Regio- and stereoselective dimerization of 1-alkynes catalyzed by an Os(II) complex

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Abstract

The complex $[(PP_3)OsH(N_2)]BPh_4$ is a catalyst precursor for the regio- and stercoselectivc dimerization of HC≡CR (R = Ph, $SiMe_3$) to (*Z*)-1,4-disubstituted-but-3-en-1-ynes ($PP_3 = P(CH_2CH_2PPh_2)_3$). In the presence of H_2O or C_2H_5OH, the catalytic reaction with $HC{\equiv}CSiMe_3$ selectively gives but-3-en-1-ynyl-trimethylsilane. A detailed study under different experimental conditions, the detection of some intermediates, and the use of isolated complexes in independent reactions, taken altogether, permit mechanistic conclusions which account for the observed products. A key-role is played by (vinylidene)σ-alkynyl complexes which transform into η^3-butenynyl derivatives via intramolecular C–C bond formation. The Os(II) η^3-butenynyl complexes are likely reagents in the rate determining step of the catalytic cycle, and produce free (*Z*)-1,4-disubstituted-but-3-en-1-ynes upon σ-bond metathesis reaction with HC≡CR. The 16-electron fragments $[(PP_3)OsX]^+$ (X = H, Cl, C≡CR) are capable of promoting the 1-alkyne to vinylidene tautomerism. In particular, the (vinylidene)hydride $[(PP_3)OsH\{C{=}C(H)\text{-}SiMe_3\}]BPh_4$ has been isolated and properly characterized. Since the stoichiometric reaction of the latter compound with $HC{\equiv}CSiMe_3$ gives vinyltrimethylsilane, the formation of (vinylidene)hydride species is suggested to be an effective step, alternative to 1-alkyne insertion, in the reduction of 1-alkynes to alkenes assisted by hydrido metal complexes.

Key words: Catalysis; Dimerization; Osmium complexes; Alkyne complexes

Introduction

The position of osmium in the Periodic Table is the principal reason for its attractive chemistry. As a metal of the third row, the outer 5d orbitals of osmium are relatively exposed and, thus, their electronic occupancy is strongly susceptible to the nature of the ligands. Furthermore, due to its central position in the d block, osmium can attain all possible electronic configurations from d^0 to d^{10} [1].

In spite of these favorable features, Os complexes are generally considered too substitution-inert to be successfully exploited in homogeneous catalysis. Indeed, only a few examples of catalytic reactions for Os complexes have been reported in the literature [2–8]. On the other hand, the kinetic sluggishness of Os compounds often permits the isolation of reactive intermediates not normally seen in analogous reactions with first- and second-row metals. Os complexes are therefore ideal compounds to carry out mechanistic studies.

In this paper, we report on the ability of $[(PP_3)OsH(N_2)]BPh_4$ (**1**) [8] to act as catalyst precursor for the regio- and stereoselective dimerization of HC≡CR (R = Ph, $SiMe_3$) to (*Z*)-1,4-disubstituted-but-3-en-1-ynes as well as the synthesis of 4-trimethylsilylbut-3-en-1-yne from $HC{\equiv}CSiMe_3$ and H_2O (or EtOH) ($PP_3 = P(CH_2CH_2PPh_2)_3$).

The formation of carbon–carbon bonds mediated by transition metals has emerged in recent years as a major goal of organometallic chemistry [9]. In this wide field of interest, understanding the primary interactions between the metal and the alkyne, particularly the

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mechanism of formation of the first C–C bond, is of key importance for developing selective processes. With the use of compound **1** and of related complexes in independent reactions, some new insight into the mechanism of 1-alkyne dimerization has been obtained.

Experimental

Materials and methods

Tetrahydrofuran, dichloromethane and n-hexane were purified just prior to use by distillation over $LiAlH_4$, P_2O_5 and Na, respectively. Ethylene glycol monomethyl ether was dried over anhydrous $CaSO_4$ and distilled twice. Phenylacetylene (Aldrich) and trimethylsilylacetylene (Fluka) were checked by ^1H NMR spectroscopy; when necessary they were distilled prior to use. All the other reagents and chemicals were reagent grade and, unless otherwise stated, were used as received by commercial suppliers. Literature methods were used for the preparations of the starting osmium complexes $[(PP_3)OsH(N_2)]BPh_4$ (**1**) [8] and $[(PP_3)OsCl_2]$ (**2**) [8]. Deuterated solvents for NMR measurements (Janssen and Merck) were dried over molecular sieves. IR spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer using samples mulled in Nujol between KBr plates. Proton NMR spectra were recorded on Varian VXR 300 and Bruker ACP 200 instruments operating at 299.94 and 200.13 MHz, respectively. Peak positions are relative to tetramethylsilane as an external reference. $^{31}P\{^1H\}$ NMR spectra were recorded on the same instruments operating at 121.42 and 81.01 MHz, respectively. Chemical shifts are relative to external 85% H_3PO_4 with downfield values reported as positive. $^{13}C\{^1H\}$ and ^{13}C-DEPT NMR spectra were run on the Bruker instrument operating at 50.32 MHz. Peak positions are relative to tetramethylsilane and were calibrated against the solvent resonance. 2D-HETCOR NMR experiments were recorded on the Bruker spectrometer using the XHCORR pulse program. The 90° ^{13}C pulse was 5.5 μs, the 90° ^1H pulse from the decoupler was 8.8 μs and the acquisition time was 0.15–0.20 s. The number of incremental spectra was determined according to the concentration of the sample and to the spectral width used for collection of the FIDs. Zero-filling and a 2D Fourier transformation resulted in a spectrum with resolution of *c.* 7 and 15 Hz in the proton and carbon dimensions, respectively. Spectra with adequate signal-to-noise ratio were obtained in *c.* 12 h. The 2D-COSY NMR experiments were performed with either Varian's and Bruker's pulse sequences on the two instruments. A delay period of 1 s was used between acquisitions. A 2D Fourier transformation gave 2D spectra with adequate signal-to-noise ratios after 4–8 h of data collection, depending on sample concentration and spectral width. Proton NMR spectra with broad-band phosphorus decoupling were recorded on the Bruker instrument equipped with a 5 mm inverse probe and a BFX-5 amplifier device. Computer simulations of NMR spectra were carried out with a locally developed package containing the programs LAOCN3 [10] and DAVINS [11] run on a Compaq Deskpro 386/25 personal computer. The initial choices of shifts and coupling constants were refined by iterative least-squares calculations using the experimental digitized spectrum. The final parameters gave a satisfactory fit between experimental and calculated spectra, the agreement factor *R* being less than 1% in all cases. Conductivities were measured with an Orion model 990101 conductance cell connected to a model 101 conductivity meter. The conductivity data were obtained at sample concentrations of *c.* 1×10^{-3} M in nitroethane solutions at room temperature (22 °C). A Shimadzu GC14 chromatograph equipped with a 2 m FFAP column (35 °C×20 min 10 °C/min 200 °C×20 min) and a Shimadzu QP2000 instrument equipped with a 50 m, 0.22 mm CP-TM-SIL8 capillary column (35 °C×15 min 2 °C/min 130 °C×1 min 5 °C/min 250 °C×10 min) were used for GC and GC-MS analysis, respectively. All reactions and manipulations were routinely performed under a dry argon or nitrogen atmosphere by using Schlenk-tube techniques. The solid complexes were collected on sintered-glass frits and washed with ethanol and petroleum ether (b.p. 40–70 °C) before being dried in a stream of nitrogen.

Preparation of (E)-[(PP_3)-$Os\{\eta^3$-$(SiMe_3)C_3$=$CH(SiMe_3)\}]BPh_4$ (3)

Method A. Neat trimethylsilylacetylene (0.42 ml, 3.03 mmol) was pipetted into a THF solution (30 ml) of **1** (1.21 g, 1.00 mmol). Stirring the solution for 1 h at room temperature produced a light yellow solution. Addition of absolute ethanol (30 ml) and slow concentration of the solution under a stream of nitrogen gave canary yellow crystals of **3**. Yield 82%. GC and ^1H NMR analysis of the reaction mixture showed total consumption of the alkyne reagent and formation of 1 equiv. of vinyltrimethylsilane as the only organic product. ^1H NMR (21 °C, $CDCl_3$, 200.13 MHz): $\delta(SiMe_3)$ 0.07 (s, 9H), $\delta(CH=CH_2)$ 6.21, 5.95, 5.70 (ABC spin system), J_{AB} 14.7 Hz, J_{AC} 20.5 Hz, J_{BC} 3.8 Hz, 3H.

Method B. Compound **3** was obtained in 93% yield by reacting **1** (0.61 g, 0.50 mmol) with 1 equiv. of 1,4-bis(trimethylsilyl)-1,3-butadiyne (0.10 g, 0.51 mmol) under comparable reaction conditions. IR: ν(C=C) 1620(w); ν(Si–C) 838(s) cm^{-1}. *Anal.* Calc. for $C_{76}H_{81}BOsP_4Si_2$: C, 66.36; H, 5.94. Found: C, 66.18; H, 5.90%. $\Lambda_M = 55\ \Omega^{-1}\ cm^2\ mol^{-1}$. $^{31}P\{^1H\}$ NMR (20 °C, CD_2Cl_2, 81.01 MHz): AMQ$_2$ system, δ_A 117.65, δ_M 43.28, δ_Q 14.54; J_{AM} 32.7 Hz, J_{AQ} 11.4 Hz, J_{MQ} 10.3

Hz. ^{1}H NMR (20 °C, CD_2Cl_2, 299.94 MHz): 6.07 (dt, 1H, C=C*H*, $^4J_{HP}$ 5.7 Hz, $^4J_{HP}$ 1.9 Hz); 0.88 (s, 9H, $SiMe_3$); −0.49 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (20 °C, CD_2Cl_2, 50.32 MHz): 155.35 [dtd, *C*=C(H)$SiMe_3$, $^2J_{CP}$ 38.3 Hz, $^2J_{CP}$ 7.1 Hz, $^2J_{CP}$ 3.8 Hz]; 140.18 [s, C=*C*(H)$SiMe_3$, assigned by DEPT and 2D-HETCOR NMR experiments]; 95.87 (dq, C≡*C*$SiMe_3$, $^2J_{CP}$ 22.7 Hz, $^2J_{CP}$ 2.8 Hz); 75.69 (s, $SiMe_3$ C≡*C*); 2.48 [s, Si(*C*H_3)$_3$, correlated by a 2D-NMR experiment with the ^{1}H resonance at 0.88 ppm]; 1.30 [s, Si(*C*H_3)$_3$, correlated by a 2D-NMR experiment with the ^{1}H resonance at −0.49 ppm].

