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Multiple Re−C Bonds at the $[\{MeC(CH_2PPh_2)_3\}Re(CO)_2]^+$ Auxiliary

Claudio Bianchini,*,† Andrea Marchi,‡ Lorenza Marvelli,‡ Maurizio Peruzzini,*,†
Antonio Romerosa,† and Roberto Rossi*,‡

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR,
Via J. Nardi 39, 50132 Firenze, Italy, and Laboratorio di Chimica Nucleare ed Inorganica,
Dipartimento di Chimica, Università di Ferrara, Via Borsari 46, 44100 Ferrara, Italy

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After displacement of the η^2-H_2 ligand from $[(triphos)Re(CO)_2(\eta^2\text{-}H_2)]BF_4$ (**2**), ethyne and various 1-alkynes, HC≡CR, are tautomerized at the Re(I) center to vinylidene ligands (R = H, Ph, *p*-tolyl, COOEt, *n*-C_6H_{13}, $SiMe_3$). A kinetic π-alkyne adduct is intercepted at low temperature during the reaction between **2** and ethyne. The primary vinylidene complex $[(triphos)Re(CO)_2(C{=}CH_2)]BF_4$ (**7**-BF_4) can also be obtained by reaction of the (trimethylsilyl)vinylidene complex $[(triphos)Re(CO)_2\{C{=}C(H)SiMe_3\}]BF_4$ with stoichiometric water. Unprecedented examples of addition of either water or alcohols to Re−vinylidene moieties to give hydroxycarbene or alkoxycarbene complexes are presented. In particular, an excess of water transforms **7**-BF_4 into the secondary hydroxycarbene complex $[(triphos)Re(CO)_2\{C(OH)CH_3\}]BF_4$ (**11**), which can be isolated in the solid state. Upon thermolysis in refluxing tetrahydrofuran, **11** selectively converts to the tricarbonyl complex $[(triphos)Re(CO)_3]BF_4$ and methane. Deprotonation of **11** by mild bases gives the acetyl derivative $(triphos)Re(CO)_2(COCH_3)$, which regenerates the hydroxycarbene precursor by protonation with strong acids. The ethoxycarbene complexes $[(triphos)Re(CO)_2\{C(OEt)CH_2R\}]BPh_4$ (R = H, COOEt) are prepared by nucleophilic addition of ethanol across the C=C double bond of the corresponding vinylidene derivatives. Neutral σ-alkynyl complexes of the general formula $(triphos)Re(CO)_2(C{\equiv}CR)$ (R = Ph, *p*-tolyl, COOEt, *n*-C_6H_{13}, H) are obtained by reaction of the vinylidene derivatives with strong bases. The reaction of the σ-alkynyl complexes with various methylating agents affords disubstituted vinylidene derivatives, herein exemplified by $[(triphos)Re(CO)_2\{C{=}C(Me)Ph\}](OSO_2CF_3)$. The structural identities in the solid state of the phenylvinylidene complex $[(triphos)Re(CO)_2\{C{=}C(H)Ph\}]BF_4$ and of the ethoxycarbene complex $[(triphos)Re(CO)_2\{C(OEt)CH_3\}]BPh_4$ have been determined by X-ray diffraction analyses. In both complexes the metal center is octahedrally coordinated by a *fac* triphos ligand, by two mutually *cis* terminal carbonyls, and by the organyl ligand.

Introduction

The chemistry of rhenium−carbon multiple bonds has experienced much progress in recent years.[1] Several vinylidene, carbene, and carbyne complexes have been synthesized and many exotic reactions have been disclosed which are made possible by the ability of rhenium to stabilize intermediates that generally have only a fleeting existence in related reactions with other transition metals.[2]

A glance through the literature shows that most of the Re−C multiple bond chemistry is based on cyclopentadienyl ligands.[1,2] In earlier work, we have demonstrated that the tripodal triphosphine $MeC(CH_2PPh_2)_3$ (triphos) is as efficient as the isolelectronic and isolobal cyclopentadienyl ligands in forming rhenium complexes in various metal oxidation states and coordination numbers.[3,4] Unlike cyclopentadienyl ligands, triphos provides its metal complexes with a much higher thermal stability and thus is more amenable to catalytic studies than cyclopentadienyl groups.[5]

Herein are reported the reactions of the $[(triphos)Re(CO)_2]^+$ fragment with ethyne and selected 1-alkynes to give primary Re(I) vinylidene complexes whose remarkable stability has allowed us to investigate their

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† ISSECC, CNR.

‡ Università di Ferrara.

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reactivity toward nucleophiles such Bronsted bases, alcohols, and water. As a result, a variety of new Re−organyl complexes have been synthesized, which includes σ-alkynyl, η^1-acyl, primary, secondary, and tertiary vinylidene, secondary hydroxycarbene, and alkoxycarbene derivatives.

Experimental Section

General Procedures. Tetrahydrofuran (THF), toluene, *n*-hexane, and diethyl ether were purified by distillation over sodium/benzophenone under a nitrogen atmosphere. Dichloromethane and ethanol were purified by distillation under nitrogen over calcium hydride. Terminal alkynes were purchased from Aldrich, their purity was checked by ^{1}H NMR spectroscopy, and, when necessary, they were distilled under a N_2 atmosphere prior to use. 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 diethyl ether or *n*-pentane before being dried in a stream of nitrogen. The ligand $CH_3C(CH_2PPh_2)_3$ (triphos)[6] and the complexes [(triphos)Re(CO)$_2$H] (**1**)[4] and [(triphos)Re(CO)$_2$(η^2-H$_2$)]BF$_4$ (**2**)[4] were prepared as described in the literature. Deuterated solvents for NMR measurements (Merck and Aldrich) were dried over molecular sieves (4 Å). ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Varian VXR 300, Bruker AC200, or Bruker AVANCE DRX 500 spectrometers operating at 299.94, 200.13, or 500.13 MHz (^{1}H) and 75.42, 50.32, or 125.80 MHz (^{13}C), respectively. Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (^{1}H) or the deuterated solvent multiplet (^{13}C). ^{13}C-DEPT and gated ^{13}C{^{1}H}-decoupled NMR experiments were run on the Bruker AC200 spectrometer. ^{1}H,^{13}C-2D HETCOR NMR experiments were recorded on either the Bruker AC200 spectrometer using the XHCORR pulse program or the Bruker AVANCE DRX 500 spectrometer equipped with a 5-mm triple resonance probe head for ^{1}H detection and inverse detection of the heteronucleus (inverse correlation mode, HMQC experiment) with no sample spinning. The ^{1}H,^{1}H-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{^{1}H} 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 broadband 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. Computer simulations of NMR spectra were carried out with a locally developed package containing the programs LAOCN3[7] and DAVINS[8] 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. Infrared spectra were recorded in KBr pellets on a Nicolet 510 P spectrometer operating in the FT mode or as Nujol mulls on a Perkin-Elmer 1600 series FT-IR spectrometer between KBr plates. 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 *ca.* 1×10^{-3} M in nitroethane solutions at room temperature (21 °C). Elemental analyses were performed with a Carlo Erba Model 1106 elemental analyzer.

