred.

Synthesis of *mer*-(PNP)RuCl(η^1-CD_2Ph)(CO) (3-d_2). Replacing H_2O with D_2O and EtOH with EtOD in the above reaction gave the isotopomer *mer*-(PNP)RuCl(η^1-CD_2Ph)(CO) (**3-d_2**) in which the selective replacement of the methylenic hydrogen atoms of the benzylic group by deuterium was shown by ^1H and ^{13}C-DEPT NMR spectroscopy.

Stepwise Reaction of 1 with Phenylacetylene and Water (*in Situ* NMR Experiment). Neat phenylacetylene (28 μL, 0.25 mmol) was added via syringe to a solution of **1** (23 mg, 0.025 mmol) in a $CDCl_3$/THF-d_8 mixture (1.0 mL 4:1 v/v) in a screw-cap 5 mm NMR tube. The tube was placed into the probe of a NMR spectrometer preheated at 60 °C. Within *ca.* 2 h, all **1** selectively transformed into the known vinylidene complex *fac,cis*-(PNP)$RuCl_2${C═C(H)Ph}[8] (**4**) (^{31}P, ^1H NMR) and free PPh_3. At this point, water (4.50 μL, 0.25 mmol) was syringed into the NMR tube cooled to room temperature. The tube was again inserted into the NMR probe at 60 °C, and $^{31}P\{^1H\}$ and ^1H NMR spectra were acquired every 30 min. The practically immediate transformation of **4** into **3** was primarily observed, followed by slow conversion of **3** into **2** (quantitative transformation in *ca.* 5 h).

Reaction of 3 with HCl. A slight excess of HCl (1 M solution in H_2O) was added via syringe into a 5-mm screw cap NMR tube containing a THF-d_8 (0.8 mL) solution of **3** (26 mg, 0.035 mmol). $^{31}P\{^1H\}$ and ^1H NMR spectroscopy showed the quantitative transformation of **3** into **2**. GC-MS analysis of the solution confirmed the formation of 1 equiv of toluene.

Replacing **3** with **3-d_2** in the above reaction, yielded 1 equiv of monodeuterated toluene, $PhCH_2D$ (^1H NMR and GC-MS analysis).

Reaction of *fac,cis*-(PNP)$RuCl_2${C═C(H)Ph} (4) with Water (*in situ* NMR Experiment). A 5-mm NMR tube was charged with a solution of the vinylidene complex **4** (20 mg, 0.026 mmol) in a $CDCl_3$/THF-d_8 mixture (1.0 mL 4:1 v/v) containing a tenfold excess of water (4.70 μL, 0.26 mmol). The tube was flame sealed under nitrogen and then inserted into the probehead of a NMR spectrometer preheated at 60 °C. The reaction was followed by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy at this temperature. The rapid conversion of **4** to **3** was observed, followed by slow conversion of **3** into **2** (complete transformation in *ca.* 5 h). ^1H NMR and GC-MS analysis showed the formation of toluene during the secondary transformation of **3** into **2**.

Reaction of *mer,trans*-(PNP)$RuCl_2${C═C(H)Ph} (4) with Water (Parr Reactor Experiment). A solution of **4** (0.40 g, 0.52 mmol) and a tenfold excess of water (0.10 mL, 5.55 mmol) in a $CHCl_3$/THF mixture (30 mL 4:1 v/v) was placed into a Parr reactor, pressurized with one atm of nitrogen, and heated to 60 °C with stirring. After 6 h, the reactor was cooled to room temperature and opened. The contents of the reactor were transferred into a Schlenk flask and a sample of the solution, analyzed by GC-MS, showed the formation of toluene. The rest of the solution was concentrated to dryness in vacuo to give a yellow powder which was authenticated by $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy as **2**.

Reaction of *mer,trans*-(PNP)$RuCl_2${C═C(H)Ph} (4) with Water (Open Reactor). A solid sample of **4** (0.20 g, 0.26 mmol) was suspended in THF (40 mL) containing 47.0 μL (2.61 mmol) of distilled

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water. The mixture was slowly brought to the boiling point and then refluxed with stirring for 3 h under a stream of nitrogen. During this time all **4** dissolved to give a pale yellow solution which after cooling to room temperature separated pale yellow crystals of **3** by addition of ethanol (30 mL) and slow concentration under nitrogen. Yield 90%.

Reaction of *fac,cis*-(PNP)RuCl$_2${C═C(H)Ph} (4) with D_2O (Schlenk-Flask Experiment). Replacing H_2O with D_2O in the above reaction at room temperature gave *fac,cis*-(PNP)RuCl$_2${C═C(D)Ph} (**4-*d*$_1$**) via H/D exchange of the vinylidene proton (disappearance of the vinylidene proton triplet at 5.32 ppm). Heating at the constant temperature of 60 °C in the spectrometer probehead produced initially **3-*d*$_2$** and ultimately **2** together with 1 equiv of toluene-d_3 (GC-MS analysis).

Reaction of 4 with $H_2{}^{18}O$ (Schlenk-Flask Experiment). A solid sample of **4** (0.10 g, 0.13 mmol) was dissolved in THF (25 mL) containing 25 μL of $H_2{}^{18}O$ (95 atom % ^{18}O, 1.25 mmol). Work up as described above for the reaction of **4** with water, gave *mer*-(PNP)-RuCl(η^1-CH_2Ph)($C^{18}O$) (**3-*^{18}O***). Yield 88%. IR: ν(C≡^{18}O) 1853 (s) cm^{-1}.

Reaction of 4 with $H_2{}^{18}O$ (*in situ* NMR Experiment). A 5-mm NMR tube was charged with a solution of **4** (20 mg, 0.026 mmol) in $CDCl_3$/THF-d_8 mixture (1.0 mL 4:1 v/v) and with a tenfold excess of $H_2{}^{18}O$ (5.20 μL, 0.26 mmol). The tube was flame sealed under nitrogen and then inserted into the probehead of the spectrometer preheated at 60 °C. The reaction was followed by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy at this temperature over a period of 6 h. A clean transformation of **4** into **3-*^{18}O*** and a secondary conversion of **3-*^{18}O*** into *fac,cis*-(PNP)RuCl$_2$($C^{18}O$) (**2-*^{18}O***) was observed. ^1H NMR and GC-MS analysis confirmed the formation of toluene during the secondary transformation of **3-*^{18}O*** into **2-*^{18}O***. IR: ν(C≡^{18}O) 1899 (s) cm^{-1}.

High-Pressure Carbonylation Reaction of the Vinylidene Complex 4 in the Presence of Water. A solution of **4** (0.20 g, 0.26 mmol) in THF (20 mL) containing 50 μL of water (2.77 mmmol) was prepared in the Parr reactor, which was pressurized with 30 atm of carbon monoxide. The reactor was heated to 60 °C and then stirred for 2 h. After this time, the reactor was cooled to room temperature and slowly depressurized under a nitrogen stream. The contents of the reactor were analyzed by GC-MS (which showed the presence of both free benzylaldehyde and phenylacetylene) and then transferred into a Schlenk flask. After the solvent was removed under reduced pressure, a pale yellow solid was obtained. $^{31}P\{^1H\}$ NMR spectroscopy of the crude product showed the formation of several ruthenium-PNP complexes: the new (η^1-acyl)carbonyl complex *mer*-(PNP)RuCl($COCH_2$Ph)(CO) (**6**) (61%) (see below), **2** (14%), and *mer,trans*-(PNP)RuCl$_2$(CO) (**5**) (12%) (some unidentified compounds were also produced). Recrystallization of the crude product from CH_2Cl_2/*n*-hexane gave **6** in almost analytically pure form (traces of **2** and **5** which may occasionally contaminate the product, can be removed by further recrystallization). Compound **6**: Anal. Calcd for $C_{40}H_{42}NClO_2P_2Ru$: C, 62.57; H, 5.52; N, 1.83. Found: C, 62.40; H, 5.38; N, 1.65. IR: ν(C≡O) 1939 (vs) cm^{-1}; ν($COCH_2$Ph) 1601 (br s) cm^{-1}. $^{31}P\{^1H\}$ NMR (22 °C, $CDCl_3$, 81.15 MHz) 32.56 (s). ^1H NMR (21 °C, CD_2Cl_2, 200.15 MHz): δ_{COCH_2Ph} 3.43 (s, 2H). $^{13}C\{^1H\}$ NMR (21 °C, $CDCl_3$, 50.32 MHz): $\delta_{COCH2Ph}$ 256.39 (t, $^2J_{CP}$ 8.7 Hz), $\delta_{C=O}$ 201.33 (t, $^2J_{CP}$ 13.1 Hz), $\delta_{Cipso\text{-}CH2Ph}$ 159.20 (t, $^3J_{CP}$ 3.3 Hz), $\delta_{CH3CH2CH2N}$ 64.19 (s), δ_{CH2Ph} 56.78 (s), $\delta_{NCH2CH2P}$ 51.28 (s), $\delta_{NCH2CH2P}$ 32.86 [vt, N = J_{CP} + $J_{CP'}$ = 12.0 Hz], $\delta_{CH3CH2CH2N}$ 13.72 (s), $\delta_{CH3CH2CH2N}$ 12.12 (s).