Preparation of [(PP$_3$)Os{η^3-(SiMe$_3$)C$_3$=CH$_2$}]BPh$_4$ (4)

Method A. Neat trimethylsilylacetylene (0.42 ml, 3.03 mmol) was pipetted into a THF/ethanol solution (30 ml, 10:1 vol./vol.) of **1** (1.21 g, 1.00 mol). The solution was stirred while the temperature was gently raised to reflux, which was maintained for 1 h. The solution was then cooled to room temperature and ethanol (30 ml) was added. Concentration of the resulting pale yellow solution gave pale cream colored crystals of **4**. Yield 80%. Formation of $EtOSiMe_3$ in the course of the reaction was shown by GC-MS.

Method B. Compound **4** was similarly obtained by substituting H_2O for EtOH in the above procedure. GC-MS analysis of the reaction mixture shown the formation of $Me_3SiOSiMe_3$.

Method C. Either EtOH (1 ml) or H_2O (1 ml) was added to a solution of **3** (0.25 g) in THF (20 ml). The resulting solutions were refluxed for 2 h during which time the color changed from light to pale yellow. Addition of ethanol (20 ml) and slow evaporation of the solvent gave **4** in almost quantitative yield. IR: ν(C≡C) 1941(w), 1906(w); ν(C=C) 1633(w), ν(Si–C) 840(s) cm^{-1}. *Anal.* Calc. for $C_{73}H_{73}BOsP_4Si$: C, 67.27; H, 5.65. Found: C, 67.08; H, 5.72%. Λ_M = 52 Ω^{-1} cm^2 mol^{-1}. $^{31}P\{^1H\}$ NMR (22 °C, CD_3CN, 121.41 MHz): AMQ_2 system, δ_A 115.36, δ_M 22.71, δ_Q 14.50; J_{AM} 15.3 Hz, J_{AQ} 7.7 Hz, J_{MQ} 8.9 Hz. ^{1}H NMR (22 °C, CD_3CN, 299.94 MHz): 5.51 (dpsq, 1H, C=C*H*$_2$, $^4J_{HP}$ 8.9 Hz, $^4J_{HP}$ 3.3 Hz, $^2J_{HH}$ 2.7 Hz); 5.00 (ddt, 1H, C=C*H*$_2$, $^4J_{HP}$ 4.5 Hz, $^4J_{HP}$ 3.8 Hz, $^2J_{HH}$ 2.7 Hz); 0.94 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (20 °C, CD_3CN, 75.43 MHz): 138.86 (dt, *C*=CH_2, $^2J_{CP}$ 38.9 Hz, $^2J_{CP}$ 2.1 Hz); 135.67 (q, C=*C*H$_2$, $^3J_{CP}$ 1.4 Hz, assigned by DEPT and 2D-HETCOR NMR experiments); 121.25 (dq, $SiMe_3$*C*≡C, J_{CP} 58.1 Hz, J_{CP} 1.9 Hz); 88.41 (s, $SiMe_3$C≡*C*); −0.61 [s, Si(*C*H_3)$_3$].

Preparation of [(PP$_3$)Os{η^3-(SiMe$_3$)C$_3$=CH(D)}]BPh$_4$ (4-d$_1$)

The monodeuterated complex **4**-d_1 was prepared using C_2H_5OD instead of C_2H_5OH in Method C.

Preparation of [(PP$_3$)OsH{C=C(H)SiMe$_3$}]BPh$_4$ (5)

A stoichiometric amount of trimethylsilylacetylene (141 μl, 1.00 mmol) in acetone (2 ml) was added dropwise (5 min) to a stirred acetone solution (20 ml) of **1** (1.21 g, 1.00 mmol) cooled at 0 °C under an argon atmosphere. After stirring for 30 min, the color of the solution changed from colorless to pale yellow. The cooling bath was then removed and n-hexane (30 ml) was added. After the solvent was partially evaporated under a brisk current of argon, ivory-colored microcrystals of **5** separated. Yield 85%. ^{31}P NMR analysis of this product invariably showed also the presence of **3** and **1** (<10%). An analytically pure sample of **5** was obtained by recrystallization of the crude material from CH_2Cl_2/n-hexane. Yield 70%. IR: ν(Os–H) 2010(w); ν(C=C) 1620(vs); ν(Si–C) 845(s) cm^{-1}. *Anal.* Calc. for $C_{71}H_{73}BOsP_4Si$: C, 66.66; H, 5.75. Found: C, 66.47; H, 5.70%. $^{31}P\{^1H\}$ NMR (−30 °C, CD_2Cl_2, 81.01 MHz): AMQ_2 system, δ_A 111.91, δ_M 42.32, δ_Q 14.38; J_{AM} 12.9 Hz, J_{AQ} ≈ 0 Hz, J_{MQ} 5.5 Hz. ^{1}H NMR (−30 °C, CD_2Cl_2, 200.13 MHz): −8.92 [m, 1H, Os–*H*, computed as the X part of an AMQQ′XY spin system (A, M, Q, Q′ = P; Y = vinylidene hydrogen), $^4J_{XY}$ 6.1 Hz, $^2J_{XA}$ 29.5 Hz, $^2J_{XM}$ 22.6 Hz, $^2J_{XQ}$ 30.6 Hz, $^2J_{XQ'}$ −15.5 Hz, $^4J_{YM}$ 6.0 Hz, $^4J_{YA}$ 1.2 Hz, $^4J_{YQ} \approx {}^4J_{YQ'} \approx {}^2J_{AQ} \approx {}^2J_{AQ'} \approx 0$ Hz, $^2J_{AM}$ 12.9 Hz, $^2J_{MQ} \approx {}^2J_{MQ'}$ 5.5 Hz, $^2J_{QQ'}$ 22.0 Hz); 0.12 (s, 9H, $SiMe_3$); 2.32 (td, 1H, C=*CH*, $^4J_{YX}$ 6.1 Hz, $^4J_{YM}$ 6.0 Hz, $^4J_{YA}$ 1.2 Hz, correlated by a 2D-COSY-90 NMR experiment with the resonance of the terminal hydride at high field). $^{13}C\{^1H\}$ NMR (−30 °C, CD_3COCD_3, 75.43 MHz): 307.30 (dt, Os=*C*=C, $^2J_{CP_A}$ 55.4 Hz, $^2J_{CP_Q}$ 11.1 Hz); 97.54 (d, Os=C=*C*, $^3J_{CP_A}$ 19.0 Hz); 0.55 [s, Si(*C*H_3)$_3$].

Reaction of [(PP$_3$)OsH(N$_2$)]BPh$_4$ with HC≡CSiMe$_3$

NMR experiments

(a) 1:1 Reaction. Solid **1** (0.06 g, 0.05 mmol) was dissolved in acetone-d_6 degassed under argon (1.0 ml) and then transferred into a screw cap 5-mm NMR tube which was then cooled to −78 °C. One equiv. of HC≡C$SiMe_3$ (7.0 μl, 0.05 mmol) was added via syringe and the tube was introduced into the spectrometer precooled at −30 °C. The reaction between **1** and trimethylsilylacetylene does not occur below 0 °C. After 30 min at 0 °C, **5** is formed in *c.* 86% yield (based on ^{31}P NMR integration) together with small amounts of **3** (*c.* 7%) and of unreacted **1** (*c.* 7%). On increasing the temperature up to 50 °C, no further reaction occurs. GC analysis and ^{1}H NMR spectroscopy showed the disappearance of the alkyne and formation of some vinyltrimethylsilane.

(b) 1:2 Reaction. A solution of **5** in acetone-d_6 prepared as previously described was cooled to −30 °C and treated with 1 equiv. of HC≡C$SiMe_3$. The reaction of **5** with the alkyne occurred already at *c.* 0 °C and

produced **3** as the only detectable osmium compound. When all the alkyne had been consumed, **5** and **3** were in an approximate ratio of 1 to 1.

A similar conversion of **1** to a 1:1 mixture of **3** and **5** was observed when an acetone-d_6 solution of **1** (0.06 g, 0.05 mmol) was treated with a double proportion of $HC{\equiv}CSiMe_3$ (14.1 μl, 0.10 mmol).

(c) 1:3 Reaction. Addition of a third equiv. of $HC{\equiv}CSiMe_3$ to the above solution completed the conversion of **5** to **3**. ^1H NMR and GC analyses of the reaction mixture showed formation of 1 equiv. of $CH_2{=}CHSiMe_3$.

*Reaction of $[(PP_3)OsD(N_2)]BPh_4$ (**1**-d_1) with $HC{\equiv}CSiMe_3$*

To a sample of the monodeuterated isotopomer **1**-d_1 (0.06 g, 0.05 mmol) dissolved in acetone-d_6 (1 ml) was added 1 equiv. of $HC{\equiv}CSiMe_3$ via syringe. ^1H NMR analysis of the resulting mixture showed formation of $[(PP_3)OsD\{C{=}C(H)SiMe_3\}]BPh_4$ (**5**-d_1) (δ 2.38, m, 1 H, C=C*H*). No resonance in the hydride region was observed. The monodeuterated reagent **1**-d_1 was synthesized according to the method reported in ref. 8 using deuterated reagents and solvents. IR: ν(Os–D) 1410 cm^{-1}.

*Preparation of $[(PP_3)OsH(C{\equiv}CSiMe_3)]$ (**6**)*

Solid KOBu^t (0.09 g, 0.80 mmol) was added to a THF solution (20 ml) of **5** (0.20 g, 0.16 mmol) under a nitrogen atmosphere. On addition of ethanol (20 ml) and concentration under a stream of nitrogen, off-white crystals of **6** precipitated. Yield 78%. IR: ν(Os–H) 1993(s); ν(C≡C) 1918(vs); ν(Si–C) 860(s) cm^{-1}. *Anal.* Calc. for $C_{47}H_{52}OsP_4Si$: C, 58.56; H, 5.47. Found: C, 58.34; H, 5.57%. $^{31}P\{^1H\}$ NMR (20 °C, CD_2Cl_2, 121.42 MHz): AMQ_2 system, δ_A 122.20, (δ_M–δ_Q) 18.0–18.4, multiplet; J_{AM} 3.8 Hz. ^1H NMR (20 °C, CD_2Cl_2, 200.13 MHz): −10.14 (dtd, 1H, Os–*H*, $^2J_{HP_M}$ 61.9 Hz, $^2J_{HP_A}$ 11.1 Hz, $^2J_{HP_Q}$ 29.3 Hz); 0.28 (s, 9H, $SiMe_3$).

*Reaction of **6** with $HOSO_2CF_3$*

Neat triflic acid (35 μl, 0.40 mmol) was syringed into a THF solution (15 ml) of **6** (0.10 g, 0.10 mmol). Addition of $NaBPh_4$ (0.20 g, 0.59 mmol) and ethanol/n-hexane (20 ml, 1:2 vol./vol.) gave pale yellow crystals of **5** in *c.* 90% yield.

*Reaction of **6** with $CPh_3BF_4/HC{\equiv}SiMe_3$*

Solid trityl tetrafluoroborate (0.10 g, 0.03 mmol) was added to a stirred THF-d_8 solution (1 ml) of **6** (0.03 g, 0.03 mmol) cooled at −10 °C in a Schlenk tube. An excess of $HC{\equiv}SiMe_3$ (100 μl, 0.71 mmol) was added to the resulting orange solution, which was transferred into an NMR tube. $^{31}P\{^1H\}$ NMR analysis showed the formation of **3** as the only osmium complex.