Synthesis of the Vinylidene Complexes [(triphos)Re(CO)$_2${C=C(H)R}]Y [R = Ph (3), *p*-tolyl (4), COOEt (5), *n*-C$_6$H$_{13}$ (6), Y = BF$_4$, BPh$_4$]. General Procedure. A dichloromethane (10 mL) solution of the complex [(triphos)Re(CO)$_2$(η^2-H$_2$)]BF$_4$ (**2**) was prepared in a 25 mL Schlenk flask by reaction of [(triphos)Re(CO)$_2$H] (**1**) (0.25 g, 0.26 mmol) with HBF$_4$·OMe$_2$ (33 μL, 0.27 mmol) at −10 °C.[4] To this solution a slight excess (*ca.* 10%) of the terminal alkyne was added with stirring. Immediately the color of the resulting solution changed from pale yellow to either deep violet (R = Ph, *p*-tolyl) or pale purple (R = COOEt, *n*-C$_6$H$_{13}$). After the reaction mixture was allowed to reach room temperature, the solvent was removed in vacuo, and the solid residue was extracted twice with 3 mL of THF. After addition of ethanol (2 mL) and partial evaporation of the solvent under a flow of nitrogen, the vinylidene complexes [(triphos)Re(CO)$_2${C=C(H)R}]BF$_4$ [R = Ph (**3**-BF$_4$), *p*-tolyl (**4**-BF$_4$), COOEt (**5**-BF$_4$), *n*-C$_6$H$_{13}$ (**6**-BF$_4$)] were obtained in very good yield (≥89%).

Addition of NaBPh$_4$ (0.10 g, 0.22 mmol) in 2 mL of ethanol and workup as above yielded the corresponding tetraphenylborate salts in yields higher than 95%.

All the vinylidene complexes are air stable in the solid state, whereas an inert atmosphere is required for their manipulation in solution (acetone, THF, chlorinated hydrocarbons, nitroethane).

[(triphos)Re(CO)$_2${C=C(H)Ph}]BPh$_4$ (3-BPh$_4$): violet, yield 98%. Anal. Calcd for $C_{75}H_{65}BO_2P_3Re$: C, 69.93; H, 5.08. Found: C, 69.82; H, 4.99. ^{1}H NMR (CD$_2$Cl$_2$, 22 °C, 200.13 MHz): δ 1.75 (q, J_{HP} 3.0 Hz, CH$_{3(\text{triphos})}$, 3H), δ 2.70 (m, CH$_{2(\text{triphos})}$, 6H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 22 °C, 75.42 MHz): δ 39.8 (q, J_{CP} 10.9 Hz, CH$_{3(\text{triphos})}$), δ 39.9 (q, J_{CP} 2.7 Hz, CH$_3$*C*$_{(\text{triphos})}$), δ 32.7 (m, CH$_2$P$_{\text{axial}}$), δ 33.2 (br d, J_{CP} 4.0 Hz, *CH$_2$*P$_{\text{equat}}$). $\Lambda_{M(\text{nitroethane})} = 55\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$.

[(triphos)Re(CO)$_2${C=C(H)(*p*-tolyl)}]BPh$_4$ (4-BPh$_4$): violet, yield 96%. Anal. Calcd for $C_{76}H_{67}BO_2P_3Re$: C, 70.09; H, 5.19. Found: C, 69.87; H, 5.09. ^{1}H NMR (CDCl$_3$, 22 °C, 299.94 MHz): δ 1.82 (br s, CH$_{3(\text{triphos})}$, 3H), δ 2.40 (s, CH$_{3(p\text{-tolyl})}$, 3H), δ 2.70 (m, CH$_{2(\text{triphos})}$, 6H). ^{13}C{^{1}H} NMR (CDCl$_3$, 22 °C, 75.42 MHz): δ 39.1 (q, J_{CP} 10.6 Hz, CH$_{3(\text{triphos})}$), δ 39.3 (q, J_{CP} 2.9 Hz, CH$_3$*C*$_{(\text{triphos})}$), δ 32.1 (br d, J_{CP} 24.5 Hz, *CH$_2$*P$_{\text{axial}}$), δ 32.2 (td, N = $J_{CPequat'} + J_{CPequat''} = 14.9$ Hz, $J_{CPaxial}$ 5.2 Hz, CH$_2$P$_{\text{equat}}$), δ 21.04 (s, CH$_{3(p\text{-tolyl})}$). $\Lambda_{M(\text{nitroethane})} = 58\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$.

[(triphos)Re(CO)$_2${C=C(H)CO$_2$Et}]BPh$_4$ (5-BPh$_4$): pink, yield 95%. Anal. Calcd for $C_{72}H_{65}BO_4P_3Re$: C, 67.35; H, 5.10. Found: C, 67.25; H, 5.15. ^{1}H NMR (CD$_2$Cl$_2$, 22 °C, 200.13 MHz): δ 1.32 (t, J_{HH} 7.1 Hz, CH$_{3(\text{ester})}$, 3H), δ 1.58 (q, J_{HP} 3.0 Hz, CH$_{3(\text{triphos})}$, 3H), δ 2.62 (m, CH$_{2(\text{triphos})}$, 6H), δ 4.30 (q, J_{HH} 7.1 Hz, CH$_{2(\text{ester})}$, 2H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 22 °C, 75.42 MHz): δ 163.4 (s, COOEt), δ 61.6 (br s, OCH$_{2(\text{ester})}$), δ 40.0 (q, J_{CP} 9.9 Hz, CH$_{3(\text{triphos})}$), δ 39.8 (q, J_{CP} 3.3 Hz, CH$_3$*C*$_{(\text{triphos})}$), δ 33.5 (br t, J_{CP} 4.0Hz, CH$_2$P$_{\text{axial}}$), δ 32.6 (td, N = $J_{CPequat'} + J_{CPequat''} = 15.9$ Hz, $J_{CPaxial}$ 5.3 Hz, CH$_2$P$_{\text{equat}}$), δ 15.1 (s, CH$_{3(\text{ester})}$). $\Lambda_{M(\text{nitroethane})} = 52\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$.

[(triphos)Re(CO)$_2${C=C(H)C$_6$H$_{13}$}]BPh$_4$ (6-BPh$_4$): pink, yield 96%. Anal. Calcd for $C_{75}H_{73}BO_2P_3Re$: C, 69.49; H, 5.68. Found: C, 69.21; H, 5.18. ^{1}H NMR (CD$_2$Cl$_2$, 22 °C, 200.13 MHz): δ 0.89 (t, J_{HH} 6.6 Hz, CH$_{3(\text{hexyl})}$, 3H), δ 1.1−1.3 (m, CH$_{2(\text{hexyl})}$, 10 H), δ 1.53 (br s, CH$_{3(\text{triphos})}$, 3H), δ 2.38 (m, CH$_{2(\text{triphos})}$, 6H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 22 °C, 75.42 MHz): δ 40.2 (q, J_{CP} 10.0 Hz, CH$_{3(\text{triphos})}$), δ 39.9 (q, J_{CP} 3.2 Hz, CH$_3$*C*$_{(\text{triphos})}$), δ 32.6 (m, CH$_2$P$_{\text{axial}}$), δ 33.4 (td, N = $J_{CPequat'} + J_{CPequat''} = 15.3$ Hz, $J_{CPaxial}$ 4.5 Hz, CH$_2$P$_{\text{equat}}$), δ 32.3, δ 32.2, δ 29.6, δ 23.4, δ 20.3 (all singlets, CH$_{2(\text{hexyl})}$), δ 14.6 (s, CH$_{3(\text{hexyl})}$). $\Lambda_{M(\text{nitroethane})} = 49\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$.