In order to confirm the presence of an −C(O)CH_2Ph ligand in **6**, a THF-d_8 solution of this complex in an NMR tube was treated with a slight excess of concentrated HCl solution. The NMR tube was sealed under nitrogen and then placed into the probehead of a spectrometer. No reaction occurred below 60 °C. At this temperature, **6** slowly but selectively converted to **5** while benzylaldehyde was liberated (GC-MS).

High-Pressure Carbonylation Reaction of 3. A solution of **3** (0.20 g, 0.27 mmol) in THF (20 mL) was placed in the Parr reactor and pressurized with 30 atm of carbon monoxide. The reactor was heated to 60 °C and then stirred at this constant trremperature for 1 h. The reactor was then cooled to room temperature and slowly depressurized under a nitrogen stream. The contents of the reactor were transferred into a Schlenk flask and then concentrated to dryness in vacuo to yield a pale yellow powder. $^{31}P\{^1H\}$ NMR spectroscopy of the crude product showed the formation of **6** (60%) and of its geometric isomer *mer*-(PNP)RuCl($COCH_2$Ph)(CO) (**7**) in which the acyl ligand is located *trans* to the chloride (40%). Heating this mixture at 60 °C for 12 h in the NMR tube transformed all **7** into **6**, which results thermally stable at the experimental temperature. Compound **7**: IR: ν(C≡O) 1916 (vs) cm^{-1}; ν($COCH_2$Ph) 1605 (br s) cm^{-1}. $^{31}P\{^1H\}$ NMR (22 °C, $CDCl_3$, 81.15 MHz) 38.96 (s). ^1H NMR (21 °C, CD_2Cl_2, 200.15 MHz): $\delta_{COCH2Ph}$ *ca.* 3.1 (s, partially masked by the aliphatic signals of the PNP ligand). $^{13}C\{^1H\}$ NMR (21 °C, $CDCl_3$, 50.32 MHz): $\delta_{COCH2Ph}$ 257.43 (t, $^2J_{CP}$ 10.9 Hz), $\delta_{C=O}$ 206.75 (t, $^2J_{CP}$ 11.9 Hz), $\delta_{Cipso\text{-}CH2Ph}$ 159.37 (t, $^3J_{CP}$ 2.3 Hz), $\delta_{CH3CH2CH2N}$ 70.80 (s), δ_{CH2Ph} 55.35 (s), $\delta_{NCH2CH2P}$ 52.79 (s), $\delta_{NCH2CH2P}$ 32.21 [vt, N = J_{CP} + $J_{CP'}$ = 11.6 Hz], $\delta_{CH3CH2CH2N}$ 13.93 (s), $\delta_{CH3CH2CH2N}$ 12.24 (s).

Synthesis of *fac,cis*-(PNP)RuCl$_2${C(NC_5H_{10})(CH_2Ph)} (8). A threefold excess of piperidine, HNC_5H_{10} (0.20 mL, 2.02 mmol), was added at room temperature to a stirred suspension of **4** (0.50 g, 0.66 mmol) in 30 mL of CH_2Cl_2. The reaction mixture was stirred in the dark overnight during which time all the starting vinylidene complex dissolved to afford a canary yellow solution which was evaporated to *ca.* 5 mL. Addition of light petroleum ether gave canary yellow microcrystals of the aminocarbene **8**, which were recrystallized from CH_2Cl_2 and light petroleum ether. Yield 96%. Anal. Calcd for $C_{44}H_{52}N_2Cl_2P_2Ru$: C, 62.70; H, 6.22; N, 3.32. Found: C, 62.48; H, 6.17; N, 3.12. $^{31}P\{^1H\}$ NMR (22 °C, C_6D_6, 81.01 MHz) 50.07 (s). ^1H NMR (22 °C, C_6D_6, 200.15 MHz): δ_{CH2Ph} 4.62 (s, 2H). $^{13}C\{^1H\}$ NMR (22 °C, C_6D_6, 50.32 MHz): $\delta_{Ru=C}$ 252.40 (t, $^2J_{CP}$ 14.2 Hz), $\delta_{CH3CH2CH2N}$ 62.94 (s), δ_{CH2Ph} 57.92 (s), $\delta_{NCH2CH2P}$ 57.41 (s), $\delta_{piperidine(CH2)\alpha}$ 51.85, $\delta_{NCH2CH2P}$ 31.64 [vt, N = J_{CP} + $J_{CP'}$ = 13.2 Hz], $\delta_{piperidine(CH2)\beta}$ 27.71, $\delta_{piperidine(CH2)\gamma}$ 25.37, $\delta_{CH3CH2CH2N}$ 16.05 (s), $\delta_{CH3CH2CH2N}$ 12.89 (s).

Reaction of 8 with Water. (A) *In Situ* NMR Experiment in THF-d_8. A fivefold excess of H_2O (3.5 μL, 0.19 mmol) was added via syringe into a 5-mm screw cap NMR tube containing a THF-d_8 (0.8 mL) solution of **8** (30 mg, 0.036 mmol). The reaction was monitored by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy in the temperature range from −40 °C to 45 °C. A slow reaction occurred already at 30 °C which transformed **8** in a 40:60 mixture of **3** and **2** within 4 h. No intermediate species was detected in the course of the transformation of **8**. After 12 h, when all the ruthenium was present in the form of **2**, GC-MS analysis of the solution showed the formation of 1 equiv of both toluene and piperidine.

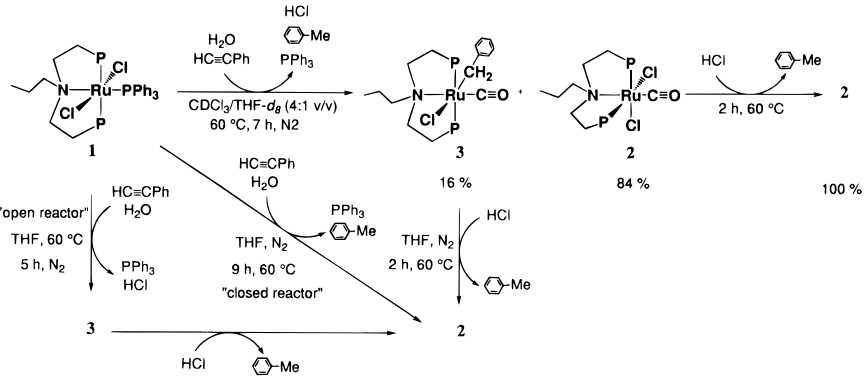
(B) Preparative Experiment with $H_2{}^{18}O$. A solid sample of **8** (0.20 g, 0.24 mmol) was dissolved in THF (25 mL) containing 25 μL of $H_2{}^{18}O$ (95 atom % ^{18}O, 1.25 mmol). The resulting solution was stirred at room temperature for 12 h. Addition of ethanol (30 mL), followed by a slow evaporation under a stream of nitrogen, gave **2-*^{18}O*** in 93% yield.

(C) Preparative Experiment in CD_2Cl_2/H_2O. The reaction between **8** (0.20 g, 0.24 mmol) and H_2O was carried out in liquid-biphase system (CH_2Cl_2/H_2O) (40 mL, 5:1 v/v) under vigorous stirring for 4 h. After phase separation, **3** was selectively obtained from the organic phase, while piperidinium chloride was found in the water phase.