*Preparation of (E)-$[(PP_3)Os\{\eta^3\text{-}PhC_3{=}C(H)Ph\}]BPh_4$ (**7a,b**)*

Method A. Neat phenylacetylene (0.40 ml, 3.60 mmol) was pipetted into a THF solution (30 ml) of **1** (1.21 g, 1.00 mmol). Stirring the solution at room temperature for 1 h produced a yellow solution. By addition of ethanol (30 ml) and slow concentration of the solvent under a stream of nitrogen, yellow crystals of the isomeric butenynyl complexes **7a,b** precipitated in a ratio of 2 to 1 (yield 91%). GC and ^1H NMR analysis of the reaction mixture showed formation of 1 equiv. of styrene.

Method B. To a stirred solution of **1** (1.21 g, 1.00 mmol) in THF (20 ml) was added 1 equiv. of 1,4-diphenylbutadiyne (0.21 g, 1.04 mmol). Work-up as above gave **7a,b** in 2:1 ratio (*c.* 95% yield). IR: reinforced phenyl vibration 1579 cm^{-1}. *Anal.* Calc. for $C_{82}H_{73}BOsP_4$: C, 71.19; H, 5.32. Found: C, 71.09; H, 5.38%. $\Lambda_M = 54\ \Omega^{-1}\ cm^2\ mol^{-1}$. Irrespective of the synthetic procedure, $^{31}P\{^1H\}$ NMR analysis of either the reaction mixtures or the isolated products showed the formation of **7a,b** in an approximate ratio of 2 to 1. Selected NMR data for the major isomer, **7a**, are as follows: $^{31}P\{^1H\}$ NMR (21 °C, CD_2Cl_2, 121.42 MHz): AMQ_2 system, δ_A 119.45, δ_M 38.75, δ_Q 13.29; J_{AM} 23.7 Hz, J_{AQ} 10.5 Hz, J_{MQ} 9.2 Hz. ^1H NMR (21 °C, CD_2Cl_2, 299.94 MHz): 5.95 (dq, 1H, C=C*H*, $^4J_{HP}$ 3.3 Hz, $^4J_{HP}$ 0.6 Hz). $^{13}C\{^1H\}$ NMR (21 °C, CD_2Cl_2, 50.32 MHz): 138.18 [dm, *C*=C(H)Ph, $^2J_{CP}$ 29.4 Hz]; 135.26 [s, C=*C*(H)Ph, assigned by DEPT and 2D-HETCOR NMR experiments]; 110.61 (dq, C≡*C*Ph, $^2J_{CP}$ 31.5 Hz, $^2J_{CP}$ 2.7 Hz); 62.76 (t, *C*≡CPh, $^2J_{CP}$ 2.9 Hz). Selected NMR data for the minor isomer, **7b**, are as follows: $^{31}P\{^1H\}$ NMR (21 °C, CD_2Cl_2, 121.42 MHz): AMQ_2 system, δ_A 118.23, δ_M 38.89, δ_Q 14.95; J_{AM} 27.8 Hz, J_{AQ} 11.6 Hz, J_{MQ} 10.6 Hz. ^1H NMR (21 °C, CD_2Cl_2, 299.94 MHz): the vinyl proton resonance was not observed. $^{13}C\{^1H\}$ NMR (21 °C, CD_2Cl_2, 50.32 MHz): 137.50 [dq, *C*=C(H)Ph, $^2J_{CP}$ 37.1 Hz, $^2J_{CP}$ 4.8 Hz]; 107.40 (dq, C≡*C*Ph, $^2J_{CP}$ 28.0 Hz, $^2J_{CP}$ 2.5 Hz); 56.22 (t, *C*≡CPh, $^2J_{CP}$ 2.7 Hz). The resonance due to the vinylic carbon atom of the butenynyl ligand in **7b** could not be assigned as it is masked by the resonances of the aromatic carbon atoms.

*Reaction of **1** with $HC{\equiv}CPh$*

NMR experiments

(a) 1:1 Reaction. Solid **1** (0.06 g, 0.05 mmol) was dissolved in CD_2Cl_2 (1.0 ml) degassed under argon and then transferred into a screw cap 5-mm NMR tube which was then cooled at −78 °C. One equiv. of $HC{\equiv}CPh$ (5.5 μl, 0.05 mmol) was added via syringe and the tube introduced into the spectrometer precooled at −50 °C. No reaction was observed below 5 °C. Above this temperature a reaction occurred which converts **1** to a 2:1 mixture of the two butenynyl

complexes **7a,b** (*c.* 31% yield), together with unreacted **1** (*c.* 62%) and a small amount (⩽8%) of the novel complex $[(PP_3)OsH\{C{=}C(H)Ph\}]BPh_4$ (**8**). GC analysis and proton NMR spectroscopy showed total consumption of the alkyne and production of *c.* 0.3 equiv. of styrene. Selected spectroscopic properties of **8**: $^{31}P\{^1H\}$ NMR (9 °C, CD_2Cl_2, 81.01 MHz): AMQ_2 system, δ_A 115.13, δ_M 18.71, δ_Q 12.02; J_{AM} 10.2 Hz, J_{AQ} 1.6 Hz, J_{MQ} 3.7 Hz. ^1H NMR (9 °C, CD_2Cl_2, 200.13 MHz): −10.59 (ddt, Os–*H*, $^2J_{HP_M}$ 37.5 Hz, $^2J_{HP_A}$ 22.8 Hz, $^2J_{HP_Q}$ 6.5 Hz). Due to the generally low concentration of **8**, we were unable to assign the vinylidene hydrogen resonance.

(b) 1:2 Reaction. Addition of a second equiv. of phenylacetylene to the above 1:1 reaction mixture decreased the concentration of **8** (⩽4%) and increased the concentration of **7a,b** (65%).

(c) 1:3 Reaction. Addition of a third equiv. of HC≡CPh to the above reaction mixture completely converted **1** to **7a,b** and produced 1 equiv. of styrene.

Reaction of 7a,b with carbon monoxide

Carbon monoxide (1 atm) was bubbled throughout a refluxing monoglyme solution (25 ml) of **7a,b** (0.28 g, 0.20 mmol) for 30 min. The solution was then cooled to room temperature and ethanol (30 ml) was added. Concentration of the resulting pale yellow solution under a brisk current of nitrogen gave pale yellow crystals of the carbonyl complex (*E*)-$[(PP_3)Os(CO)\{\eta^1\text{-}PhC_3{=}C(H)Ph\}]BPh_4$ (**9**). Yield 89%. IR: ν(C≡O) 1939(s), ν(C=C) 1620(w) cm^{-1}. *Anal.* Calc. for $C_{83}H_{73}BOOsP_4$: C, 70.63; H, 5.21. Found: C, 70.51; H, 5.27%. $^{31}P\{^1H\}$ NMR (20 °C, CD_2Cl_2, 81.01 MHz): AMQ_2 system, δ_A 119.11, δ_M 24.48, δ_Q 20.30; J_{AM} 6.7 Hz, $J_{AQ}\approx 0$ Hz, J_{MQ} 6.6 Hz. ^1H NMR (20 °C, CD_2Cl_2, 200.13 MHz): 6.24 (dm, 1H, C=C*H*, $^4J_{HP}$ 5.6 Hz). $^{13}C\{^1H\}$ NMR (20 °C, CD_2Cl_2, 50.32 MHz): 193.28 (dq, Os–*C*≡O, $^2J_{CP_M}$ 81.7 Hz, $^2J_{CP_A}\approx{}^2J_{CP_Q}$ 7.1 Hz); 158.59 (m, Os–*C*=C), 141.68 (dt, Os–C=*C*, $^3J_{CP}$ 4.9 Hz, $^3J_{CP}$ 2.1 Hz), 102.88 (t, C≡*C*Ph, $^4J_{CP}$ 1.7 Hz), 94.09 (brd, *C*≡CPh, $^3J_{CP}$ 2.8 Hz).

Preparation of $[(PP_3)OsCl\{C{=}C(H)Ph\}]BPh_4$ (10)

Solid $NaBPh_4$ (0.80 g, 2.34 mmol) and an excess of HC≡CPh (0.05 ml, 4.5 mmol) dissolved in 5 ml of ethanol, were added portionwise over 5 min to a well stirred THF solution (30 ml) of **3** (0.93 g, 1.00 mmol) thermostatted at 20 °C. Addition of ethanol (30 ml) and slow concentration under nitrogen gave orange crystals of **10**. Yield 76%. IR: ν(C=C) 1661(m), 1634(m) cm^{-1}. *Anal.* Calc. for $C_{74}H_{68}BClOsP_4$: C, 67.45; H, 5.20; Cl, 2.69. Found: C, 67.35; H, 5.22; Cl, 2.51%. $^{31}P\{^1H\}$ NMR (20 °C, CD_2Cl_2, 81.01 MHz): AMQ_2 system, δ_A 98.04, δ_M −7.46, δ_Q −5.05; J_{AM} 1.5 Hz, J_{AQ} 9.8 Hz, J_{MQ} 12.8 Hz. ^1H NMR (20 °C, CD_2Cl_2, 200.13 MHz): 1.31 (dq, 1H, C=C*H*, $^4J_{HP_A}$ 4.4 Hz, $^4J_{HP_M}\approx{}^4J_{HP_Q}$ 2.4 Hz, assigned by a 2D-HETCOR NMR experiment). $^{13}C\{^1H\}$ NMR (20 °C, CD_3COCD_3, 50.32 MHz): 323.60 (dt, Os=*C*=C, $^2J_{CP_A}$ 75.0 Hz, $^2J_{CP_Q}$ 8.3 Hz); 115.88 (dt, Os=C=*C*, $^3J_{CP_A}$ 16.7 Hz, $^3J_{CP_Q}$ 5.4 Hz, correlated by a 2D-HETCOR NMR experiment with the proton resonance at 1.31 ppm).

Preparation of $[(PP_3)OsCl(C{\equiv}CPh)]BPh_4$ (11)

Method A. To a stirred suspension of **2** (0.93 g, 1.00 mmol) in THF (30 ml) was added solid $NaBPh_4$ (0.80 g, 2.34 mmol). Within a few minutes, the osmium dichloride dissolved to produce a deep green solution which on addition of LiC≡CPh (1.0 M THF solution, 1.0 ml) became yellow. By addition of ethanol (30 ml) and slow evaporation of the solvent in a stream of nitrogen, yellow crystals of **11** precipitated. Yield 80%.