[(triphos)Re(CO)$_2${C=C(H)Ph}]BF$_4$ (3-BF$_4$): violet, yield 92%. Anal. Calcd for $C_{51}H_{45}BF_4O_2P_3Re$: C, 58.02; H, 5.20. Found: C, 57.73; H, 5.15. $\Lambda_{M(\text{nitroethane})} = 80\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$.

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Table 1. $^{31}P\{^1H\}$ NMR Spectral Data and Selected IR Absorptions for the Complexes

	chem shift (ppm)^a			IR (cm^{-1})	
compd	$\delta(P_A)$	$\delta(P_M)$	J_{AM} (Hz)	ν(CO)	ν(other)
[(triphos)Re(CO)$_2${C$=$C(H)Ph}]Y^b (**3**)	−20.46	−15.98	25.5	2013, 1961	C$=$C 1654
[(triphos)Re(CO)$_2${C$=$C(H)(*p*-tolyl)}]Y^{b,c} (**4**)	−20.27	−16.04	25.6	2016, 1958	C$=$C 1639
[(triphos)Re(CO)$_2${C$=$C(H)CO$_2$Et}]Y^b (**5**)	−21.80	−15.22	25.9	2036, 1970	CO$_{ester}$ 1701, C$=$C 1607, COC 1223
[(triphos)Re(CO)$_2${C$=$C(H)C$_6$H$_{13}$}]Y^b (**6**)	−18.99	−15.24	24.2	2007, 1952	C$=$C 1663
[(triphos)Re(CO)$_2$(C$=$CH$_2$)]Y^b (**7**)	−19.78	−16.23	24.5	2011, 1946	C$=$C 1624
[(triphos)Re(CO)$_2${C(OEt)(CH$_3$)}]Y^b (**8**)	−16.62	−12.87	20.6	1968, 1900	COC 1269
[(triphos)Re(CO)$_2${C$=$C(H)SiMe$_3$}]BF$_4$ (**9**)	−19.49	−16.73	24.3		
[(triphos)Re(CO)$_2$(π-HC$\equiv$CH)]BF$_4$ (**10**)	−11.18	−22.49	24.5		
[(triphos)Re(CO)$_2${C(OH)CH$_3$}]BF$_4$^{d} (**11**)	−12.70	−13.82	19.1	1962, 1886	OH 3510
(triphos)Re(CO)$_2$(COCH$_3$)^d (**13**)	−9.07	−15.47	17.1	1939, 1866	CO$_{acetyl}$ 1621
(triphos)Re(CO)$_2$(C$\equiv$CPh) (**14**)	−7.14	−19.94	17.5	1942, 1881	C$\equiv$C 2079
(triphos)Re(CO)$_2${C$\equiv$C(*p*-tolyl)} (**15**)	−6.77	−20.10	25.6	1937, 1879	C$\equiv$C 2081
(triphos)Re(CO)$_2$(C$\equiv$CCO$_2$Et) (**16**)	−7.60	−19.00	18.9	1947, 1888	C$\equiv$C 2062, CO$_{ester}$ 1659, COC 1200
(triphos)Re(CO)$_2${C$\equiv$C(*n*-C$_6$H$_{13}$)} (**17**)	−6.99	−17.16	17.2	1937, 1881	C$\equiv$C 2101
(triphos)Re(CO)$_2$(C$\equiv$CH) (**18**)	−6.79	−20.08	17.8	1926, 1875	C$\equiv$C 1954
[(triphos)Re(CO)$_2${C$=$C(Me)Ph}]OSO$_2$CF$_3$ (**19**)	−20.52	−16.47	25.2	2004, 1940	C$=$C 1643
[(triphos)Re(CO)$_2${C(OEt)(CH$_2$CO$_2$Et)}]BPh$_4$ (**20**)	−18.09	−13.36	21.3	1962, 1902	CO$_{ester}$ 1734, COC 1290

[a] All measurements were recorded at room temperature in CD_2Cl_2 unless otherwise stated. All the $^{31}P\{^1H\}$ NMR spectra exhibit an AM$_2$ splitting pattern. [b] Y = BF4, BPh4. [c] In $CDCl_3$. [d] In THF-d_8.

[(triphos)Re(CO)$_2${C$=$C(H)(*p*-tolyl)}]BF$_4$ (4-BF$_4$): violet, yield 94%. Anal. Calcd for $C_{52}H_{47}BF_4O_2P_3Re$: C, 58.38; H, 4.43. Found: C, 58.07; H, 4.38. $\Lambda_{M(nitroethane)} = 81\ \Omega^{-1}$ cm^2 mol^{-1}.

[(triphos)Re(CO)$_2${C$=$C(H)CO$_2$Et}]BF$_4$ (5-BF$_4$): pink, yield 92%. Anal. Calcd for $C_{48}H_{45}BF_4O_4P_3Re$: C, 54.81; H, 4.31. Found: C, 54.69; H, 4.43. $\Lambda_{M(nitroethane)} = 76\ \Omega^{-1}$ cm^2 mol^{-1}.

[(triphos)Re(CO)$_2${C$=$C(H)C$_6$H$_{13}$}]BF$_4$ (6-BF$_4$): pink, yield 89%. Anal. Calcd for $C_{51}H_{53}BF_4O_2P_3Re$: C, 57.58; H, 5.02. Found: C, 57.54; H, 5.12. $\Lambda_{M(nitroethane)} = 77\ \Omega^{-1}$ cm^2 mol^{-1}.

Reaction of [(triphos)Re(CO)$_2$(η^2-H$_2$)]BF$_4$ (2) with Ethynyltrimethylsilane and NaBPh$_4$. Neat ethynyltrimethylsilane, HC$\equiv$CSiMe$_3$ (40 μL, 0.29 mmol), was syringed into a dichloromethane (10 mL) solution of **2** prepared as described above. Analogous workup gave rust-colored crystals of the unsubstituted vinylidene complex [(triphos)Re(CO)$_2$(C$=$CH$_2$)]BPh$_4$ (**7**-BPh$_4$) invariably contaminated by the alkoxycarbene complex [(triphos)Re(CO)$_2${C(OEt)(CH$_3$)}]BPh$_4$ (**8**-BPh$_4$) (5−10%) (*vide infra*).