Reaction of 8 with Water under Carbon Monoxide. (A) *In Situ* NMR Experiment at Room Temperature. A THF-d_8 (1.0 mL) solution of **8** (30 mg, 0.036 mmol), prepared in a screw cap 5-mm NMR tube, was saturated with carbon monoxide (1 atm) at room temperature and analyzed by $^{31}P\{^1H\}$ NMR spectroscopy. The NMR study showed no reaction within 3 h. Addition of H_2O (3.5 μL, 0.19 mmol) *via* syringe almost immediately transformed **8** into a mixture of the two complexes *fac*-(PNP)RuCl($COCH_2$Ph)(CO) (**9**) (see below) and **7** in a kinetic ratio of 89:11 [$^{31}P\{^1H\}$ NMR integration after 10 min]. With time, **9** transformed into **7** (complete transformation in 3 h at room temperature). After N_2 was substituted for CO, the NMR tube was heated at 60 °C for 12 h during which time **7** completely transformed into **6**.

(B) *In Situ* NMR Experiment at Low Temperature. A THF-d_8 (1.0 mL) solution of **8** (90 mg, 0.11 mmol), prepared as above, was saturated with carbon monoxide (1 atm) at −78 °C and treated with 5 equiv of H_2O (9.9 μL, 0.55 mmol). Monitoring the reaction by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy at −20 °C, revealed that **8** immediately disappeared to give **9**. After 12 h at this temperature,

Scheme 1



only a small amount of **7** (< 5%) was present in the solution [$^{31}P\{^1H\}$ NMR integration].

(C) Synthesis of *fac*-(PNP)RuCl(η^1-COCH$_2$Ph)(CO) (9). A steady stream of carbon monoxide (1 atm) was bubbled throughout a THF solution (20 mL) of **8** (0.30 g, 0.36 mmol) cooled at −20 °C. After 15 min, 5 equiv of water (32 μL in 1.0 mL of THF) were added under vigorous stirring. Stirring was continued for 30 min. Addition of light petroleum ether (30 mL) and concentration of the resulting solution under a brisk current of CO gave off-white microcrystals of **9**. Yield 76%. Anal. Calcd for $C_{40}H_{42}NCl_2O_2P_2Ru$: C, 59.85; H, 5.27; N, 1.74. Found: C, 59.58; H, 5.11; N, 1.67. IR: ν(C≡O) 1932 (s) cm^{-1}; ν(COCH$_2$Ph) 1630 (br s) cm^{-1}. $^{31}P\{^1H\}$ NMR (-20 °C, THF-d_8, 121.42 MHz) AM spin system: δ_A 54.01, δ_M 38.46, $^2J_{PP}$ 17.0 Hz. ^1H NMR (−20 °C, THF-d_8, 200.15 MHz): δ_{CH2Ph} (ABX system): δ_A 5.34, δ_B 5.13, $^2J_{AB}$ 12.6 Hz, $^2J_{AX} \approx {}^2J_{BX}$ 4.9 Hz. $^{13}C\{^1H\}$ NMR (-20 °C, THF-d_8, 75.42 MHz): $\delta_{COCH2Ph}$ 249.20 (dd, $^2J_{CPtrans}$ 94.1, $^2J_{CPcis}$ 11.2 Hz), $\delta_{C\equiv O}$ 208.22 (dd, $^2J_{CP}$ 16.0 and 14.1 Hz), $\delta_{CH3CH2CH2N}$ 63.38 (s), $\delta_{NCH2CH2P}$ 58.99 (s), δ_{CH2Ph} 56.00 (s), $\delta_{NCH2CH2P}$ 30.53 [vt, N = J_{CP} + $J_{CP'}$ = 11.6 Hz], $\delta_{CH3CH2CH2N}$ 15.70 (s), $\delta_{CH3CH2CH2N}$ 12.24 (s).

Synthesis of *fac*-(PNP)RuCl(C≡CPh)(OH$_2$) (10) and *fac*-(PNP)-RuCl(C≡CPh)(OD$_2$) (10-d$_2$). Compound **4** (0.40 g, 0.53 mmol) was dissolved in 25 mL of CH_2Cl_2. Three equiv of triethylamine, (0.22 mL, 1.59 mmol) in water (25 mL) were added at room temperature, and the resulting biphase system was vigorously stirred for 2 h. The organic layer was separated, dried over magnesium sulfate, and concentrated to *ca.* 5 mL under vacuum. Addition of light petroleum ether (10 mL) gave orange microcrystals of *fac*-(PNP)RuCl(C≡CPh)-(OH$_2$) (**10**). The crude product was recrystallized from CH_2Cl_2/*n*-hexane solution. Yield 72%. Anal. Calcd for $C_{39}H_{42}NClOP_2Ru$: C, 63.37; H, 5.73; N, 1.89. Found: C, 63.06; H, 5.65; N, 1.70. IR: ν(OH) 3374 cm^{-1} (br w), ν(C≡C) 2074 cm^{-1} (s). $^{31}P\{^1H\}$ NMR (22 °C, CD_2Cl_2, 81.01 MHz) AM system: δ_A 77.57 (br), δ_M 64.84 (br); (−50 °C, CD_2Cl_2, 81.01 MHz) AM system: δ_A 76.85, δ_M 62.72, $^2J_{PP}$ 41.1 Hz. ^1H NMR (−50 °C, CD_2Cl_2, 200.15 MHz): δ_{OH2} 4.69 (br t, $^3J_{HP}$ 8.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (20 °C, CD_2Cl_2, 50.32 MHz): $\delta_{C\equiv CPh}$ 108.93 (t, $^2J_{CPA} \approx {}^2J_{CPM}$ 12.6 Hz), $\delta_{C\equiv CPh}$ 114.12 (s), $\delta_{CH3CH2CH2N}$ 62.25 (s), $\delta_{NCH2CH2P}$ 53.45 (s), $\delta_{NCH2CH2P}$ 31.09 [vt, N = J_{CP} + $J_{CP'}$ = 11.5 Hz], $\delta_{CH3CH2CH2N}$ 14.87 (s), $\delta_{CH3CH2CH2N}$ 12.06 (s).

After concentration under reduced pressure, the water phase gave the ammonium salt [NEt$_3$H]Cl. Substitution of H_2O for H_2O in the above reaction gave **10-*d*$_2$** (contaminated by *ca.* 10% of **10**).

Reaction of 10 and 10-*d*$_2$ with HCl. A stoichiometric amount of gaseous HCl (1.3 mL, 0.06 mmol) was syringed into a screw cap 5-mm NMR tube containing a $CDCl_3$ (1.0 mL) solution of **10** (42 mg, 0.057 mmol). Monitoring the reaction by $^{31}P\{^1H\}$ and ^1H NMR spectroscopies at room temperature showed the transformation of **10** into the (dichloride)carbonyl complex **2** and toluene *via* the intermediacy of the (benzyl)carbonyl complex **3**. Some vinylidene complex **4** (20%) is also formed as a result of protonation of the C$_\beta$ carbon atom of the σ-alkynyl ligand in **10**, followed by displacement of the coordinated water by chloride. Just the HCl consumed in this reaction allows the formation of a comparable amount of **3**. As a matter of fact, the use of an excess of HCl produces only **2** and **4**.

When the isotopomer **10-*d*$_2$** was used in the place of **10**, the reaction gave **3-*d*$_2$** and toluene-d_2 (GC-MS).