Method B. Solid $KOBu^t$ (0.09 g, 0.80 mmol) was added to a stirred THF solution (30 ml) of **10** (0.66 g, 0.50 mmol). Immediately, the orange color turned yellow. Addition of ethanol (30 ml) and concentration of the resulting solution gave **11** in quantitative yield. IR: ν(C≡C) 2085(s) cm^{-1}. *Anal.* Calc. for $C_{50}H_{47}ClOsP_4$: C, 60.21; H, 4.75; Cl, 3.55. Found: C, 60.11; H, 4.78; Cl, 3.43%. $^{31}P\{^1H\}$ NMR (20 °C, THF-d_8, 81.01 MHz): AMQ_2 system, δ_A 113.37, δ_M 10.72, δ_Q 9.69; J_{AM} 8.9 Hz, J_{AQ} 8.3 Hz, J_{MQ} 12.7 Hz.

Reaction of 11 with $HOSO_2CF_3$

Neat triflic acid (35 μl, 0.40 mmol) was syringed into a THF solution (12 ml) of **11** (0.10 g, 0.10 mmol) which immediately turned orange. Addition of $NaBPh_4$ (0.20 g, 0.59 mmol) and ethanol (20 ml) gave **10** in *c.* 90% yield.

Reaction of 11 with $TlPF_6$ and HC≡CPh

Solid $TlPF_6$ (0.13 g, 0.36 mmol) was added to a stirred THF solution (20 ml) of **11** (0.33 g, 0.33 mmol) and HC≡CPh (0.50 ml, 4.50 mmol). The solution was gently heated to *c.* 40 °C. After the precipitate of TlCl was removed by filtration, an excess of $NaBPh_4$ in ethanol (30 ml) was added to the resulting yellow solution to give crystals of the butenynyl complexes **7a,b**. Yield 90%.

Reaction of 5 with HC≡CPh

(a) 1:1 Reaction. Solid **5** (0.05 g, 0.04 mmol) was dissolved in deaerated acetone-d_6 (1.0 ml) and then transferred into a screw cap 5-mm NMR tube. One equiv. of HC≡CPh (4.4 μl, 0.04 mmol) was added via syringe and a proton NMR spectrum was immediately recorded at room temperature which showed total consumption of the added alkyne and formation of one half equiv. of vinyltrimethylsilane. A $^{31}P\{^1H\}$ NMR

spectrum showed the conversion of 50% of **5** to the butenynyl complexes **7a,b** (ratio 2:1).

(b) 1:2 Reaction. Addition of a second equiv. of HC≡CPh to the above reaction mixture transformed all **5** into **7a,b** and CH_2=$CHSiMe_3$.

Reaction of 3 with HC≡CPh

Neat phenylacetylene (0.50 ml, 4.50 mmol) was pipetted into a THF solution (20 ml) of **3** (0.42 g, 0.31 mmol). The solution was gently heated to reflux temperature and then stirred for 15 min. Addition of ethanol (20 ml) and slow concentration of the solvent under nitrogen gave **7a,b** and (*Z*)-Me_3SiC≡C–CH=$CHSiMe_3$ (see below) in almost quantitative yield.

Preparation of [$(PP_3)OsCl${C=C(CH_3)Ph}]BPh_4 (14)

Neat $MeOSO_2CF_3$ (55 μl, 0.49 mmol) was syringed into a THF solution (20 ml) of **11** (0.50 g, 0.50 mmol) which immediately turned orange. Addition of an ethanol/n-hexane mixture (25 ml, 1:3 vol./vol.) gave an orange microcrystalline product containing the (vinylidene)chloride **14** as the largely predominant component (≥85%). The crude product invariably contains **10** (≤10%) due to the competitive reaction of $HOSO_2CF_3$ (formed by hydrolysis of the triflic ester) with **11**, and some unknown osmium complexes (≤5%). Repeated recrystallizations from CH_2Cl_2/EtOH removed most of the unknown impurities but never afforded an analytically pure sample of **14**. IR: ν(C=C) 1578(m) cm^{-1}. $^{31}P\{^1H\}$ NMR (−50 °C, CD_2Cl_2, 81.01 MHz): AMQ_2 system, δ_A 100.95, δ_M −7.82, δ_Q −5.56; J_{AM}≈0 Hz, J_{AQ} 12.2 Hz, J_{MQ} 13.4 Hz. ^1H NMR (20 °C, CD_2Cl_2, 200.13 MHz): 1.64 (t, 3H, CH_3, $^5J_{HP}$ 1.1 Hz). $^{13}C\{^1H\}$ NMR (23 °C, CD_2Cl_2, 50.32 MHz): 329.21 (dt, Os=*C*=C, $^2J_{CP_A}$ 70.0 Hz, $^2J_{CP_Q}$ 8.9 Hz); 119.69 (dt, Os=C≡*C*, $^3J_{CP_A}$ 17.2 Hz, $^3J_{CP_Q}$ 6.4 Hz); 5.24 (s, CH_3).

Preparation of (E)-[(PP_3)-Os{η^3-PhC_3=C(CH_3)Ph}]BPh_4 (15a,b)

To a stirred THF solution (20 ml) of **14** and **11** (*c.* 9:1 ratio) (0.25 g, 0.19 mmol) at 0 °C was added one equiv. of LiC≡CPh (1.0 M THF solution, 0.20 mmol). Stirring was continued for 30 min while the starting orange color disappeared to produce a clear yellow solution. Addition of ethanol (30 ml) and concentration of the resulting solution at room temperature gave yellow crystals of the butenynyl complexes **15a,b** and **7a,b** in a ratio of 9 to 1. Overall yield 80%. Like **7a,b**, the methyl-substituted congeners **15a,b** constitute a pair of geometric isomers in a ratio of 3 to 1 (see text). Selected NMR data for the major isomer **15a**: $^{31}P\{^1H\}$ NMR (22 °C, CD_2Cl_2, 81.01 MHz): AMQ_2 system, δ_A 122.52, δ_M 43.08, δ_Q 16.27; J_{AM} 23.7 Hz, J_{AQ} 11.7 Hz, J_{MQ} 9.7 Hz. ^1H NMR (22 °C, CD_2Cl_2, 200.13 MHz): 1.83 [s, 3H, C=C(CH_3)]. $^{13}C\{^1H\}$ NMR (22 °C, CD_2Cl_2, 50.32 MHz): 161.07 [dt, *C*=C(CH_3)Ph, $^2J_{CP}$ 33.1 Hz, $^2J_{CP}$ 1.9 Hz]; 138.46 [s, C=*C*(CH_3)Ph]; 111.53 (dm, C≡*C*Ph, $^2J_{CP}$ 30.6 Hz); 67.25 (s, *C*≡CPh); 14.56 (s, CH_3). Selected NMR data for the minor isomer **15b**: $^{31}P\{^1H\}$ NMR (22 °C, CD_2Cl_2, 81.01 MHz): AMQ_2 system, δ_A 117.97, δ_M 41.02, δ_Q 14.02; J_{AM} 25.6 Hz, J_{AQ} 12.0 Hz, J_{MQ} 10.9 Hz. ^1H NMR (22 °C, CD_2Cl_2, 200.13 MHz): 1.74 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (22 °C, CD_2Cl_2, 50.32 MHz): 156.95 [dt, *C*=C(CH_3)Ph, $^2J_{CP}$ 32.6 Hz, $^2J_{CP}$ 2.4 Hz]; 112.05 (dm, C≡*C*Ph, $^2J_{CP}$ 22.5 Hz); 68.50 (s, *C*≡CPh). The resonance due to the vinyl carbon atom of the butenynyl ligand in **15b** could not be assigned as it is masked by the resonances of the aromatic carbon atoms.

Reaction of 15a,b with HC≡CPh

To a stirred THF solution (20 ml) of a 9:1 mixture of **15a,b** and **7a,b** (0.25 g, 0.19 mmol) was added a five-fold excess of HC≡CPh. The reaction mixture was heated at reflux temperature for 1 h and then cooled to room temperature. Addition of ethanol and concentration under a brisk current of argon quantitatively gave **7a,b** (2:1 ratio). GC-MS analysis of the reaction mixture prior to addition of ethanol showed formation of 1,4-diphenyl-pent-3-en-1-yne. [M^+ = 218(30), $M-CH_3^+$ = 203(100)].

Catalytic experiments

Catalytic reactions were performed by using the following procedure. The catalyst precursor **1** was dissolved in THF (or THF/H_2O) and the resulting solution was stirred under nitrogen or argon at reflux temperature. A 100-fold excess of the substrate in THF was then added and the mixture was stirred for 6 h (HC≡CPh) or 18 h (HC≡$CSiMe_3$). The reactions were quenched by contemporaneous cooling to 0 °C and exposure to air. The organic product compositions were determined by GC and GC-MS analyses.

Reaction between HC≡$CSiMe_3$ and 1 in dry THF

Organic product composition: HC≡$CSiMe_3$ (58.1%), CH_2=$CHSiMe_3$ (0.1%), (*Z*)-Me_3SiC≡C–CH=$CHSiMe_3$ (36.5%), (*E*)-Me_3SiC≡C–CH=$CHSiMe_3$ (5.3%). The reaction crude was distilled under reduced pressure to eliminate the solvent and the unreacted substrate. (*Z*)-1,4-Bis(trimethylsilyl)but-3-en-1-yne (b.p. 100 °C/30 torr) was isolated by fractional distillation. ^1H NMR (20 °C, $CDCl_3$, 299.94 MHz): 0.184 (s, 9H, $SiMe_3$); 0.187 (s, 9H, $SiMe_3$); 6.16, 6.24 (AB spin system, 2H, *CH*=*CH*, $^3J_{HH}$ 15.1 Hz [12]. $^{13}C\{^1H\}$ NMR (20 °C, $CDCl_3$, 50.32 MHz): −1.15 [Si(CH_3)]; −0.31 [Si(CH_3)]; 98.57 (*C*≡$CSiMe_3$); 105.10 (C≡*C*$SiMe_3$); 124.56 (CH=*C*H$SiMe_3$); 146.47 (Me_3SiCH=*C*H). [M^+ = 196] [13].

*Reaction between $HC{\equiv}CSiMe_3$ and **1** in THF/H_2O (10:1)*

Organic product composition: $HC{\equiv}CSiMe_3$ (62.3%), $CH_2{=}CHSiMe_3$ (0.3%), $CH_2{=}CH{-}C{\equiv}CSiMe_3$ (37.5%), $Me_3SiC{\equiv}C{-}CH{=}CHSiMe_3$ (traces). The reaction crude was distilled under reduced pressure to eliminate the solvent and the unreacted substrate. Trimethylsilylbut-3-en-1-yne (b.p. 52 °C/80 torr) [14], $CH_2{=}CH{-}C{\equiv}CSiMe_3$, was separated by fractional distillation. ^1H NMR (20 °C, $CDCl_3$, 299.94 MHz): 0.15 (s, 9H, $SiMe_3$); 5.77, 5.65, 5.45 (ABC spin system, 3H, $CH_2{=}CH$, J_{AB} 11.4 Hz, J_{AC} 17.6 Hz, J_{BC} 2.0 Hz). $^{13}C\{^1H\}$ NMR (22 °C, $CDCl_3$, 50.32 MHz): 128.43 ($CH_2{=}CH$, assigned by a DEPT NMR experiment); 117.89 ($CH_2{=}CH$, assigned by a DEPT NMR experiment); 107.60 ($C{=}CSiMe_3$); 60.41 ($C{\equiv}CSiMe_3$); 2.51 [$Si(CH_3)$]. [$M^+ = 124(45)$, $M - CH_3^+ = 109(100)$, $C{\equiv}CSiMe_3^+ = 83(35)$].