Reaction of [(triphos)Re(CO)$_2$(η^2-H$_2$)]BF$_4$ (2) with Ethynyltrimethylsilane in a Sealed NMR Tube. CD_2Cl_2 (0.8 mL) was transferred under nitrogen into a 5-mm NMR tube previously charged with **1** (0.025 g, 0.028 mmol). Addition of 3.3 μL (0.027 mmol) of HBF$_4$·OMe$_2$ completely dissolved the monohydride to give a solution of **2** which was cooled to −78 °C. After 4.0 μL (0.029 mmol) of HC$\equiv$CSiMe$_3$ was syringed into the tube, this was flame-sealed in a dry-ice bath and then introduced into a NMR probe precooled at −45 °C. The reaction progress was monitored by variable-temperature ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy. A slow reaction occurred already at −18 °C to give the (trimethylsilyl)vinylidene complex [(triphos)Re(CO)$_2${C$=$C(H)SiMe$_3$}]BF$_4$ (**9**) and the vinylidene complex [(triphos)Re(CO)$_2$(C$=$CH$_2$)]BF$_4$ (**7**-BF$_4$) in a ratio of 1 to 1.5 since the acquisition of the first $^{31}P\{^1H\}$ NMR spectrum. The ^{1}H NMR spectrum showed the presence of free hydrogen (4.61 ppm). With time the concentration of **7**-BF$_4$ increased at the expense of that of **9**. Within 30 min at −15 °C, **7** was the only product detected by $^{31}P\{^1H\}$NMR spectroscopy. On warming of the NMR tube to room temperature, no change in the product composition was observed. GC-MS analysis of the reaction mixture showed the formation of HOSiMe$_3$ together with traces of O(SiMe$_3$)$_2$. NMR data for **9** (see also Tables 1 and 2): ^{1}H NMR (CD_2Cl_2, −15 °C, 200.13 MHz) δ 0.35 (s, SiMe$_3$, 9H), δ 1.66 (q, J_{HP} 1.7 Hz, CH$_{3(triphos)}$, 3H), δ 2.62 (d, $J_{HPaxial}$ 9.2 Hz, CH$_2$P$_{axial}$, 2H), δ 2.69 (m, CH$_2$P$_{equat}$, 4H).

Synthesis of [(triphos)Re(CO)$_2$(C$=$CH$_2$)]BF$_4$ (7-BF$_4$). Method A. To a CH_2Cl_2 solution of **2** prepared at −10 °C as described above, a slight excess of HC$\equiv$CSiMe$_3$ (40 μL, 0.29 mmol) and a few drops of water were added with stirring. After being stirred for 30 min at −10 °C, the solvent was removed in vacuo to give a rust-colored solid which was washed with ethanol and *n*-pentane. The crude product was crystallized from dichloromethane/*n*-hexane to afford **7**-BF$_4$ in analytically pure form. Yield: 92%.

Method B. A steady stream of ethyne was bubbled for *ca.* 1 min into a dichloromethane solution (10 mL) of **2** cooled at *ca.* 0 °C. After ethyne was replaced by nitrogen, the solution was heated to room temperature. The resulting red-orange solution was stirred for 30 min, and then the solvent was removed in vacuo to give a rust-colored residue of **7**-BF$_4$. Crystallization from dichloromethane/*n*-hexane gave crystals of **7**-BF$_4$. Yield: 90%. Anal. Calcd for $C_{45}H_{41}BF_4O_2P_3Re$: C, 55.17; H, 4.22. Found: C, 54.85; H, 4.16. $\Lambda_{M(nitroethane)} = 82\ \Omega^{-1}$ cm^2 mol^{-1}.

Prolonged bubbling of ethyne must be avoided as it causes extensive decomposition of **7**-BF$_4$ to unidentified products.

The tetraphenylborate salt **7**-BPh$_4$ was obtained by crystallization of the crude product from THF/*n*-hexane (2:1) in the presence of NaBPh$_4$ (1.1 equiv). Anal. Calcd for $C_{69}H_{61}BO_2P_3Re$: C, 68.37; H, 5.07. Found: C, 68.46; H, 4.90. $\Lambda_{M(nitroethane)} = 53\ \Omega^{-1}$ cm^2 mol^{-1}. ^{1}H NMR (CD_2Cl_2, 22 °C, 200.13 MHz): δ 1.72 (q, J_{HP} 4.2 Hz, CH$_{3(triphos)}$, 3H), δ 2.67 (d, $J_{HPaxial}$ 4.2 Hz, CH$_2$P$_{axial}$, 2H), δ 2.70 (m, CH$_2$P$_{equat}$, 4H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C, 50.32 MHz): δ 39.8 (q, J_{CP} 10.4 Hz, CH$_{3(triphos)}$), δ 39.2 (q, J_{CP} 3.0 Hz, CH$_3$*C*$_{(triphos)}$), δ 32.6−35.3 (m, CH$_{2(triphos)}$).

Reaction of [(triphos)Re(CO)$_2$(η^2-H$_2$)]BF$_4$ (2) with Ethyne in a Sealed NMR Tube. A solution of **2** (0.028 mmol) in CD_2Cl_2 (1.0 mL) was prepared in a 5-mm NMR tube as described above. After two freeze/pump thaw cycles at −196 °C, the solution was frozen and pumped on at −196 °C. After adding ethyne (*ca.* 4 equiv) via syringe, the tube was flame-sealed and then introduced into a NMR probe precooled at −50 °C. The reaction was followed by variable-temperature ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy. The reaction between **2** and HC$\equiv$CH already occurred at −15 °C to give an intermediate species which we assign the formula [(triphos)Re(CO)$_2$(π-HC$\equiv$CH)]BF$_4$ (**10**). With time, **10** converted to **7**-BF$_4$. A complete transformation of **2** into **10** and **7**-BF$_4$ was observed after 30 min at −15 °C, while the secondary transformation of **10** into **7**-BF$_4$ completely occurred in further 30 min. NMR data for **10** (see also Tables 1 and 2): ^{1}H NMR (CD_2Cl_2, −15 °C, 200.13 MHz) δ 1.72 (q, J_{HP} 1.8 Hz, CH$_{3(triphos)}$, 3H), δ 2.69 (m, CH$_{2(triphos)}$, 6H).

Reaction of [(triphos)Re(CO)$_2$(C$=$CH$_2$)]BF$_4$ with H$_2$O in a Sealed NMR Tube. A 3 equiv amount of distilled water (3.5 μL, 0.19 mmol) was introduced via syringe into a THF-d_8

(1.0 mL) solution of **7**-BF_4 (0.06 g, 0.06 mmol) in a 5-mm NMR tube cooled at −78 °C. The tube was flame-sealed under nitrogen and then introduced into a NMR probe at 20 °C. The reaction was monitored at this constant temperature by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. Within 5 min a new species was formed, which was identified as the hydroxycarbene complex [(triphos)Re(CO)$_2${C(OH)CH$_3$}]BF$_4$ (**11**). The complete conversion of **7**-BF_4 to **11** occurred in *ca.* 1 h. On long standing in the NMR tube, the secondary transformation of **11** into the known tricarbonyl complex [(triphos)Re(CO)$_3$]BF$_4$ (**12**)[4] and free methane (^1H NMR singlet at *ca.* 0.18 ppm) slowly occurred (*ca.* 23% conversion in 72 h as determined by ^{31}P NMR integration). At 60 °C, the complete transformation of **11** into **12** and free methane occurred in 30 min. NMR data for **11** (see also Tables 1 and 2): ^1H NMR (THF-d_8, 21 °C, 200.13 MHz) δ 1.73 (q, J_{HP} 2.7 Hz, $CH_{3(triphos)}$, 3H), δ 2.74 (m, $CH_{2(triphos)}$, 6H) (the resonance due to the hydroxy proton was not observed); $^{13}C\{^1H\}$ NMR (THF-d_8, 21 °C, 50.32 MHz) δ 53.6 (d, $J_{CPtrans}$ 5.6 Hz, $CH_{3(carbene)}$), δ 40.6 (q, J_{CP} 10.0 Hz, $CH_{3(triphos)}$), δ 41.0 (q, J_{CP} 5.3 Hz, $CH_3C_{(triphos)}$), δ 36.1 (m, CH_2P_{axial}), δ 36.4 (td, $N = J_{CPequat'} + J_{CPequat''} = 14.1$ Hz, $J_{CPaxial}$ 5.9 Hz, CH_2P_{equat}).