Reaction of 1 with Benzylaldehyde. A solution of **1** (0.20 g, 0.25 mmol) and a tenfold excess of freshly distilled benzylaldehyde (0.3 mL, 2.55 mmol) in THF (30 mL) were refluxed with stirring for 2 h. After the reactor was cooled to room temperature, addition of *n*-hexane gave orange crystals of the dimer [Ru$_2$(μ-Cl)$_3$(PNP)$_2$]Cl, which can be obtained by simple thermolysis of **1** in refluxing THF.[7,8]

Results

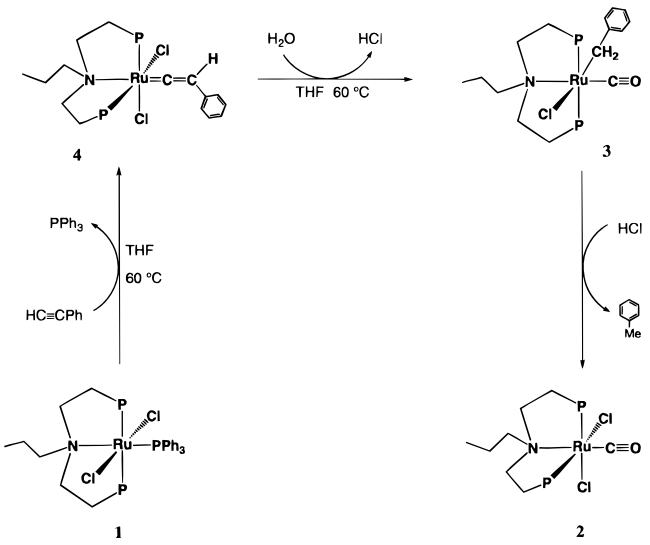
Reaction of *mer,trans*-(PNP)RuCl$_2$(PPh$_3$) (1) with Phenylacetylene and Water. Treatment of the complex *mer,trans*-(PNP)RuCl$_2$(PPh$_3$) (**1**)[7] in THF with a mixture of phenylacetylene and water in a closed reactor at a constant temperature of 60 °C results in the quantitative formation of the known carbonyl complex *fac,cis*-(PNP)RuCl$_2$(CO) (**2**),[8] PPh$_3$, and toluene. Monitoring the reaction in a sealed NMR tube ($CDCl_3$/THF-d_8 mixture) by NMR spectroscopy ($^{31}P\{^1H\}$, ^1H) shows that **2** is formed at the expense of the intermediate (benzyl)carbonyl complex *mer*-(PNP)RuCl(η^1-CH$_2$Ph)(CO) (**3**). The NMR analysis shows also that the formation of **3** is accompanied by formation of free PPh$_3$, while the formation of **2** is accompanied by formation of toluene. Once formed, **2** is indefinitely stable under the experimental conditions (Scheme 1).

The (benzyl)carbonyl complex **3** can be isolated in analytically pure form by performing the reaction in an open reactor under a constant bubbling of dinitrogen. This experiment also shows that the formation of **3** is accompanied by evolution of HCl, which is removed from the reaction mixture by the stream of inert gas. If HCl is not removed, as occurs in the reaction carried out in a closed system, it reacts with **3** producing **2** and toluene (*vide infra*). Once isolated, **3** is thermally stable in THF. Unambiguous characterization of **3** is provided by IR and NMR spectroscopies. In particular, a singlet at 30.64 ppm in the $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, 20 °C) is consistent with a *meridional* arrangement of the PNP ligand,[8,9] while a triplet resonance at δ 3.00 ($^3J_{HP}$ 4.2 Hz) in the ^1H NMR spectrum shows that the two benzylic protons are magnetically equivalent. This signal collapses to a singlet in the broad-band decoupled $^1H\{^{31}P\}$ NMR spectrum and does not show any cross-peak in the ^1H,^1H-2D COSY spectrum. A ^1H,^{13}C-2D HETCOR experiment clearly correlates this signal with an upfield triplet at 11.04 ppm in the $^{13}C\{^1H\}$ NMR spectrum which is assigned to the Ru−CH$_2$ carbon atom of the benzyl group. The relatively low magnitude of the carbon to phosphorus geminal coupling ($^2J_{CP}$ 6.2 Hz) agrees with the *meridional* geometry of PNP and indicates also that the benzyl and chloride ligands are mutually trans. A ^{13}C-DEPT experiment, unambiguosly confirms this assignment.

Finally, the $^{13}C\{^1H\}$ NMR spectrum of **3** shows the presence of a carbonyl resonance at δ 204.50 and of a narrower triplet at

(9) Meek, D. W.; Mazanec, T. *Acc. Chem. Res.* **1981**, *14*, 266.

Scheme 2



159.21 ppm ($^3J_{CP}$ 2.9 Hz) due to the *ipso* carbon of the benzylic group. It is worth mentioning that both the position and the $^2J_{CP}$ value (14.1 Hz) of the carbonyl resonance suggest that the CO group is *trans* to the N donor of PNP[8,10] (the X-ray authenticated carbonyl **2** exhibits a similar triplet signal at δ 203.61 ppm with $^2J_{CP}$ 15.9 Hz).[8]

Reactions of the Vinylidene Complex *fac,cis*-(PNP)$RuCl_2$-{C═C(H)Ph} (4) with H_2O, D_2O, or $H_2{}^{18}O$. In the absence of water, the reaction between **1** and HC≡CPh in THF at 60 °C gives exclusively the vinylidene complex *fac,cis*-(PNP)-$RuCl_2${C═C(H)Ph} (**4**).[8] In keeping with this previous finding, the vinylidene **4** is the first compound which is formed in the stepwise reaction of **1** with HC≡CPh and H_2O illustrated in Scheme 2. However, **4** cannot be intercepted in the course of the one-pot reaction of **1** with HC≡CPh and H_2O as it rapidly reacts with H_2O to give **3** which slowly converts to **2**.

The independent synthesis of the vinylidene complex **4**[8] has allowed us to use this key compound in the elucidation of the mechanism of the C−C triple bond cleavage of phenylacetylene. In particular, valuable information has been obtained by a variety of isotope labeling experiments (Scheme 3).

Reaction of **4** with D_2O in an open reactor in the experimental conditions used for H_2O gives the isotopomer *mer*-(PNP)RuCl(η^1-CD_2Ph)(CO) (**3-*d*$_2$**) in which the selective incorporation of deuterium into the benzylic group is unequivocally demonstrated by ^{1}H NMR spectroscopy. A standard ^{13}C-DEPT experiment confirms this result demonstrating about 100% incorporation of deuterium into the benzylic multiplet at *ca.* 11 ppm which, in fact, disappears in the DEPT spectrum of **3-*d*$_2$**.

Deuterium labeling experiments carried out directly in the NMR tube (closed system) show that **2** and 1 equiv of $PhCD_3$ (^{1}H NMR spectroscopy; GC-MS) are selectively formed. Incorporation of deuterium occurs neither into the phenyl ring of the benzyl ligand nor the PNP ligand. The formation of $PhCD_3$ instead of the expected isotopomer $PhCD_2H$ occurs because of a fast intermolecular exchange of the vinylidene hydrogen atom with deuterium which precedes the incorporation of D_2O into the complex. Indeed, at room temperature **4** completely transforms into *fac,cis*-(PNP)$RuCl_2${C═C(D)Ph} (**4-*d*$_1$**) when a drop of D_2O is added to a $CDCl_3$/THF-d_8 solution (4:1 v/v).

The reaction of **4** with $H_2{}^{18}O$ in either open or closed reactors results in the selective incorporation of ^{18}O in the carbonyl ligand, thus confirming that the C−C bond scission of the vinylidene ligand is caused by water and not by adventitious O_2. In fact, vinylidene metal complexes are known to react with O_2 yielding carbonyl derivatives and aldehydes *via* oxidative cleavage of the C−C bond.[8,11]

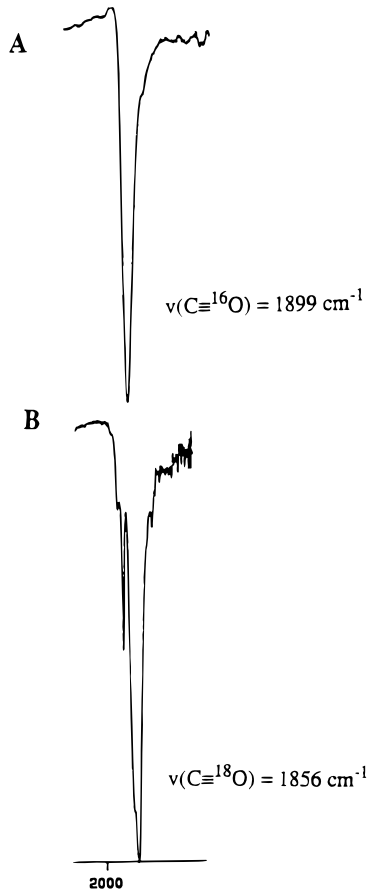


Figure 1. Infrared spectra (Nujol mull between KBr plates) of **3** (A) and **3-*18*O** (B) in the carbonyl stretching region.