*Reaction between $HC{\equiv}CPh$ and **1** in THF*

Organic product composition: $HC{\equiv}CPh$ (10.6%), (*Z*)-$PhC{\equiv}C{-}CH{=}CHPh$ (89.4%). After the solvent was removed under reduced pressure, the products were separated by tlc on alumina plates using n-hexane as eluent. 1,4-Diphenylbut-3-en-1-yne was isolated. ^1H NMR (20 °C, $CDCl_3$, 299.94 MHz): 6.00 (d, 1H, $PhCH{=}CH$, $^3J_{HH}$ 11.9 Hz); 6.76 (d, 1H, $PhCH{=}CH$, $^3J_{HH}$ 11.9 Hz); 7.36–7.62 (m, 8H, Ph); 7.96–8.06 (m, 2H, Ph) [15]. $^{13}C\{^1H\}$ NMR (22 °C, $CDCl_3$, 75.14 MHz): 138.71 ($PhCH{=}CH$, correlated by a 2D-NMR experiment with the ^1H resonance at 6.76 ppm); 136.60 (Ph); 131.50 ($PhCH{=}CH$, correlated by a 2D-NMR experiment with the ^1H resonance at 6.00 ppm); 123.4–128.9 (Ph); 95.90 ($PhC{\equiv}C$); 88.29 ($PhC{\equiv}C$). [$M^+ = 204$].

Results and discussion

Preparation and characterization of osmium enynyl complexes

Reaction of $[(PP_3)Os(H)(N_2)]BPh_4$ (1) with $HC{\equiv}CSiMe_3$

Reaction of 3 equiv. of trimethylsilylacetylene with **1** in THF at room temperature yields the enynyl complex (*E*)-$[(PP_3)Os\{\eta^3\text{-}Me_3SiC_3{=}C(H)SiMe_3\}]BPh_4$ (**3**) as a result of a C–C bond-forming reaction between two alkyne molecules (Scheme 1). One equiv. of trimethylvinylsilane is also formed as shown by both GC-MS analysis and ^1H NMR spectroscopy.

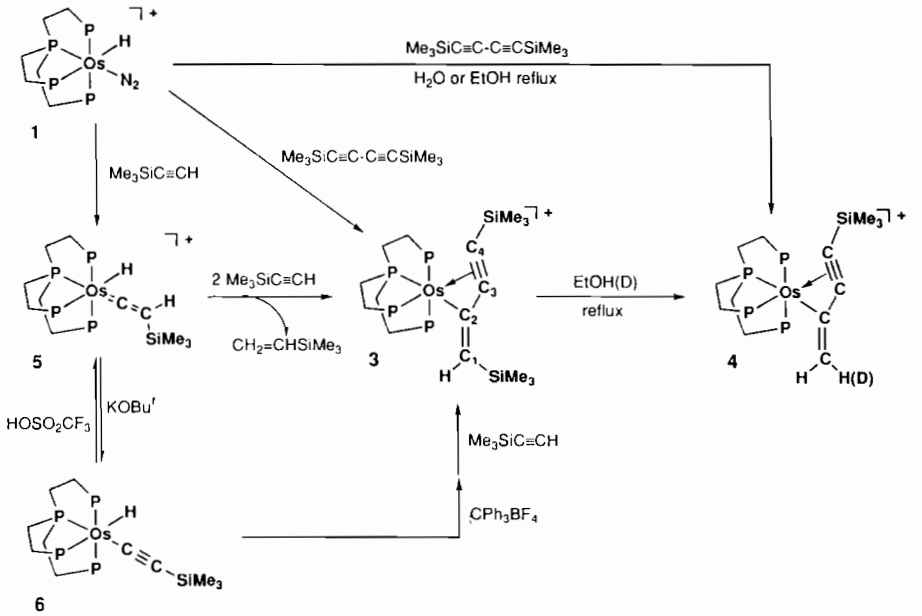
The $^{31}P\{^1H\}$ NMR spectrum of **3** exhibits a temperature-invariant first order AMQ_2 splitting pattern which is typical of octahedral PP_3 metal complexes [8, 16]. The presence of a 1,4-trimethylsilylbutenynyl ligand trihapto bonded to the osmium atom is unambiguously shown by IR, ^1H and $^{13}C\{^1H\}$ NMR data which are in excellent correlation with those of (*E*)-$[(PP_3)Ru\{\eta^3\text{-}Me_3SiC_3{=}C(H)SiMe_3\}]BPh_4$ recently authenticated by an X-ray analysis [17], as well as a number of η^3-enynyl metal complexes [18–28]. In particular, the ^1H NMR spectrum shows that the two $SiMe_3$ groups are inequivalent (δ 0.88 and −0.49), while the vinyl hydrogen of the enynyl ligand appears as a doublet of triplets at δ 6.07 (1H). In keeping with this assignment, the latter resonance does not show any cross-peak in the homonuclear correlated 2D-COSY NMR spectrum and transforms into a narrow singlet with no discernible coupling in the broad-band phosphorus-decoupled ^1H NMR spectrum.

The $^{13}C\{^1H\}$ NMR spectrum contains two singlets (δ 2.48 and 1.30) due to the methyl carbons of the two inequivalent $SiMe_3$ substituents, which, in fact, correlate in a 2D-HETCOR NMR experiment with the two hydrogen singlets at 0.88 and −0.49 ppm, respectively. A set of three carbon resonances, which disappear in a DEPT-^{13}C experiment, are readily assigned to the C_2, C_4 and C_3 quaternary carbons of an η^3-butenynyl ligand, respectively (Scheme 1). Notably, the two acetylenic carbons C_3 and C_4 of the η^3-enynyl fragment (δ 75.69 and 95.87) are significantly shifted as compared to the corresponding carbons in free (*Z*)-1,4-bis(trimethylsilyl)but-3-en-1-yne (δ 60.41 and 107.60) suggesting a consistent deviation from sp hybridization. The remaining carbon atom of the skeleton of the enynyl moiety, namely C_1, was identified by a 2D-HETCOR NMR experiment which provides evidence for a C–H correlation of the singlet at 140.18 ppm with the vinyl hydrogen resonance at δ 6.07.

Indirect but conclusive evidence supporting the structure of **3** as shown in Scheme 1 is provided by the reaction of **1** with a stoichiometric amount of 1,4-bis(trimethylsilyl)butadiyne which gives **3**. Indeed, hydrometallation of butadiynes to give η^1- or η^3-butenynyl complexes is a well-known route to the synthesis of enynyl metal complexes [21, 22, 29–33].

In some preparations of **3** when no particular care was paid to remove moisture from either the solvent or the reaction apparatus, a minor product, namely the monosubstituted-trimethylsilyl butenynyl complex $[(PP_3)Os(\eta^3\text{-}Me_3SiC_3{=}CH_2)]BPh_4$ (**4**), is formed (3–5% yield). In view of this finding, the reaction between **1** and $HC{\equiv}CSiMe_3$ or $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ was purposefully performed in the presence of some water or ethanol. As a result, **5** is selectively produced and is isolated as pale yellow needles. GC-MS analyses of the reaction mixtures showed the formation of $Me_3SiOSiMe_3$ and $EtOSiMe_3$, respectively.

Complex **4** shares most of its chemo-physical properties with **3** from which it can straightforwardly be synthesized by gentle heating in THF containing some drops of either water or ethanol. Relevant to the



Scheme 1. All reactions were performed in THF at room temperature unless otherwise stated. All cations were employed as BPh_4^- salts.

identification of **4** is the presence in the ^1H NMR spectrum of only one singlet (δ 0.94) due to the $SiMe_3$ substituent and of two low-field multiplets (δ 5.51 and 5.00) integrating as 1H. These multiplets are correlated with an inverted peak at δ 135.67 in the DEPT-135 ^{13}C spectrum. Accordingly, the two hydrogen resonances at 5.51 and 5.00 ppm can safely be assigned to the two geminal protons of the vinyl moiety of the η^3-$Me_3SiC_3{=}CH_2$ ligand. In keeping with this formulation, the two proton signals show a strong correlation in the 2D-COSY NMR spectrum and transform into a pair of doublets in the $^1H\{^{31}P\}$ NMR spectrum ($^2J_{HH}$ 2.7 Hz).

On the basis of these data, it is therefore apparent that cleavage of the vinyl carbon–silicon bond occurs upon reaction of **3** with either H_2O or C_2H_5OH. The chemospecific character of the reaction is clearly shown by a deuterium labelling experiment with the use of C_2H_5OD. In fact, when a THF solution of **3** is treated with C_2H_5OD, incorporation of deuterium selectively occurs on one of the two geminal positions of the vinyl moiety as shown by the ^1H NMR spectrum of $[(PP_3)Os(\eta^3\text{-}Me_3SiC_3{=}CHD)]BPh_4$ (**4**-d_1) which contains only the vinyl hydrogen resonance at δ 5.51.

The conversion of **3** to **4** is quite interesting as it provides access to catalytic production of the butenynylsilane $CH_2{=}CH{-}C{\equiv}CSiMe_3$ (see below).

From a mechanistic viewpoint, the reaction may be seen as an electrophilic addition of either water or ethanol to the vinylsilane moiety in **3**, followed by thermal elimination of Me_3SiOH (which later condenses to $Me_3SiOSiMe_3$) or Me_3SiOEt*. Indeed, vinylsilanes are known to react with a wide range of electrophiles to give products of substitution or addition; in the latter case, *syn*-elimination generally occurs as a thermal step [35–38].

The chemoselectivity of the attack by H_2O and C_2H_5OH is remarkable in view of the potential of the trimethylsilylalkynyl moiety of the butenynyl ligand in **3** to undergo cleavage of the Si–C bond by hydrolysis or ethanolysis.