Substitution of D_2O for H_2O in the above reaction gave [(triphos)Re(CO)$_2${C(OD)CD$_3$}]BF$_4$ (**11**-d_4).

Synthesis of [(triphos)Re(CO)$_2${C(OH)CH$_3$}]BF$_4$ (11). A 10 equiv amount of water (46 μL, 2.55 mmol) was syringed into a THF solution (3 mL) of **7**-BF_4 (0.25 g, 0.25 mmol) at 0 °C under vigorous stirring. Within a few minutes, the red-orange solution turned red-yellow. Removal of the solvent in vacuo gave a yellow-orange powder which was washed with 2 × 2 mL of a *n*-hexane/ethanol mixture (4:1 v/v) and then with *n*-pentane (2 × 2 mL). $^{31}P\{^1H\}$ NMR analysis of this product showed it to be a *ca.* 9.5:0.5 mixture of the hydroxycarbene derivative **11** and of the acetyl derivative (triphos)Re(CO)$_2$(COCH$_3$) (**13**) (*vide infra*).

Thermolysis of 11 in THF. A solid sample of **11** (0.10 g, 0.10 mmol; contaminated by *ca.* 5% of **13**) was dissolved in 5 mL of THF and gently refluxed for 1 h. On cooling of the sample to room temperature, amber colored crystals of the tricarbonyl complex **12** separated. Yield: 90%. An independent experiment performed on an authentic specimen of the acetyl complex **13** showed that this product is thermally stable in refluxig THF.

Synthesis of (triphos)Re(CO)$_2$(COCH$_3$) (13). A slight excess of triethylamine (45 μL, 0.32 mmol) was syringed into a stirred THF solution (8 mL) of **11** prepared as described above from **7**-BF_4 (0.25 g, 0.26 mmol) and water (14.0 μL, 0.78 mmol). Addition of *n*-hexane (10 mL) and evaporation of the solvent under a brisk current of nitrogen gave a mixture of the acetyl complex **13** and of [HNEt$_3$]BF$_4$. Recrystallization of the crude reaction mixture from THF/EtOH gave yellow crystals of **13** in 73% yield. Anal. Calcd for $C_{45}H_{42}O_3P_3Re$: C, 59.40; H, 4.65. Found: C, 59.28; H, 4.72. ^1H NMR (THF-d_8, 20 °C, 200.13 MHz): δ 1.44 (q, J_{HP} 2.7 Hz, $CH_{3(triphos)}$, 3H), δ 2.3−2.5 (m, $CH_{2(triphos)}$, 6H). $^{13}C\{^1H\}$ NMR (THF-d_8, 20 °C, 50.32 MHz): δ 57.2 (d, $J_{CPtrans}$ 10.4 Hz, $CH_{3(acetyl)}$), δ 41.3 (q, J_{CP} 3.7 Hz, $CH_3C_{(triphos)}$), δ 41.1 (q, J_{CP} 9.3 Hz, $CH_{3(triphos)}$), δ 37.7 (dt, $J_{CPaxial}$ 18.9 Hz, $J_{CPequat}$ 3.1 Hz, CH_2P_{axial}), δ 36.9 (td, $N = J_{CPequat'} + J_{CPequat''} = 14.0$ Hz, $J_{CPaxial}$ 7.3 Hz, CH_2P_{equat}).

Reaction of 13 with HBF$_4$·OMe$_2$. A stoichiometric amount of HBF$_4$·OMe$_2$ was syringed into a THF-d_8 solution (0.8 mL) of **13** (0.030 g, 0.033 mmol) in a 5-mm screw-cap NMR tube. $^{31}P\{^1H\}$ and ^1H NMR analysis of the resulting yellow solution showed the complete transformation of **13** into the hydroxycarbene complex **11.**

Synthesis of the σ-Alkynyl Complexes (triphos)Re(CO)$_2$(C≡CR) [R = Ph (14), *p*-tolyl (15), COOEt (16), *n*-C$_6$H$_{13}$ (17), H (18)]. A Schlenk tube was charged with the appropriate vinylidene complex (**3**−**7**) (*ca.* 0.25 mmol) in THF (5 mL) at −78 °C. Solid KO^{t}Bu (0.03 g, 0.27 mmol) was added with stirring. As a result, an immediate reaction occurred to give a colorless solution (occasionally pale yellow). The reaction mixture was stirred for 30 min at room temperature. After the solvent was removed in vacuo, the off-white (occasionally yellowish) residue was extracted with dichloromethane (2 × 3 mL). Addition of ethanol/*n*-hexane (10 mL, 1:1 v/v) to the CH_2Cl_2 solution caused the precipitation of the alkynyl derivatives **14**−**18** as off-white microcrystals. Replacing solid KO^{t}Bu with LiHBEt$_3$ or NEt$_3$ in the above preparations gave the alkynyl derivatives in similar yields.

(triphos)Re(CO)$_2$(C≡CPh) (14): off-white, yield 90%. Anal. Calcd for $C_{51}H_{44}O_2P_3Re$: C, 63.28; H, 4.58. Found: C, 63.06; H, 4.64. ^1H NMR (CD_2Cl_2, 22 °C, 200.13 MHz): δ 1.45 (br s, $CH_{3(triphos)}$, 3H), δ 2.46 (m, $CH_{2(triphos)}$, 6H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C, 50.32 MHz): δ 40.9 (q, J_{CP} 9.7 Hz, $CH_{3(triphos)}$), δ 40.1 (q, J_{CP} 4.2 Hz, $CH_3C_{(triphos)}$), δ 36.1 (dt, $J_{CPaxial}$ 22.4 Hz, $J_{CPequat}$ 3.0 Hz, CH_2P_{axial}), δ 34.5 (td, $N = J_{CPequat} + J_{CPequat'} = 15.4$ Hz, $J_{CPaxial}$ 4.5 Hz, CH_2P_{equat}).

(triphos)Re(CO)$_2${C≡C(*p*-tolyl)} (15): off-white, yield 92%. Anal. Calcd for $C_{52}H_{46}O_2P_3Re$: C, 63.60; H, 4.72. Found: C, 63.47; H, 4.81. ^1H NMR (CD_2Cl_2, 22 °C, 299.94 MHz): δ 1.41 (br s, $CH_{3(triphos)}$, 3H), δ 2.41 (m, $CH_{2(triphos)}$, 6H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C, 50.32 MHz): δ 41.0 (q, J_{CP} 11.1 Hz, $CH_{3(triphos)}$), δ 40.2 (q, J_{CP} 2.4 Hz, $CH_3C_{(triphos)}$), δ 35.2 (br d, $J_{CPaxial}$ 21.0 Hz, CH_2P_{axial}), δ 34.6 (m, CH_2P_{equat}).

(triphos)Re(CO)$_2$(C≡CCO$_2$Et) (16): off-white, yield 92%. Anal. Calcd for $C_{48}H_{44}O_4P_3Re$: C, 59.81; H, 4.60. Found: C, 59.62; H, 4.55. ^1H NMR (CD_2Cl_2, 22 °C, 200.13 MHz): δ 1.46 (br s, $CH_{3(triphos)}$, 3H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C, 50.32 MHz): δ 42.3 (q, J_{CP} 8.4 Hz, $CH_{3(triphos)}$), δ 41.9 (q, J_{CP} 4.2 Hz, $CH_3C_{(triphos)}$), δ 37.3 (br d, $J_{CPaxial}$ 23.3 Hz, CH_2P_{axial}), δ 36.2 (td, $N = J_{CPequat} + J_{CPequat'} = 15.2$ Hz, $J_{CPaxial}$ 6.1 Hz, CH_2P_{equat}).