When the reaction between **4** and $H_2{}^{18}O$ is carried out in an open system, the only Ru product obtained is *mer*-(PNP)RuCl-(CH_2Ph)($C^{18}O$) (**3-*18*O**) as shown also by the red-field shift (Figure 1) exhibited by the stretching vibration of the carbonyl group [$\nu_{(C\equiv O)}$ = 1853 cm^{-1} (s)]. The frequency-change in this absorption, $\Delta\nu_{(C\equiv O)} = \nu_{(C\equiv{}^{16}O)} - \nu_{(C\equiv{}^{18}O)}$ = (1899−1853) cm^{-1} = 46 cm^{-1}, is in excellent agreement with the value that may be figured out from the change in reduced mass [$\Delta\nu_{(C\equiv O)}$ = 47 cm^{-1}].[12]

Addition of $H_2{}^{18}O$ to a solution of **4** ($CDCl_3$/THF-d_8 4:1 v/v) in an NMR tube, followed by heating to 60 °C leads to formation of *fac,cis*-(PNP)$RuCl_2$($C^{18}O$) (**2-*18*O**) [IR: $\nu_{(C\equiv{}^{18}O)}$ 1899 cm^{-1} (s)]. Again, the energy change of the C≡O stretching frequency, $\Delta\nu_{(C\equiv O)}$ = 43 cm^{-1} as compared to **2**, is in accord with the incorporation of ^{18}O into the carbonyl ligand.

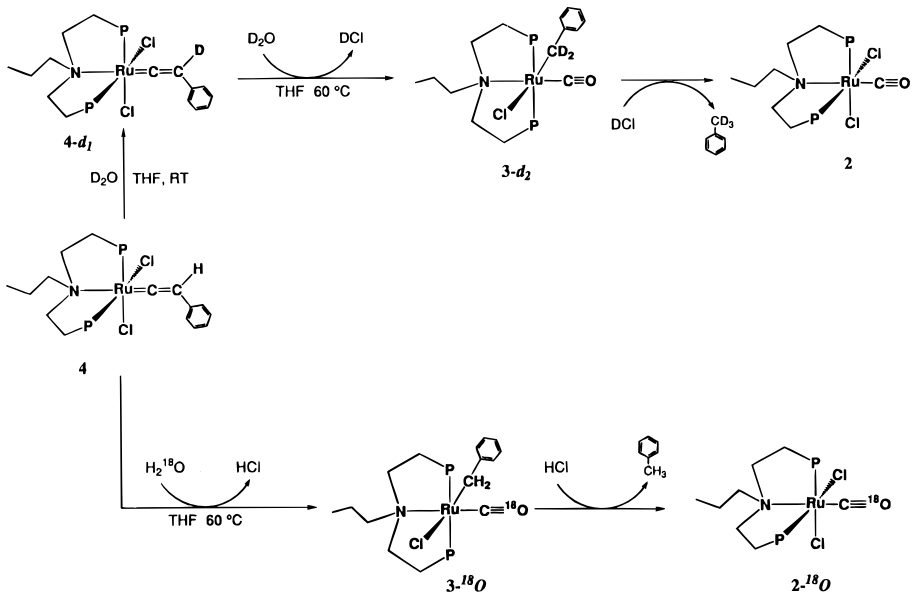
Modeling Studies Relevant to the Mechanism of the Ru-Assisted Cleavage of the C−C Bond of Phenyacetylene by Water. Reaction of the Vinylidene Complex 4 with Water in the Presence of CO. When **4** is reacted with a slight excess

(10) See for example, Hommeltoft, S. J.; Baird M. C. *Organometallics* **1986**, *5*, 190.

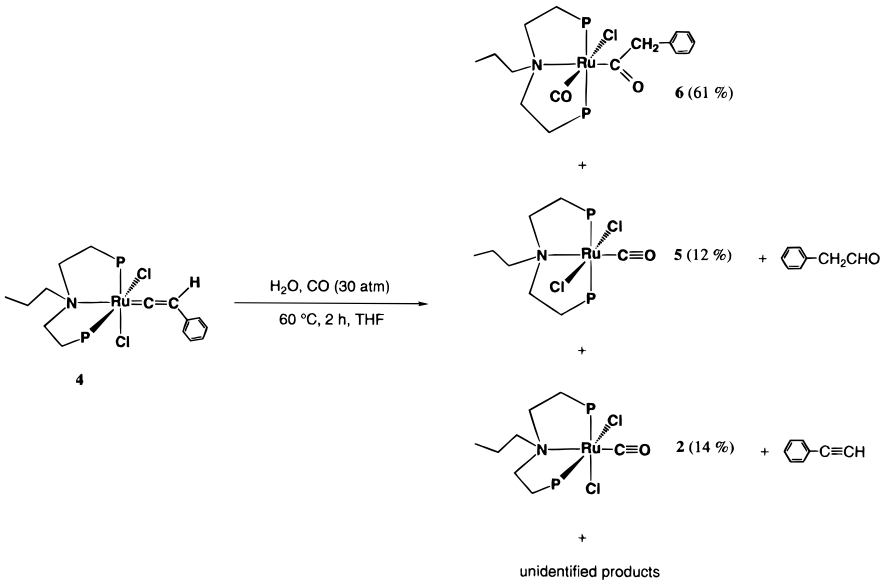
(11) Several examples of oxidation of Ru(II) vinylidene complexes by molecular oxygen have been reported, see for example: (a) Bruce, M. I.; Swincer, A. G.; Wallis, R. C. *J. Organomet. Chem.* **1979**, *171*, C5. (b) Oro, L. A.; Ciriano, M. A.; Foces-Foces, C.; Cano, F. M. *J. Organomet. Chem.* **1985**, *289*, 117. (c) Mezzetti, A.; Consiglio, G.; Morandini, F. *J. Organomet. Chem.* **1992**, *430*, C15. (d) Le Lagadec, R.; Roman, E.; Toupet, L.; Müller, U.; Dixneuf, P. H. *Organometallics* **1994**, *13*, 5030.

(12) Mingos, D. M. P. in *Comprehensive Organometallic Chemistry* Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, UK, 1982; Vol. 3, p 1.

Scheme 3



Scheme 4



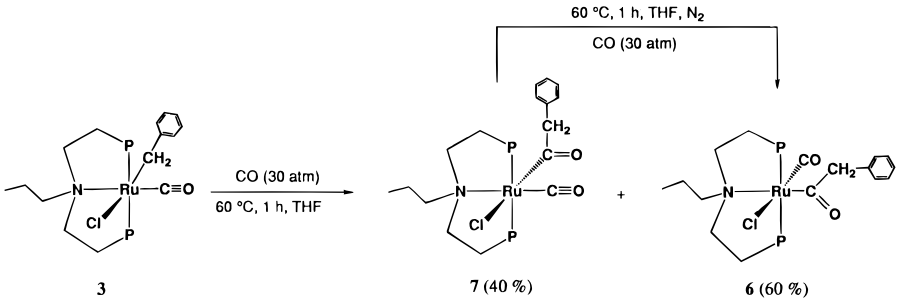
of H_2O in the Parr reactor pressurized with 30 atm of CO at 60 °C for 2 h, several products are formed. Among these, the most abundant (61%) is the new (η^1-*C*-phenylacetyl)carbonyl complex *mer*-(PNP)RuCl(η^1-$COCH_2Ph$)(CO) (**6**). The (carbonyl)dichloride **2** and its *meridional* isomer *mer*,*trans*-(PNP)$RuCl_2$(CO) (**5**)[8] are also produced in 14 and 12% yield, respectively, together with phenylacetylene, benzylaldehyde, and some unidentified Ru-PNP products (overall yield 13%).