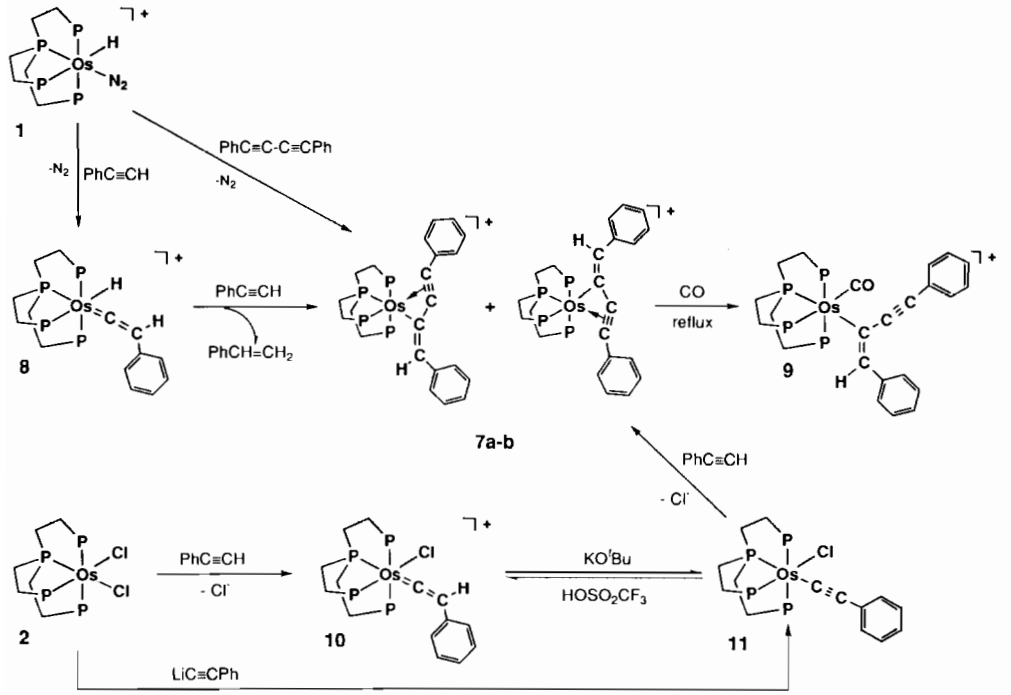
Reaction of 1 with HC≡CPh

Stirring **1** in THF with either 3 equiv. of HC≡CPh or 1 equiv. of 1,4-diphenylbutadiyne gives yellow crystals analyzing as $[(PP_3)Os\{\eta^3\text{-}PhC_3{=}C(H)Ph\}]BPh_4$ (**7**) (Scheme 2). One equiv. of styrene is produced in the reaction.

The $^{31}P\{^1H\}$ NMR spectrum of **7** shows the presence of two distinct osmium complexes in an approximate ratio of 2 to 1. Both osmium compounds exhibit $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and ^1H NMR data in excellent correlation with those of the pair of geometric isomers of the formula $[(PP_3)Ru\{\eta^3\text{-}PhC_3{=}C(H)Ph\}]BPh_4$ [18]. The two Ru complexes, recently prepared by an analogous procedure, differ from each other only in the anchoring mode of the PhC_3CHPh ligand to the metal as shown in structures **I** and **II**.

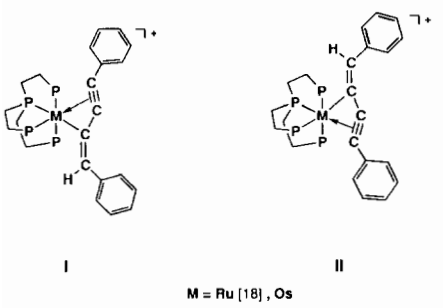
Reaction of **7** in either THF or glycol monomethyl ether with CO (1 atm) at reflux temperature yields a

*Selective cleavage of C–Si bond by water in a vinylidene rhodium(I) complex has been recently reported [34].



Scheme 2. All reactions were performed in THF at room temperature unless otherwise stated. All cations were employed as BPh_4^- salts.

unique carbonyl complex, $[(PP_3)Os(CO)\{\eta^1\text{-}PhC_3{=}C(H)Ph\}]BPh_4$ (**9**), in which the butenynyl ligand uses only the vinyl carbon to bind the metal. The formation of a unique carbonyl complex is obviously consistent with a single C_1,C_2 stereochemistry within the butenynyl ligands in the starting compound **7**. A further piece of experimental evidence in favor of the structural formulation proposed for the **7a,b** couple is provided by the selective production of (*Z*)-1,4-diphenylbut-3-en-1-yne when **1** is reacted with HC≡CPh in catalytic conditions (see below). Accordingly, one may reasonably conclude that **7** is also a mixture of two species, hereafter **7a,b**, containing 1,4-diphenylbutenynyl ligands displaying identical stereochemistry but different anchoring modes to the metal. As previously suggested for Ru, repulsive interaction with the six phenyl rings of the tripodal phosphine ligand may account for the observed *trans* arrangement adopted by the substituents on the enynyl ligands in **3** and **7a,b**.



Unlike the $SiMe_3$-substituted analogue **3**, the 1,4-diphenyl derivatives **7a,b** are stable when heated in THF containing either H_2O or C_2H_5OH.

Catalytic dimerization of terminal alkynes

Reaction of **1** with an excess (100 equiv.) of phenylacetylene in refluxing THF for 6 h results in catalytic, selective conversion of the alkyne to (*Z*)-1,4-diphenylbut-3-en-1-yne (89.4%) [27, 39, 40]. In the catalytic reaction, phenylacetylene is thus regio- and stereoselectively dimerized via head-to-head coupling. No trace of either the 1,3-disubstituted regioisomer (head-to-tail coupling) or the *E*-1,4-diphenylbut-3-en-1-yne stereoisomer was detected in the reaction mixture. The selective formation of the *Z*-butenyne is clearly consistent with the suggested *E* structure of **7a,b**, which are, in fact, the termination metal products and catalyst precursors for the catalytic dimerization of phenylacetylene as well.

Compound **1** is a less efficient catalyst, in terms of both activity and selectivity, for the dimerization of $HC{\equiv}CSiMe_3$ to the corresponding butenyne. In fact, not only the conversion of the alkyne is much lower (41.8% in 18 h) but is also less selective as the formation of (*Z*)-1,4-bis(trimethylsilyl)but-3-en-1-yne (36.5%) is accompanied by appreciable formation of the *E* stereoisomer (5.3%). In contrast, the reaction of **1** with $HC{\equiv}CSiMe_3$ in the presence of water (THF/H_2O, 10:1 vol./vol.) selectively produces the partially desilylated trimethylsilylbut-3-en-1-yne, $CH_2{=}CH{-}C{\equiv}CSiMe_3$

(37.5% in 18 h). Only traces of the disubstituted enynes were detected, while there was no evidence for the formation of other mono- or disilylated organic products.

In situ NMR experiments

In an attempt to gather information on the mechanism of formation of the Os butenynyl complexes as well as the catalysis cycle of 1-alkyne dimerization, **1** was treated with incremental amounts of either $HC{\equiv}CSiMe_3$ or $HC{\equiv}CPh$, and the subsequent reactions were monitored with the use of variable-temperature ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

The reaction between **1** and 1 equiv. of $HC{\equiv}CSiMe_3$ occurs already at 0 °C. At this temperature 93% of **1** disappears within *c.* 30 min. Formed in its place are the (vinylidene)hydride $[(PP_3)OsH\{C{=}C(H)SiMe_3\}]BPh_4$ (**5**) and the butenynyl complex **3** in a 86:7 ratio, while all the alkyne is consumed. This product composition changes neither with time nor with temperature up to 52 °C. On addition of a second equiv. of alkyne, **1** completely disappears while almost one half of **5** transforms into **3**. Complete conversion of **5** to **3** occurs when a third equiv. of alkyne is syringed into the reaction mixture. ^1H NMR analysis shows the formation of 1 equiv. of $CH_2{=}CHSiMe_3$ as the only organic product.

A similar reaction sequence is observed when $PhC{\equiv}CH$ is substituted for $HC{\equiv}CSiMe_3$, the only difference being that the concentration of the (vinylidene)hydride complex $[(PP_3)OsH\{C{=}C(H)Ph\}BPh_4$ (**8**) is invariably very low ($\leqslant 8\%$). The low concentration of **8**, even when the alkyne is the limiting reagent, suggests that the reaction of **1** with $PhC{\equiv}CH$ to give **8** is slower than the subsequent reaction of the latter species with the alkyne. As a consequence, no attempt was made to isolate **8** in the solid state, whereas a large-scale preparation of **5** was successfully carried out in THF using n-hexane as precipitant.

Synthesis and characterization of the cis-(vinylidene)hydride complex $[(PP_3)OsH\{C{=}C(H)SiMe_3\}]BPh_4$ (5) and of the (σ-alkynyl)hydride $[(PP_3)OsH(C{\equiv}CSiMe_3)]$ (6)

Compound **5** which appears as ivory-colored microcrystals, is fairly stable in both the solid-state and solution.

The IR spectrum exhibits a strong absorption at 1620 cm^{-1} typical of a $\nu(C{=}C)$ vibration and, in principle, ascribable to either σ-vinyl or vinylidene ligands. The former assignment is readily ruled out by the presence of a weak ν(Os–H) band at 2010 cm^{-1} which is shifted to 1445 cm^{-1} in the IR spectrum of the isotopomer $[(PP_3)OsD\{C{=}C(H)SiMe_3\}]BPh_4$ (**5**-d_1) ($k_{H/D} = 1.39$). In fact, a σ-vinyl ligand might have been formed only by insertion of the alkyne into the Os–H bond in **1** and thus no terminal hydride absorption should be present in the IR spectrum [41–43]. Finally, a strong band at 845 cm^{-1} is consistent with the presence of the trimethylsilyl substituent in the organyl fragment attached to osmium.

Conclusive evidence of the presence of *cis*-disposed hydride and vinylidene ligands in **5** was provided by NMR spectroscopy and reactivity tests as well.

The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 shows **5** to be fluxional on the NMR time scale. At room temperature, the spectrum consists of three featureless resonances of which only the one at lowest field (δ 112.84), assigned to the bridgehead phosphorus atom, is partially resolved into a broad doublet with $^2J_{P_AP_M} = 10.6$ Hz. Upon a decrease in the temperature, the fluxional process is rapidly slowed down and, at −35 °C, the slow-exchange spectrum (AMQ_2 pattern) is obtained, which shows no coupling of the apical phosphorus P_A to the two equivalent terminal phosphorus atoms P_Q. In the temperature window of dichloromethane, the fast-exchange regime cannot be observed. Substitution of C_6D_5Cl for CD_2Cl_2 allowed us to record spectra at high temperature. At 76 °C, coalescence of the two high field resonances occurs, which suggests an AM_3 spin system for the fast motion regime. Unfortunately, at higher temperatures **5** extensively decomposes to unknown compounds.