(triphos)Re(CO)$_2${C≡C(*n*-C$_6$H$_{13}$)} (17): off-white, yield 86%. Anal. Calcd for $C_{51}H_{52}O_2P_3Re$: C, 62.76; H, 5.37. Found: C, 62.58; H, 5.50. ^1H NMR (CD_2Cl_2, 22 °C, 200.13 MHz): δ 1.53 (br s, $CH_{3(triphos)}$, 3H), δ 2.46 (m, $CH_{2(triphos)}$, 6H).

(triphos)Re(CO)$_2$(C≡CH) (18): off-white, yield 90%. Anal. Calcd for $C_{45}H_{40}O_2P_3Re$: C, 60.60; H, 4.52. Found: C, 60.51; H, 4.42. ^1H NMR (CD_2Cl_2, 22 °C, 200.13 MHz): δ 1.44 (q, J_{HP} 2.7 Hz, $CH_{3(triphos)}$, 3H), δ 2.41 (m, $CH_{2(triphos)}$, 6H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C, 50.32 MHz): δ 40.5 (q, J_{CP} 9.8 Hz, $CH_{3(triphos)}$), δ 39.9 (q, J_{CP} 4.3 Hz, $CH_3C_{(triphos)}$), δ 37.3 (dt, $J_{CPaxial}$ 23.2 Hz, $J_{CPequat}$ 2.8 Hz, CH_2P_{axial}), δ 34.3 (td, $N = J_{CPequat} + J_{CPequat'} = 14.7$ Hz, $J_{CPaxial}$ 6.1 Hz, CH_2P_{equat}).

Reaction of (triphos)Re(CO)$_2$(C≡CR) (R = H, Ph, *p*-tolyl, COOEt, *n*-C$_6$H$_{13}$) with HBF$_4$·OMe$_2$. A Schlenk flask was charged with the appropriate alkynyl derivative (**14**−**18**) (*ca.* 0.2 mmol) in dichloromethane (5 mL) at −20 °C. A 1 equiv amount of HBF$_4$·OMe$_2$ (25 μL, 0.20 mmol) was syringed under vigorous stirring. To the resulting dark violet or pale purple solutions was added NaBPh$_4$ (0.10 g, 0.22 mmol) in 5 mL of ethanol. Concentration under a brisk current of nitrogen gave the vinylidene complexes **3**−**7** in almost quantitative yield.

Synthesis of [(triphos)Re(CO)$_2${C=C(Me)Ph}](OSO$_2$CF$_3$) (19-OSO$_2$CF$_3$). By addition of methyl triflate (45 μL, 0.41 mmol) to a solution of **14** (0.40 g, 0.41 mmol) in dichloromethane (20 mL) at −20 °C, a deep violet solution was obtained from which violet crystals of the disubstituted vinylidene complex **19**-OSO$_2$CF$_3$ separated at room temperature after addition of ethanol (20 mL) and slow evaporation of the solvent under a nitrogen stream. Yield: 96%. Anal. Calcd for $C_{53}H_{47}F_3O_5P_3ReS$: C, 56.23; H, 4.18. Found: C, 56.08; H, 4.14. The vinylidene iodide salt **19**-I was obtained using CH_3I (28 μL, 0.41 mmol) instead of methyl triflate as methylating agent. Yield: 91%. Anal. Calcd for $C_{52}H_{47}IO_2P_3Re$: C, 56.27; H, 4.27. Found: C, 56.11; H, 4.20. ^1H NMR (CD_2Cl_2, 22 °C, 299.94 MHz): δ 1.72 (q, J_{HP} 2.8 Hz, $CH_{3(triphos)}$, 3H), δ 2.60 (m, CH_2P_{equat}, 2H), δ 2.70 (d, $J_{HPaxial}$ 9.4 Hz, CH_2P_{axial}, 2H), δ 2.78 (m, CH_2P_{equat}, 2H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C, 75.42 MHz): δ 40.0 (q, J_{CP} 10.6 Hz, $CH_{3(triphos)}$), δ 39.8 (br s, $CH_3C_{(triphos)}$), δ 32.8 (dt, $J_{CPaxial}$ 22.8 Hz, $J_{CPequat}$ 2.5 Hz, CH_2P_{axial}), δ 33.4 (td, $N = J_{CPequat'} + J_{CPequat''} = 15.2$ Hz, $J_{CPaxial}$ 5.3 Hz, CH_2P_{equat}).

Synthesis of [(triphos)Re(CO)$_2${C(OEt)(CH$_3$)}]BF$_4$ (8-BF$_4$). Method A (One-Pot Procedure). Neat ethynyltrimethylsilane, HC≡CSiMe$_3$, (40 μL, 0.29 mmol), was syringed

Table 2. Selected ^{1}H and ^{13}C{^{1}H} NMR Spectral Data for the Complexes[a]