Recrystallization of the reaction mixture from CH_2Cl_2/*n*-hexane gives **6** sufficiently pure to allow its unambiguous spectroscopic characterization. The presence of both a terminal carbonyl ligand and an η^1-*C*-acyl ligand in this complex is shown by IR bands at 1939 cm^{-1} [$\nu_{C\equiv O}$] and 1601 cm^{-1} [$\nu_{C=O}$] as well as the $^{13}C\{^1H\}$ NMR spectrum which contains the typical resonances for Ru-*C(O)R* [256.39 ppm, $^2J_{CP}$ 8.7 Hz] and Ru-*C*≡O [201.33 ppm, $^2J_{CP}$ 13.1 Hz] carbon atoms.[13] In addition, the resonance of the Ru-CH_2Ph carbon atom is remarkably shifted to lower field (56.78 ppm) as compared to the analogous resonance in **3** in which there is a direct Ru−CH_2Ph bond (δ_{CH2} 11.04). Conclusive experimental evidence for the presence of a phenylacetyl group in **6** is finally provided by the reaction with HCl which gives benzylaldehyde and **5**. This result indicates that, at a certain stage of the reaction of **4** with water in the presence of CO, HCl is evolved which later reacts with **6** to give **5**. The formation of both **2** and free phenylacetylene are consistent with the occurrence of a side-reaction, namely the displacement of the vinylidene ligand in **4** by CO, which has previously been observed[8] (once displaced, the vinylidene moiety spontaneously tautomerizes to alkyne).[14]

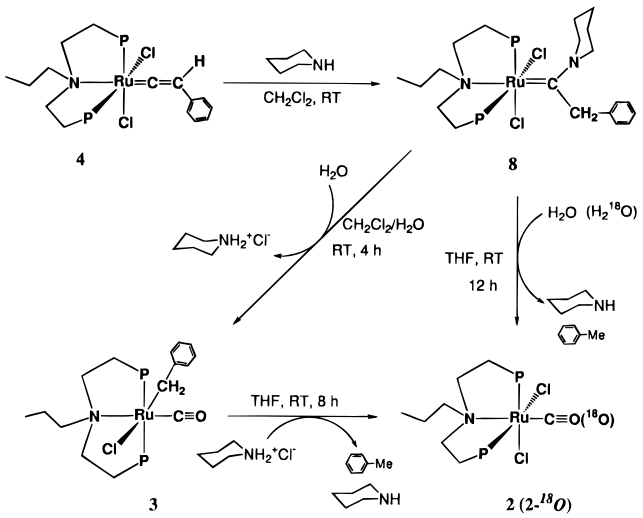
(13) See for example, McCooey, K. M.; Probitts, E. J.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1987**, 1713.

(14) A sizable number of metal assisted acetylene to vinylidene tautomerization have been reported. Key references include the following: (a) Bruce, M. I. *Chem Rev.* **1991**, *91*, 197. (b) Antonova, A. B.; Ioganson, A. A. *Russ. Chem. Rev.* **1989**, *58*, 593. (c) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (d) Fryzuk, M. D.; Huang, L.; McManus, N. T.; Paglia, P.; Rettig, S. J.; White, G. S. *Organometallics* **1992**, *11*, 2979. (b) Lumprey, J. R.; Selegue, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 5518. (c) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1077. (d) Bianchini, C.; Peruzzini, M.; Vacca, A.; Zanobini, F. *Organometallics* **1991**, *10*, 463. (e) Xiao, J.; Cowie, M. *Organometallics* **1993**, *12*, 463. (f) Bianchini, C.; Marchi, A.; Marvelli, L.; Peruzzini, M.; Romerosa, A.; Rossi, R.; Vacca, A. *Organometallics* **1995**, *14*, 3203.

Scheme 5



Scheme 6



Carbonylation Reaction of the (Benzyl)carbonyl Complex 3. In order to exclude that, in the reaction described above, **6** is formed by the straightforward carbonylation of the (benzyl)-carbonyl complex **3** (which, in fact, is an intermediate in the reaction of **4** with water, *vide supra*), a THF solution of isolated **3** was reacted with CO (30 atm) at 60 °C in the Parr reactor for 1 h. As a result, two isomeric (phenylacetyl)carbonyl complexes of the formula *mer*-(PNP)RuCl(η^1-$COCH_2Ph$)(CO) are obtained in a ratio of 40:60 (Scheme 5).

The minor product **7** is a geometric isomer of **6** in which the phenylacetyl group is still located *trans* to chloride as shown by ^{13}C NMR spectroscopy. Also, **7** is thermodynamically unstable and spontaneously converts to **6** at the working temperature. This experiment thus shows that the added CO forces the migratory insertion of the carbonyl ligand of **3** into the Ru−CH_2Ph bond to give the acyl complex **7**, which subsequently rearranges to the thermodynamic isomer **6**. The driving force for this isomerization is most likely electronic in nature and originated by the need of eliminating the strong *trans* interaction between the Cl and acyl ligands.

Reaction of the Vinylidene Complex 4 with Piperidine. Treatment of **4** in CH_2Cl_2 with a slight excess of piperidine at room temperature gives the aminocarbene complex *fac,cis*-(PNP)$RuCl_2${C(NC_5H_{10})(CH_2Ph)} (**8**) in almost quantitative yield (Scheme 6).

Recently, Ru(II) aminocarbenes of the general formula *fac,cis*-(PNP)$RuCl_2${C(NHR)(CH_2Ph)} [R = *n*-Pr, *cyclo*-C_6H_{11}, *(R)-(+)*-CHMePh, *(R)-(−)*-CHMeEt, *(S)-(−)*-CHMeNaphthyl] have been prepared by reaction of **4** with primary amines.[15]

From a comparison of the spectroscopic characteristics of **8** with those of the primary aminocarbenes mentioned above, one may readily infer that all the complexes exhibit the same primary geometry.[15] In particular, the retention of the *facial* stereochemistry of the PNP ligand in the precursor **4** is confirmed by the $^{31}P\{^1H\}$ NMR spectrum of **8** which consists of a singlet at 50.07 ppm (indeed, the chemical shift of the PNP phosphorus atoms can be used as a diagnostic tool for discriminating between *mer* and *fac* stereochemistries).[8,15,16] The presence of the aminocarbene ligand *trans* to the PNP-nitrogen atom is unequivocally demonstrated by the $^{13}C\{^1H\}$ NMR spectrum which contains a well-resolved triplet in the low-field region [δ 252.40, $^2J_{CP}$ 14.2 Hz] typical of Ru(II) carbene carbon atoms.[15,17]

Unlike the analogous aminocarbene complexes obtained by reaction of primary amines with **4** (*vide infra*), **8** is thermally stable in refluxing THF.

Reaction of the Aminocarbene 8 with H_2O or $H_2{}^{18}O$. Treatment of **8** in THF with H_2O (or $H_2{}^{18}O$) at room temperature for 12 h results in the quantitative formation of the (carbonyl)dichloride complex **2** (or ***2-18O***), piperidine and toluene (Scheme 6).

Intermediate in this reaction is the (benzyl)carbonyl complex **3** (or ***3-18O***) which can be isolated when the reaction is carried out in a liquid-biphase system (CH_2Cl_2/H_2O) to extract piperidinium hydrochloride. In fact, the latter species is the primary product, and, if not removed from the reaction mixture, it reacts with the benzyl complex **3** to give **2** and toluene. An isotope labeling experiment with $H_2{}^{18}O$ confirms that the oxygen atom of the carbonyl ligand in **2** is provided by water.

The overall reactivity pathway toward H_2O exhibited by **8** is thus quite similar to that observed for the vinylidene **4**, the only difference being that the evolved HCl is trapped by the piperidine.

The aminocarbene complexes *fac,cis*-(PNP)$RuCl_2${C(NHR)-(CH_2Ph)} obtained from primary amines[15] do not exhibit this type of reactivity toward H_2O. Due to the acidic character of the NH hydrogen they are deprotonated by water to give iminoacyl complexes.[18]

Reaction of the Aminocarbene 8 with H_2O in the Presence of CO. In the presence of a CO atmosphere, **8** in THF reacts with H_2O at −20 °C to give a new isomer of the (phenylacetyl)-carbonyl complexes of the general formula (PNP)RuCl($COCH_2$-Ph)(CO) (Scheme 7). This new isomer, **9**, contains a *fac*-PNP ligand as shown by the magnetic inequivalence and chemical shifts of the two phosphorus nuclei [$^{31}P\{^1H\}$ NMR AM pattern with δ_{P_A} 54.01 and δ_{P_M} 38.46]. The presence of an η^1-*C*-phenylacetyl ligand *trans* to a P donor is unequivocally confirmed by $^{13}C\{^1H\}$ NMR spectroscopy ($\delta_{COCH2Ph}$ 249.20, dd, $^2J_{CPtrans}$ 94.1 Hz, $^2J_{CPcis}$ 11.2 Hz).