In the ^1H NMR spectrum of **5** at −30 °C, the terminal hydride ligand (δ −8.92) gives rise to a complex resonance which has properly been computed as the X part of an AMQQ'XY spin system (Fig. 1). In the $^1H\{^{31}P\}$ NMR spectrum, the hydride resonance transforms into a doublet with a separation of 6.1 Hz.This additional homonuclear coupling assigned to the four-bond coupling interaction between the terminal hydride and the vinylidene proton ($^4J_{H_XH_Y}$) is remarkable and reflects the unsaturation of the metal–vinylidene moiety. In order to unambiguously prove this assignment, a homonuclear correlated 2D-COSY spectrum was recorded. Indeed, the hydride resonance is coupled to the vinylidene hydrogen resonance (triplet of doublets at 2.32 ppm) which, in turn, reduces to a doublet with a separation of 6.1 Hz in the broad-band phosphorus-decoupled ^1H NMR spectrum. No anomalous bonding interaction is observed between the two scalarly coupled hydride and vinylidene hydrogen atoms, as shown by the relatively long longitudinal relaxation time of the hydride atom ($T_1(C_6D_5Cl$, 35 °C, 300 MHz, inversion-recovery sequence) = 250 ± 5 ms). This value is comparable to the one measured for the hydride ligand in **1** ($T_1 = 280 \pm 5$ ms) and thus rules out the existence of any anomalous dipolar interaction with the vinylidene hydrogen atom [44].

Finally, $^{13}C\{^1H\}$ NMR and DEPT-^{13}C spectra of **5** (−30 °C, acetone-d_6) showed the C_β carbon of the

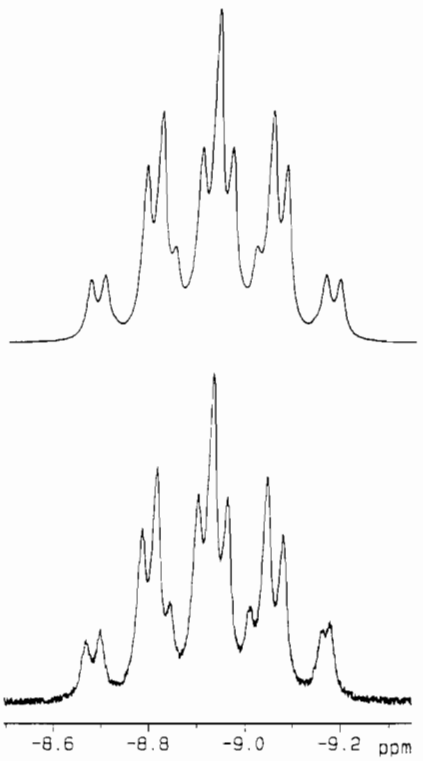


Fig. 1. Experimental and computed (upper) resonance of the terminal hydride ligand in **5** (CD_2Cl_2, −30 °C).

vinylidene ligand to originate a doublet at 97.54 ppm and the electron-deficient quaternary C_α carbon to originate a low-field shifted multiplet (δ 307.30). All the other chemical shifts and coupling constants (see 'Experimental') are in good agreement with those reported for vinylidene metal complexes [45].

A peculiar reaction of monosubstituted vinylidene complexes is their proclivity to undergo deprotonation by bases to the corresponding σ-alkynyl derivatives [45–47]. In accord with the general trend, treatment of **5** with KO^{t}Bu in THF readily produces off-white crystals of the neutral *cis*-(hydride)(σ-trimethylsilylethynyl) complex $[(PP_3)OsH(C{\equiv}CSiMe_3)]$ (**6**) which reversibly regenerates **5** upon reaction with protic acids like $HBF_4 \cdot OEt_2$ or $HOSO_2CF_3$. The spectroscopic properties of **6** nicely correlate with those of a number of octahedral *cis*-(hydride)(alkynyl) complexes of the formula $[(L_4)MH(C{\equiv}CR)]^{0/+}$ ($L_4 = PP_3$, NP_3; M = Co [47], Rh [16c], Ir [48], Fe [48], Ru [48]), some of which, namely $[(PP_3)CoH(C{\equiv}CSiMe_3)]BPh_4$ [47b] and $[(NP_3)RhH(C{\equiv}CH)]BPh_4$ [16c], have been authenticated by X-ray analyses ($NP_3 = N(CH_2CH_2PPh_2)_3$).

The 1-alkyne to vinylidene tautomerism occurs widely in organometallic chemistry. It is generally agreed that in the initial step the alkyne molecule coordinates in an η^2 mode to the metal center. From this π-intermediate, the system can eventually convert to hydride alkynyl (C–H oxidative addition) and/or vinylidene (1,3-hydrogen shift/1,2-hydrogen shift) derivatives [45–49]. In the Os case at hand, a C–H oxidative addition step can be ruled out on the basis of the reaction of **1**-d_1 with 1 equiv. of $HC{\equiv}CSiMe_3$ as it exclusively affords **5**-d_1. Indeed, were the C–H bond of the alkyne cleaved to give an Os(IV) (alkynyl)dihydride intermediate, the subsequent hydride migration from the metal to the β-carbon of the alkynyl ligand would reasonably produce a mixture of $[(PP_3)OsD\{C{=}C(H)SiMe_3\}]BPh_4$ and $[(PP_3)OsH\{C{=}C(D)SiMe_3\}]BPh_4$, which in fact is not observed. In conclusion, the 16-electron fragment $[(PP_3)OsH]^+$ seems to belong to the numerous family of transition metal systems which are capable of converting 1-alkynes to vinylidene ligands via 1,2-hydrogen shift.

The isolation and characterization of **5** is not only useful to gain insight into the mechanism of the reaction between **1** and terminal alkynes (*vide infra*) but is also of fundamental relevance. In fact, despite their elusive nature, (vinylidene)hydride complexes are considered important intermediates in several homogeneous and heterogenous catalytic reactions, including alkene oligomerization, polymerization, metathesis of olefins [50] and Fischer–Tropsch synthesis [51]. To the best of our knowledge, the only (vinylidene)hydride complex described so far is the permethyltantalocene derivative $Cp^*_2TaH(C{=}CH_2)$ obtained by Bercaw and co-workers by reaction of $Cp^*_2TaCl_2$ with vinylmagnesium bromide in THF [52]. Remarkably, this tantalum complex reacts with CO to give the carbonyl vinyl complex $Cp^*_2Ta(CO)(CH{=}CH_2)$ via hydride migration from the metal to the vinylidene α-carbon. This reaction correlates with the results described in this paper and suggests that the rearrangement of 1-alkynes to vinylidene at metal centers may be a key step along the reaction path of alkyne reduction to alkene. In fact, there is little doubt that the formation of **5** precedes the hydrogenation of the alkyne as shown by the reactions of **5** with 2 equiv. of $HC{\equiv}CR$ (R = $SiMe_3$, Ph) which give the butenynyl complexes **3** and **7a,b** and the alkenes $CH_2{=}CHSiMe_3$ and $CH_2{=}CHPh$, respectively. The reaction between **5** and $HC{\equiv}CPh$ is of particular importance as it unambiguously shows that the alkene is formed from the starting vinylidene ligand.

Model reactions for the dimerization of terminal alkynes to 1,4-disubstituted butenynes

As shown above, (vinylidene)hydride complexes are important species for the conversion of **1** to η^3-butenynyls **3** and **7a,b**. The role of the (vinylidene)hydride complexes in the catalytic cycle for phenylacetylene and trimethylsilylacetylene dimerization is conversely marginal as apparently they are sacrificed to generate the catalyst via reduction of the first equivalent of alkyne (see the reaction of **5** with $HC{\equiv}CPh$). The latter process

necessarily requires hydrogen transfer from a second equiv. of alkyne to generate free alkene and a σ-alkynyl complex, which however has not been detected. Thus, some questions still need to be addressed to rationalize the catalysis cycle, in particular it remains to establish the structure of the catalyst and the intimate mechanism of the C–C bond-forming reaction leading to butenynyl ligand formation.

With the use of isolated compounds in independent reactions we have accumulated convincing evidence of the effective role of a σ-alkynyl Os(II) complex in the catalysis cycle and of the occurrence of a C–C bond coupling reaction between σ-alkynyl and vinylidene ligands.

Synthesis and characterization of the (vinylidene)chloride [(PP$_3$)OsCl{C=C(H)Ph}]BPh$_4$ (10)

One-pot reaction of the dichloride complex [(PP$_3$)OsCl$_2$] (**2**) with a slight excess of HC≡CPh in THF/EtOH at room temperature in the presence of a mild chloride scavenger such as NaBPh$_4$, gives orange crystals of the octahedral (vinylidene)chloride complex [(PP$_3$)OsCl{C=C(H)Ph}]BPh$_4$ (**10**). Alternatively, **10** can be synthesized by treatment of isolated [(PP$_3$)OsCl]BPh$_4$ [48] with phenylacetylene.

The occurrence of HC≡CPh to C=C(H)Ph tautomerism at the [(PP$_3$)OsCl]$^+$ system is shown by IR and NMR data. In particular, the $^{13}C\{^1H\}$ NMR spectrum contains the expected low-field resonance of the quaternary α-carbon of the vinylidene ligand (δ 323.60), while a doublet of triplets at 115.88 ppm is readily assigned to the C$_\beta$ atom. Finally, a C,H-heterocorrelated 2D NMR spectrum showing a cross peak between the latter carbon and a proton resonance at 1.31 ppm, discloses the position of the vinylidene hydrogen. Interestingly, the position of this hydrogen in the ^1H NMR spectrum appears at higher field than the analogous resonance of the (vinylidene)hydride **5** (δ 2.32) and, in general, of cationic metal vinylidene complexes [45–49]. In a similar way, the $^{31}P\{^1H\}$ NMR spectrum of **10** is consistent with the proposed structure (AMQ_2 spin system), but is featured by a remarkable high-field shift of all phosphorus resonances (δ_A 98.04, δ_M −7.46, δ_Q −5.05), which is not observed for the related (vinylidene)hydrides complexes **5** and **8**. This unusual magnetic shielding of the vinylidene hydrogen and phosphorus nuclei in **10** is not clear, particularly as we note no similar high-field shift of the ^{13}C NMR signals of the vinylidene carbon atoms. Relevant to this anomalous shielding effect may be the presence of the chloride ligand in **10** as the chloride is a better σ and π donor than the hydride. The substitution of chloride for hydride may thus increase the electronic density on the metal and, ultimately, cause a more efficient shielding of the other ligands. Indeed, there is little doubt that chloride π-donation to osmium is the driving force for the stabilization of the coordinatively unsaturated complex [(PP$_3$)OsCl]BPh$_4$ [48].