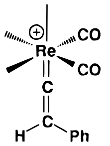
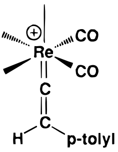
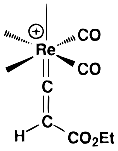
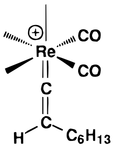
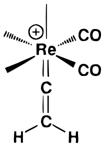
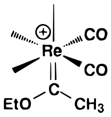
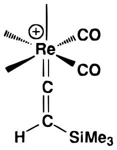
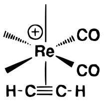
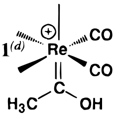
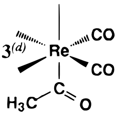
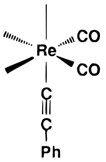
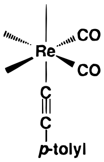
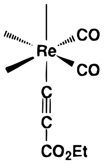
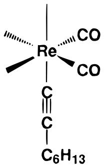
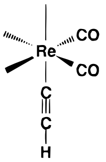
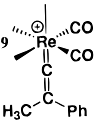
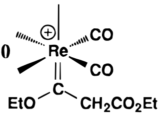
	^{1}H NMR			^{13}C{^{1}H} NMR		
complex	assgnt	δ (multiplicity)[b]	J (Hz)	assgnt	δ (multiplicity)[b]	J (Hz)
3 	CH	4.23 (q)	J_{HP} 2.9	Cα	351.0 (dt)	$J_{CPtrans}$ 30.7, J_{CPcis} 11.6
				CO	191.6 (AXX′Y)	J_{AX} 47.4, $J_{AX'}$ −12.0, J_{AY} 8.4, $J_{XX'}$ 24.9
				Cβ	116.3 (dt)	$J_{CPtrans}$ 13.3, J_{CPcis} 2.7
4(c) 	CH	4.12 (q)	J_{HP} 3.2	Cα	351.9 (dt)	$J_{CPtrans}$ 32.0, J_{CPcis} 11.4
				CO	191.1 (AXX′Y)	J_{AX} 46.9, $J_{AX'}$ −11.4, J_{AY} 8.6, $J_{XX'}$ 20.6
				Cβ	115.4 (br b)	$J_{CPtrans}$ 13.7
5 	CH	3.92 (q)	J_{HP} 3.0	Cα	339.5 (dt)	$J_{CPtrans}$ 33.8, J_{CPcis} 10.6
				CO	189.6 (AXX′Y)	J_{AX} 45.7, $J_{AX'}$ −10.0, J_{AY} 8.8, $J_{XX'}$ 25.6
				CO_2Et	163.4 (s)	
				Cβ	109.2 (dt)	$J_{CPtrans}$ 13.9, J_{CPcis} 2.0
				OCH_2	61.6 (br s)	
				CH_3	15.1 (s)	
6 	CH	3.41 (tq)	J_{HH} 8.3, J_{HP} 2.8	Cα	344.6 (dt)	$J_{CPtrans}$ 32.6, J_{CPcis} 9.9
				CO	191.9 (br m)	
				Cβ	111.5 (dt)	$J_{CPtrans}$ 13.3, J_{CPcis} 2.9
7 	C=CH$_2$	3.09 (q)	J_{HP} 2.8	Cα	340.9 (dt)	$J_{CPtrans}$ 32.3, J_{CPcis} 10.7
				CO	191.3 (m)	
				Cβ	95.8 (dt)	$J_{CPtrans}$ 14.0, J_{CPcis} 2.4
8 	CH_3	0.90 (t)	J_{HH} 7.1	Re=C	306.2 (dt)	$J_{CPtrans}$ 37.7, J_{CPcis} 8.3
	CH_3 carbene	2.79 (s)				
	OCH_2	4.03 (q)	J_{HH} 7.1	CO	197.1 (AXX′Y)	J_{AX} 48.2, $J_{AX'}$ −12.3, J_{AY} 9.0, $J_{XX'}$ 26.1
				OCH_2	73.7 (s)	
				CH_3 carbene	48.0 (dt)	$J_{CPtrans}$ 5.6, J_{CPcis} 1.8
				CH_3	14.2 (s)	
9 	SiMe$_3$	0.35 (s)				
	CH	3.14 (dt)	$J_{HPtrans}$ 4.3, J_{HPcis} 1.9			
10 	HC≡CH	5.27 (td)	J_{HPM} 3.3, J_{HPA} 2.2			
11(d) 	CH_3	2.82 (s)		Re=C	296.3 (dt)	$J_{CPtrans}$ 32.1, J_{CPcis} 10.3
				CO	200.5 (AXX′Y)	J_{AX} 42.8, $J_{AX'}$ −10.8, J_{AY} 8.9, $J_{XX'}$ 20.1
				CH_3	53.6 (d)	$J_{CPtrans}$ 5.0
13(d) 	CH_3	2.53 (s)		Re=C	295.5 (dt)	$J_{CPtrans}$ 30.1, J_{CPcis} 9.0
				CO	203.1 (AXX′Y)	J_{AX} 47.0, $J_{AX'}$ −8.7, J_{AY} 5.2, $J_{XX'}$ 27.1
				CH_3	57.2 (d)	$J_{CPtrans}$ 10.4
14 				CO	198.4 (m)	
				Cβ	123.8 (s)	
				Cα	108.7 (dt)	$J_{CPtrans}$ 32.8, J_{CPcis} 14.2
15 	CH_3 *p*-tolyl	2.22 (s)		CO	198.6 (m)	
				Cβ	116.0 (br s)	
				Cα	106.9 (dt)	$J_{CPtrans}$ 33.2, J_{CPcis} 14.6
				CH_3 *p*-tolyl	34.5 (s)	

Table 2 (Continued)

	^{1}H NMR			^{13}C{^{1}H} NMR		
complex	assgnt	δ (multiplicity)[b]	J (Hz)	assgnt	δ (multiplicity)[b]	J (Hz)
16 	CH_3 ester	1.21 (t)	J_{HH} 7.1	CO	199.6 (AXX′Y)	J_{AX} 44.2, $J_{AX'}$ −8.8, J_{AY} 5.6, $J_{XX'}$ 27.2
	OCH_2 ester	4.04 (q)				
				CO_2Et	168.6 (s)	
				Cα	123.6 (dt)	$J_{CPtrans}$ 33.9, J_{CPcis} 13.3
				Cβ	11.1 (s)	
				OCH_2	62.3 (s)	
				CH_3	16.9 (s)	
17 	CH_3 hexyl	0.89 (t)				
	CH_2 hexyl	1.2−1.4 (m)				
18 	CH	2.09 (q)	J_{HP} 2.4	CO	199.0 (m)	
				Cα	100.3 (dt)	$J_{CPtrans}$ 12.8, J_{CPcis} 1.5
				Cβ	not detected	
19 	CH_3 vinylidene	2.11 (s)		Cα	349.7 (dt)	$J_{CPtrans}$ 33.9, J_{CPcis} 11.9
				CO	192.3 (AXX′Y)	J_{AX} 55.1, $J_{AX'}$ −10.7, J_{AY} 9.3, $J_{XX'}$ 23.9
				Cβ	122.2 (dt)	$J_{CPtrans}$ 13.3, J_{CPcis} 2.7
				CH_3 vinylidene	10.4 (s)	
20 	CH_3 ethoxy	0.74 (t)	J_{HH} 7.2	Re=C	296.7 (dt)	$J_{CPtrans}$ 40.5, J_{CPcis} 8.1
	CH_3 ester	1.38 (t)	J_{HH} 7.2			
	OCH_2 ethoxy	4.17 (q)	J_{HH} 7.2	CO	196.8 (m)	
	OCH_2 ester	4.31 (q)	J_{HH} 6.9	CO_2Et	189.6 (s)	
	CH_2CO_2Et	4.53 (s)		OCH_2 ester	75.7 (s)	
				OCH_2 ethoxy	63.2 (s)	
				CH_2CO_2Et	63.0 (s)	
				CH_3 ester	14.7 (s)	
				CH_3 ethoxy	14.0 (s)	

[a] At room temperature in CD_2Cl_2 unless otherwise stated. [b] Key: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br broad. [c] In $CDCl_3$. [d] In THF-d_8.

into a dichloromethane (10 mL) solution of **2** (0.26 mmol) at −10 °C prepared as described above. After 30 min, when all the rhenium was present in the form of **7**, ethanol (2 mL) was added at room temperature. The reaction mixture was stirred for 2 h during which time the red-orange color turned yellow. Addition of ethanol/diethyl ether (10 mL, 1:2 v/v) gave the ethoxycarbene complex **8**-BF_4 as light yellow crystals. Yield: 94%. Anal. Calcd for $C_{47}H_{47}BF_4O_3P_3Re$: C, 55.03; H, 4.62. Found: C, 54.88; H, 4.73. $\Lambda_{M(nitroethane)}$ (for **8**-BF_4) = 76 Ω^{-1} cm^2 mol^{-1}. The tetraphenylborate salt **8**-BPh_4 can be obtained by recrystallization of **8**-BF_4 from dichloromethane/ethanol (2:1 v/v) in the presence of $NaBPh_4$ (1.1 equiv). Yield: 95%. Anal. Calcd for $C_{71}H_{67}BO_3P_3Re$: C, 67.78; H, 5.37. Found: C, 67.54; H, 5.36. $\Lambda_{M(nitroethane)}$ (for **8**-BPh_4) = 50 Ω^{-1} cm^2 mol^{-1}.