(15) Bianchini, C.; Peruzzini, M.; Romerosa, A; Zanobini, F. *Organometallics* **1995**, *14*, 3152.
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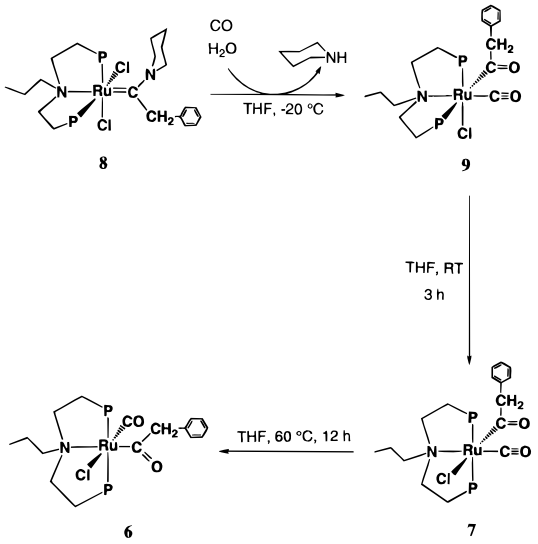
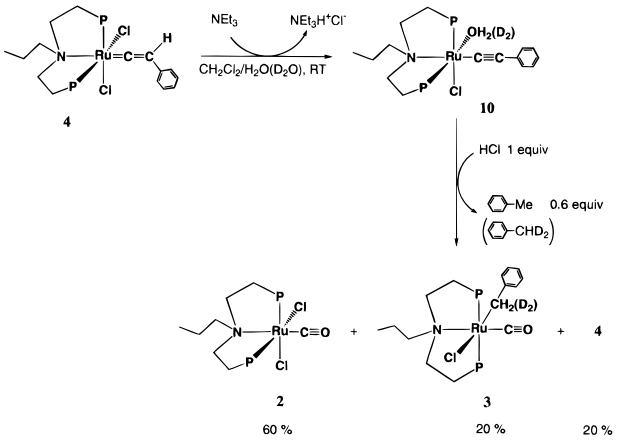
(17) (a) Gamasa, M. P.; Gimeno, J.; Martín-Vaca, B. M.; Borger, J.; García-Granda, S.; Perez-Carreño, E. *Organometallics* **1994**, *13*, 4045. (b) Singh, M., M.; Angelici, R. J. *Inorg. Chem.* **1984**, *23*, 2691. (c) McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 1111.
(18) Bianchini, C.; Peruzzini, M. manuscript in preparation.

Scheme 7



Scheme 8



Compound **9** is stable and isolable at low temperature, whereas it spontaneously converts to the *mer* isomer **7** at room temperature, which in turn transforms into the thermodynamic isomer **6** at 60 °C.

A low energy barrier to isomerization of *fac*-PNP complexes to *mer*-derivatives has previously been observed and interpreted in terms of the minor steric congestion in the *meridional* complexes.[8]

Reaction of the Vinylidene Complex 4 with NEt_3 in a CH_2Cl_2/H_2O Biphase System. Under vigorous stirring, complex **4** reacts with NEt_3 in a CH_2Cl_2/H_2O biphase system at room temperature to give the (aquo)σ-phenylethynyl complex *fac*-(PNP)RuCl(C≡CPh)(OH_2) (**10**) (Scheme 8). This compound is obtained as orange crystals from the organic phase, while [NEt_3H]Cl is found in the aqueous phase.

Complex **10** is fluxional on the NMR time scale. The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 at room temperature displays two broad humps that resolve at −50 °C into an AM pattern with $^2J_{PP}$ of 41 Hz. At this temperature, the ^1H NMR spectrum contains a broad triplet at 4.69 ppm ($^2J_{HP}$ 8.8 Hz) which disappears by adding D_2O and is thus assigned to the coordinated water molecule. Finally, a strong IR absorption at 2052 cm^{-1} as well as ^{13}C NMR resonances at 108.93 ppm (t, $^2J_{CP}$ 12.6 Hz, C_α) and 114.12 ppm (s, C_β) are consistent with the presence in **10** of a σ-alkynyl ligand[19] as a result of the deprotonation of the vinylidene ligand of **4** by the tertiary amine.

(19) See for example: Bianchini, C.; Frediani, P.; Masi, D.; Peruzzini, M.; Zanobini, F. *Organometallics* **1994**, *13*, 4616.

Treatment of **10** in anhydrous chloroform (NMR experiment) with a stoichiometric amount of HCl at room temperature transforms the starting complex into the (dichloride)carbonyl complex **2** and toluene (Scheme 8). The reaction proceeds through the intermediacy of the (benzyl)carbonyl complex **3** which is found as a minor product in the final reaction mixture only because part of the added HCl is consumed to form the vinylidene complex **4** (*via* protonation of the C_β carbon atom of the σ-alkynyl in **10**, followed by displacement of the coordinated water molecule by chloride).

Consistently, the reaction of the isotopomer *fac*-(PNP)RuCl(C≡CPh)(OD_2) (**10-*d*$_2$**) with HCl gives **3-*d*$_2$** and $PhCHD_2$.

Discussion

For a better understanding of the overall mechanism of the present C−C bond cleavage of phenylacetylene by water, it may be helpful to discuss some relevant literature precedents as well as summarize the results of the modeling studies reported above.

The Ru(II) aminocarbene complexes obtained by treatment of the vinylidene **4** with primary amines are thermally unstable in refluxing THF in which they degrade to the (dichloride)-isonitrile complexes *fac,cis*-(PNP)$RuCl_2$(CNR) (R = *n*-Pr, *cyclo*-C_6H_{11}, *(R)-(+)*-CHMePh, *(R)-(−)*-CHMeEt, *(S)-(−)*-CHMeNaphthyl) *via* toluene elimination (Scheme 9).[15] Indeed, this reaction parallels that of **4** with water and supports the intermediacy of carbene species (*i.e.*, hydroxycarbene) also in the latter reaction.

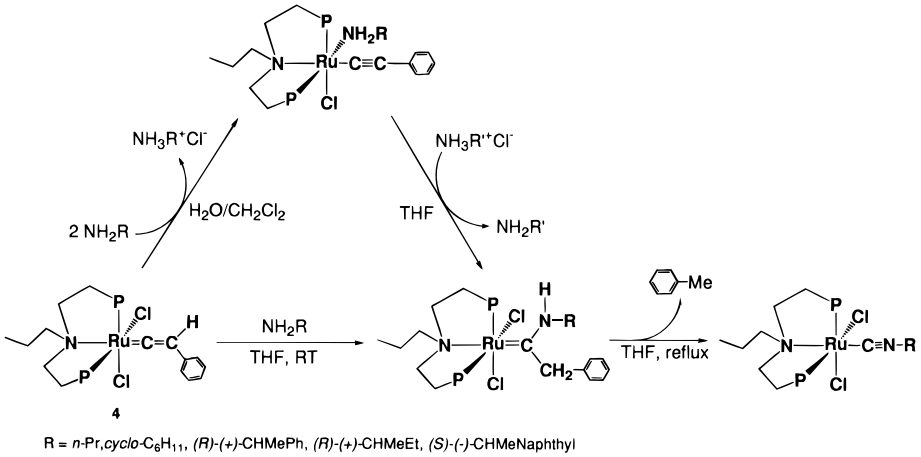
As shown in Scheme 9, the formation of the aminocarbene complexes require the use of 2 equiv of primary amine as 1 equiv serves to deprotonate the vinylidene ligand to alkynyl. The resulting σ-alkynyl complexes are coordinatively unsaturated because of the removal of a chloride ligand as alkylammonium salt, and thus pick up a second molecule of primary amine to form stable (σ-alkynyl)(primary amine) derivatives (these can be isolated using a CH_2Cl_2/H_2O biphase system).[18] Only at this stage, the ammonium chloride (if not removed) reprotonates the C_β carbon of the alkynyl ligand to form a vinylidene ligand *cis* to the coordinated amine. This rapidly attacks the vinylidene C_α atom to give the aminocarbene product (unequivocal evidence for intramolecular amine migration has been provided by treatment of isolated (σ-alkynyl)(primary amine) complexes with different alkylammonium chlorides; see Scheme 9).[18]

The reaction sequence shown in Scheme 9 is thus quite similar to that illustrated in Scheme 8: dehydrohalogenation of **4** by NEt_3 gives a coordinatively unsaturated σ-alkynyl complex which coordinates a water molecule (instead of NEt_3 for steric reasons). Like primary amines, the coordinated water (see the deuterium labeling experiment), after protonation of the σ-alkynyl ligand, apparently attacks the C_α atom of the resulting vinylidene and ultimately leads to the C−C bond cleavage.