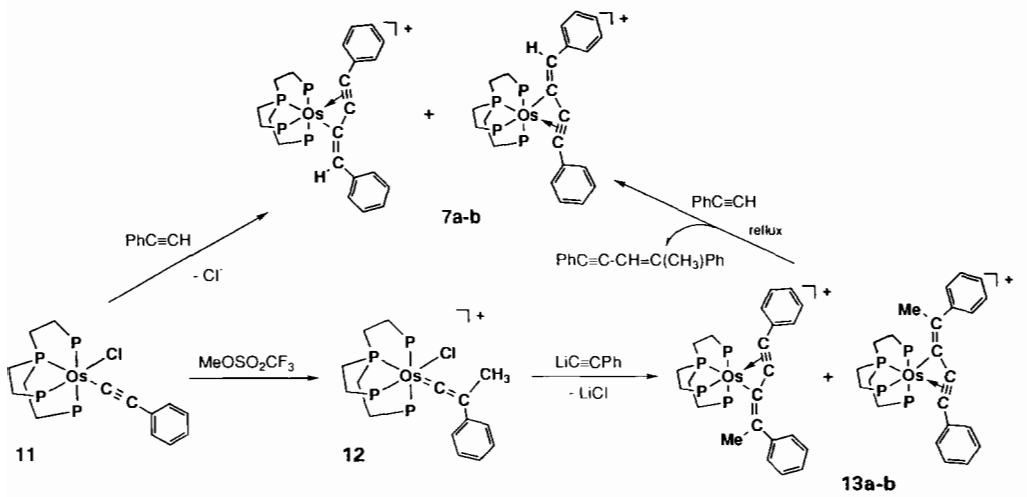
Synthesis, characterization and reactions of the (alkynyl)chloride complex [(PP$_3$)OsCl(C≡CPh)] (11)

As is expected for a vinylidene complex, **10** undergoes a clean deprotonation reaction with strong bases such as KOBu^t. As a result, the neutral *cis*-(alkynyl)chloride complex [(PP$_3$)OsCl(C≡CPh)] (**11**) (ν(C≡C) 2085 cm^{-1}) is obtained, which regenerates the vinylidene **10** by treatment with a protic acid. Complex **11** can also be prepared by reaction of LiC≡CPh with either **2** or [(PP$_3$)OsCl]BPh$_4$ in THF.

Remarkably, the reaction of **11** with phenylacetylene in the presence of an efficient chloride scavenger such as TlPF$_6$ yields the butenynyl complexes **7a,b**. This is an interesting result, which shows that the enynyl ligand is formed via a formal coupling reaction between alkynyl and 1-alkyne ligands. On the other hand, the ascertained ability of unsaturated Os(II) systems of the formula [(PP$_3$)OsX]$^+$ (X = H, Cl) to promote the HC≡CR (R = Ph, SiMe$_3$) to C=C(H)R tautomerism suggests that the coupling of alkynyl and 1-alkyne actually proceeds via a (vinylidene)alkynyl intermediate. Indeed, (vinylidene)alkynyl metal complexes are considered key-intermediates for the synthesis of butenynyl derivatives via intramolecular C–C bond formation [17, 18, 27, 39]. This route to butenynyl complexes and, therefore, to catalytic production of but-3-en-1-ynes, is alternative to alkyne insertion into metal–carbon(alkynyl) bonds, which is generally assisted by early transition metals and lanthanides [40].

In order to prove the occurrence of a C–C bond coupling between σ-alkynyl and vinylidene ligands at osmium, we attempted a metathesis reaction between the (vinylidene)chloride **10** and LiC≡CPh. Unfortunately, the reaction was unsuccessful as **10** was simply deprotonated to **11**. To overcome the competing acid–base reaction between the acidic vinylidene hydrogen and LiC≡CPh, the disubstituted vinylidene complex [(PP$_3$)OsCl{C=C(CH$_3$)Ph}]BPh$_4$ (**12**) was synthesized by alkylation of **11** in THF with MeOSO$_2$CF$_3$ and then reacted with 1 equiv. of LiC≡CPh. As a result, the trisubstituted butenynyl complexes **13a,b** were obtained, which like the disubstituted congeners **7a,b** constitute a pair of geometric isomers in a *c.* 3:1 ratio (Scheme 3).

A detailed description of the spectroscopic properties of the butenynyl complexes **13a,b** and of their vinylidene precursor **12** is not in order as most of their relevant spectroscopic data, reported in 'Experimental' nicely correlate with those of the butenynyl complexes **7a,b** and the vinylidene complex **10**, respectively.



Scheme 3. All reactions were performed in THF at room temperature unless otherwise stated. All cations were employed as BPh_4^- salts.

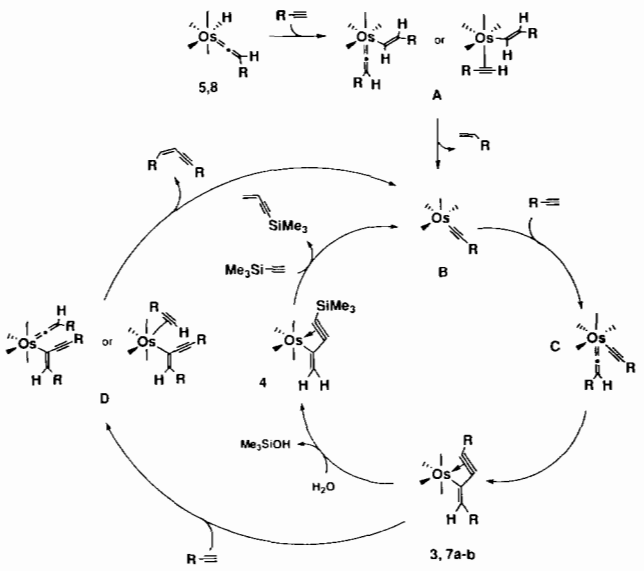
It is therefore reasonable to conclude that the butenynyl ligands **7a,b** are formed by C–C coupling reactions between C≡CPh and C=C(H)Ph ligands. Identical mechanistic conclusions can be arrived at for the trimethylsilyl-substituted complex **3**. In fact, the (alkynyl)hydride complex **6** reacts with trityl tetrafluoroborate in THF in the presence of $HC{\equiv}CSiMe_3$ to give $CHPh_3$ and the butenynyl **3**.

The latter reaction is of particular interest as it may serve as a simple, alternative method for the preparation of butenynyl metal complexes via (alkynyl)hydrides which constitute an ubiquitous class or organometallic compounds.

Mechanism of 1-alkyne dimerization to 1,4-disubstituted-but-3-en-1-ynes

Incorporation of the above experimental evidence leads to the mechanism shown in Scheme 4 for the osmium-catalyzed dimerization of HC≡CR (R = Ph, $SiMe_3$) to either 1,4-disubstituted- or monosubstituted-but-3-en-1-ynes. In Scheme 4, the skeleton of the tripodal ligand and the phosphorus donor atoms are omitted for clarity.

Once the dinitrogen ligand in **1** has been displaced by the 1-alkyne, the latter rearranges to vinylidene via 1,2-hydrogen shift. The resulting (vinylidene)hydride complex (**5** or **8**) reacts with a second alkyne molecule, which promotes migration of hydride to the C_α vinylidene carbon. As a result, a σ-vinyl complex is formed in which the added alkyne may be either π-bonded or rearranged to vinylidene. Actually, in view of the proclivity of $[(PP_3)OsX]^+$ systems (X = H, Cl, C≡CR) to promote the 1-alkyne to vinylidene tautomerism, a (vinylidene)vinyl intermediate cannot be excluded a priori.



Scheme 4. Suggested mechanism for the regio- and stereocontrolled dimerization of phenylacetylene and trimethylsilylacetylene to 1,4-disubstituted-but-3-en-1-ynes. The internal cycle refers to the synthesis of trimethylsilylbut-3-en-1-yne.

Whatever its structure, intermediate **A** undergoes a fast intramolecular reaction to give free alkene and an unsaturated σ-alkynyl species. Indeed, σ-bond metathesis reactions between alkyne C–H and metal–C bonds to give σ-alkynyl complexes have a large occurrence in organometallic chemistry [40c, 53]. Thermodynamic data for such processes are available [54]. On the other hand, free alkenes have also been reported to form by intramolecular acid–base interaction between σ-vinyl ligands and *cis* ligands bearing acidic hydrogen atoms; see for example the conversion of $[(PP_3)Fe(H_2)(CH{=}CHPh)]^+$ to styrene and $[(PP_3)FeH]^+$ for which

kinetic studies are available [55]. Accordingly, alkene formation may also be envisaged as occurring via intramolecular reaction between the acidic vinylidene hydrogen and the basic vinyl α-carbon.

Even though a σ-alkynyl complex of the formula $[(PP_3)Os(C{\equiv}CR)]^+$ has not been detected along the reaction path that converts **1** to either **3** or **7a,b**, its formation as initial step of the catalysis cycle can safely be proposed on the basis of several literature reports [17, 18]. In particular, the σ-alkynyl $[(PP_3)Ru(C{\equiv}CSiMe_3)]BPh_4$ has been isolated along the reaction sequence that converts $[(PP_3)Ru(H)(N_2)]BPh_4$ to (*E*)-$[(PP_3)Ru\{\eta^3\text{-}(Me_3Si)C_3CH(SiMe_3)\}]BPh_4$ [17]. The capability of σ-alkynyl metal complexes to catalyze the dimerization of 1-alkynes has been demonstrated, *inter alia*, by Horton [39c] for the regioselective synthesis of 2,4-disubstituted-but-1-en-3-ynes, and by Wakatsuki *et al.* for the regio- and stereocontrolled dimerization of tert-butylacetylene to (*Z*)-1,4-di-tert-butylbutatriene [27].

In view of the experimental evidence reported above, the formation of an η^3-butenynyl complex (**3** or **7a,b**) from the σ-alkynyl intermediate **B** indeed occurs via a (vinylidene)alkynyl intermediate (**C**). A change in the hapticity from η^3 to η^1 of the hemilabile butenynyl ligand in intermediate **C** provides a free coordination site at which an incoming alkyne molecule may either coordinate in π fashion or rearrange to vinylidene. Irrespective of the bonding mode of the alkyne in intermediate **D**, a formal σ-bond metathesis reaction finally gives free (*Z*)-1,4-disubstituted-but-3-en-2-yne and the σ-alkynyl catalyst. This reaction has several precedents in the literature (see also the reactions of **3** and **13** with HC≡CPh) [17, 18, 28].

As mentioned in a previous section, the η^3-butenynyl complexes **3** and **7a,b** are the only metal species detected by $^{31}P\{^1H\}$ NMR spectroscopy in the course of the catalytic reactions. This suggests that the η^3-butenynyl complexes are reagents in the rate determining step. Even though kinetic studies have not been carried out, this hypothesis is sound and corroborated by the observation that the η^3-butenynyl complexes are rapidly formed at low temperature (0–5 °C), whereas their further reaction with 1-alkynes to give free butenynes requires the use of a higher temperature (*c.* 66 °C).

The catalytic formation of 1,4-bis(trimethylsilyl)but-3-en-1-ynes is quenched when the reaction between **1** and $HC{\equiv}CSiMe_3$ is performed in the presence of either water of ethanol. Both reagents, in fact, are able to selectively cleave the C–Si bond of the vinyl moiety at the stage of formation of the 1,4-disubstituted-butenynyl complex. As a result, a monosubstituted-trimethylsilyl butenynyl complex is formed, which then reacts with further $HC{\equiv}CSiMe_3$ to give $CH_2{=}CH{-}C{\equiv}CSiMe_3$ and the σ-alkynyl catalyst. Indirectly, the latter reaction provides additional experimental support to the suggested participation of the butenynyl complexes in the rate determining step of the catalysis cycle.

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