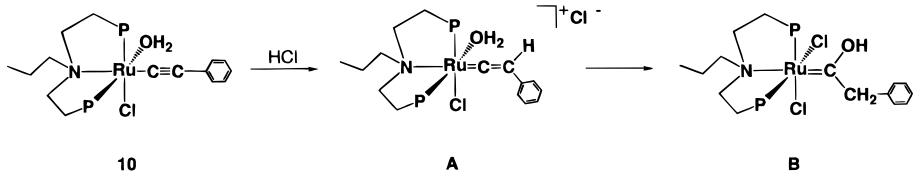
By analogy with the reaction of **4** with primary amines, an intermediate hydroxycarbene complex of the formula *fac,cis*-(PNP)$RuCl_2${C(OH)(CH_2Ph)} (**B**) is proposed to form upon intramolecular migration of the coordinated H_2O to the C_α atom of the vinylidene ligand (Scheme 10).

The key role of the hydroxycarbene **B** in the Ru-assisted C−C bond cleavage of phenylacetylene is also supported by the reaction of the secondary aminocarbene **8** with water (Scheme 6). Unlike the primary aminocarbene analogs, **8** is thermally stable in THF (the absence of an NH group impedes the rearrangement to isonitrile and toluene). However, it reacts with water to give toluene, piperidine, and the carbonyl **2** (or the benzyl complex **3** and piperidinium chloride in a liquid biphase system, see Scheme 6). Although not seen in the course of the reaction of either **8** or **4** with water, the intermediacy of a

Scheme 9



Scheme 10



hydroxycarbene species is thus highly probable in both cases. Indeed, it is well-known that vinylidene metal complexes may react with alcohols to give alkoxycarbene derivatives.[4,20]

If one takes for granted the intermediacy of the hydroxycarbene **B** in the reaction of **4** with water, the following stepwise degradation to acyl (deprotonation of the hydroxycarbene) and benzyl(carbonyl) complexes (C−C bond cleavage) can readily be rationalized in light of several literature reports. In fact, hydroxycarbene metal complexes[21] are generally unstable and thermally degrade to give acyl derivatives (*via* HCl elimination when chloride ligands are present in the complex framework).[22] Formyl complexes are also formed by deprotonation of hydroxycarbene complexes with weak bases.[21c] In some cases, the thermal degradation of hydroxycarbenes yields carbonyl complexes (*via* acyl intermediates).[21ac,23] Finally, it is worth mentioning that Fischer carbenes react with water to give aldehydes *via* hydroxycarbene intermediates formed by nucleophilic substitution of the alkoxy group (eliminated as alcohol).[24]

In the case at hand, we exclude that the hydroxycarbene ligand in **B** rearranges to benzylaldehyde also because the reaction of the thermally generated [(PNP)$RuCl_2$] fragment with benzylaldehyde does not lead to formation of either **3** or **2**. Thus, the conversion of **B** to the σ-acyl product (intercepted with CO as **6**) proceeds *via* HCl elimination which, in fact, has been detected in the "open reactor" experiment.

Incorporation of all the experimental evidence leads to the mechanism shown in Scheme 11 for the reaction between water and phenylacetylene in the presence of **1** in THF at 60 °C.

The dissociation of PPh_3 from **1** occurs as a thermal step.[8] As a result, a free coordination site becomes available at the Ru center for interaction with phenylacetylene, which is rapidly tautomerized to vinylidene (step **a**) to give **4**. For Ru(II) systems, this step generally occurs *via* a 1,2-hydrogen shift mechanism involving π-alkyne intermediates.[14] The alternative mechanism involving C−H oxidative addition, followed by 1,3-hydrogen shift, in fact, would require a much more electron-rich metal center.[25] At this stage, water comes into play: a water molecule deprotonates the vinylidene ligands to σ-alkynyl and also promotes the elimination of one chloride as $H_3O^+Cl^-$ (step **b**) (the acidic character of the C_β−H hydrogen of vinylidene ligands is well-known;[14a−c] the acidic character of this hydrogen atom in **4** is shown by the rapid H/D exchange observed when a solution of **4** is treated with D_2O at room temperature). A second water molecule occupies the resulting coordination vacancy to give the alkynyl complex **10** (step **b**), which is transformed into the cationic vinylidene intermediate **A** (step **c**) by the proton released in the preceding step. Complex **A** cannot be intercepted due to fast intramolecular attack by the coordinated H_2O to the vinylidene C_α atom (step **d**). The hydroxycarbene intermediate **B** thus is formed, which eliminates HCl (or $H_3O^+Cl^-$) to give an unsaturated σ-acyl complex (step **e**), intercepted as the saturated carbonyl complex **6** when the reaction is carried out in the presence of CO (Schemes 4 and 5). From intermediate **C** the formation of the (benzyl)carbonyl complex **3** and subsequently of the carbonyl **2** are readily

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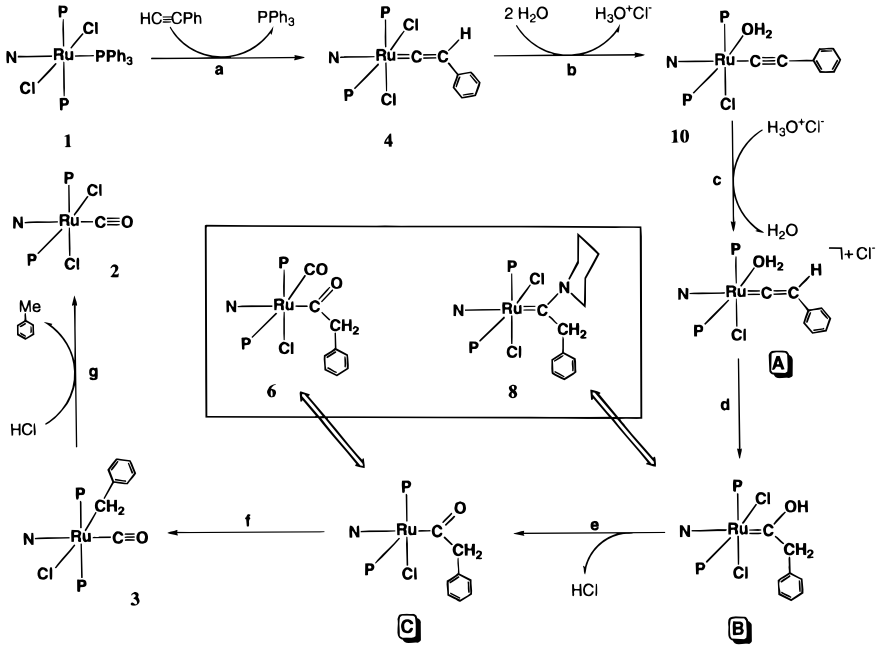
Scheme 11



explained by CO deinsertion (step **f**), followed by reaction with the previously generated HCl which removes the benzyl ligand as toluene and saturates the metal coordination sphere with the chloride (step **g**).

Conclusions

In this paper we have shown that the hydration of phenylacetylene in the presence of a Ru(II) complex may lead to the cleavage of the C−C triple bond with formation of CO and toluene.

A study under different experimental conditions, the use of model and isotope labeling experiments, and the detection of several intermediates, taken altogether, show that the C−C bond cleavage reaction comprises a number of steps: 1-alkyne to vinylidene tautomerism, conversion of a vinylidene ligand to hydroxycarbene by intramolecular attack of water, deprotonation of hydroxycarbene to σ-acyl, deinsertion of CO from the acyl ligand, and hydrocarbon elimination by protonation of the metal-alkyl moiety. While most of these elemental reactions have precedents in organometallic chemistry and catalysis, the present system is unique in that they all occur at the same metal-ligand fragment. This allows one to draw similar mechanistic conclusions on other relevant reactions such as the recently reported Ir-assisted hydrolysis of allenylidene ligand to CO and σ-vinyl,[26] and, more in general, the Fischer-Tropsch chemistry.[27] In fact, both vinylidene[28] and hydroxycarbene[29] species are key intermediates in the hydrogenation of CO catalyzed by iron-group metals, to give a variety of organic products. In light of the results described in this paper, one cannot disregard the possibility that water (produced in Fischer-Tropsch reactions)[30] may interact with vinylidene intermediates to give either hydrocarbons and further CO or aldehydes and ketones.

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