Method B. Ethanol (2 mL) was added to a solution of isolated **7**-BF_4 (or **7**-BPh_4) (*ca.* 0.20 mmol) in dichloromethane (10 mL). The solution was stirred for 2 h at room temperature during which time the red-orange color of the initial solution turned bright yellow. Addition of ethanol/diethyl ether (10 mL, 1:2 v/v) gave yellow crystals of **8**-BF_4 (or **8**-BPh_4) in almost quantitative yield. ^{1}H NMR (CD_2Cl_2, 28 °C, 500.13 MHz): δ 1.52 (q, J_{HP} 2.8 Hz, $CH_{3(triphos)}$, 3H), δ 2.44 (m, CH_2P_{equat}, 2H), δ 2.50 (d, $J_{HPaxial}$ 8.7 Hz, CH_2P_{axial}, 2H), δ 2.61 (m, CH_2P_{equat}, 2H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 28 °C, 125.75 MHz): δ 40.3 (q, J_{CP} 9.9 Hz, $CH_{3(triphos)}$), δ 39.6 (q, J_{CP} 4.2 Hz, $CH_3C_{(triphos)}$), δ 33.0 (dt, $J_{CPaxial}$ 22.2 Hz, $J_{CPequat}$ 4.8 Hz, CH_2P_{axial}), δ 35.6 (td, N = $J_{CPequat'}$ + $J_{CPequat''}$ = 14.9 Hz, $J_{CPaxial}$ 5.1 Hz, CH_2P_{equat}).

Synthesis of [(triphos)Re(CO)$_2${C(OEt)(CH_2CO_2Et)}]-BPh_4 (20). Ethanol was added to a solution of **5** (0.25 g, 0.19 mmol) in dichloromethane (10 mL). The reaction mixture was stirred overnight at room temperature to give a yellow solution from which crystals of the disubstituted carbene complex **20** separated by addition of ethanol/diethyl ether (10 mL, 1:2 v/v). Yield: 72%. Anal. Calcd for $C_{74}H_{71}BO_5P_3Re$: C, 66.81; H, 5.38. Found: C, 66.65; H, 5.46. ^{1}H NMR (CD_2Cl_2, 22 °C, 299.94 MHz): δ 1.57 (br s, $CH_{3(triphos)}$, 3H), δ 2.57 (m, $CH_{2(triphos)}$, 6H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 75.42 MHz): δ 39.7 (q, J_{CP} 10.7 Hz, $CH_{3(triphos)}$), δ 39.5 (q, J_{CP} 3.0 Hz, $CH_3C_{(triphos)}$), δ 32.4 (br d, $J_{CPaxial}$ 22.2 Hz, CH_2P_{axial}), δ 35.3 (td, N = $J_{CPequat'}$ + $J_{CPequat''}$ = 14.8 Hz, $J_{CPaxial}$ 5.0 Hz, CH_2P_{equat}). $\Lambda_{M(nitroethane)}$ = 47 Ω^{-1} cm^2 mol^{-1}.

X-ray Diffraction Studies. A summary of crystal and intensity data for the compounds **3**-BF_4 and **8**-BPh_4 is presented in Table 4. Experimental data were recorded at room temperature (21 °C) on a Enraf-Nonius CAD4 (**3**-BF_4) or a Philips-PW1100 diffractometer with an upgraded computer control (FEBO system) (**8**-BPh_4·0.5CH_2Cl_2). A set of 25 carefully centered reflections in the range 7° ≤ θ ≤ 12° (**3**-BF_4) and 15.5° ≤ θ ≤ 18.5° (**8**-BPh_4·0.5CH_2Cl_2), respectively, was used for determining the lattice constants. As a general procedure, the intensities of three standard reflections were measured periodically every 200 reflections for orientation and intensity control. This procedure did not reveal an appreciable decay of intensities. The data were corrected for Lorentz and polarization effects. Atomic scattering factors were those tabulated by Cromer and Waber[9] with anomalous dispersion corrections taken from ref 10. An empirical absorptions correction was applied via ψ scan for compound **8**-BPh_4·0.5CH_2Cl_2 with transmission factors in the range 1.006−2.158. The computational work was performed with a Digital Dec 5000/

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(9) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(10) *International Tables of Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 3-BF$_4$ and 8-BPh$_4$·0.5CH$_2$Cl$_2$

[(triphos)Re(CO)$_2${C=CH(Ph)}]BF$_4$ (**3**-BF$_4$)			
Re−P1	2.469(2)	Re−P2	2.480(2)
Re−P3	2.523(2)	Re−C6	1.944(7)
Re−C7	1.949(7)	Re−C8	1.925(6)
C6−O1	1.136(8)	C7−O2	1.138(8)
C8−C9	1.289(9)	C9−C1G	1.494(11)
C8−Re−C6	87.7(3)	C8−Re−C7	85.1(3)
C6−Re−C7	87.8(3)	C8−Re−P1	91.2(2)
C6−Re−P1	172.0(2)	C7−Re−P1	99.9(2)
C8−Re−P2	96.9(2)	C6−Re−P2	87.1(2)
C7−Re−P2	174.5(2)	P1−Re−P2	85.15(6)
C8−Re−P3	174.1(2)	C6−Re−P3	97.6(2)
C7−Re−P3	92.3(2)	P1−Re−P3	84.03(7)
P2−Re−P3	86.16(6)	O2−C7−Re	174.1(6)
C9−C8−Re	173.0(6)	C8−C9−C1G	122.3(7)
[(triphos)Re(CO)$_2${C(OEt)CH$_3$}]BPh$_4$ (**8**−BPh$_4$·0.5CH$_2$Cl$_2$)			
Re−P1	2.478(2)	Re−P2	2.482(2)
Re−P3	2.478(2)	Re−C10	1.892(9)
Re−C11	1.904(10)	Re−C6	2.071(8)
C6−O3	1.319(10)	C6−C7	1.478(13)
O3−C8	1.481(12)	C8−C9	1.48(2)
C10−O1	1.180(11)	C11−O2	1.171(11)
C10−Re−C11	90.8(4)	C10−Re−C6	87.0(4)
C11−Re−C6	83.9(4)	C10−Re−P1	93.2(3)
C11−Re−P1	176.0(3)	C6−Re−P1	96.1(2)
C10−Re−P3	178.4(3)	C11−Re−P3	88.8(3)
C6−Re−P3	91.5(2)	P1−Re−P3	87.18(7)
C10−Re−P2	96.7(3)	C11−Re−P2	96.2(3)
C6−Re−P2	176.4(2)	P1−Re−P2	83.54(8)
P3−Re−P2	84.89(8)		

Table 4. Summary of Crystal Data and Structure Refinement for 3-BF$_4$, and 8-BPh$_4$·0.5CH$_2$Cl$_2$

	3-BF$_4$	**8**-BPh$_4$·0.5CH$_2$Cl$_2$
formula	$C_{51}H_{45}BF_4O_2P_3Re$	$C_{71.5}H_{68}BClO_3P_3Re$
fw	1055.85	1300.72
cryst size, mm	0.225 × 0.200 × 0.075	0.25 × 0.25 × 0.50
cryst system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	10.693(2)	10.2710(10)
b, Å	13.387(3)	16.3936(5)
c, Å	17.785(4)	37.257(9)
α, deg	111.19(3)	90
β, deg	94.10(3)	97.49(3)
γ, deg	104.84(4)	90
V, Å^3	2256.2(8)	6426(3)
Z	2	4
ρ_{calcd}, g cm^{-3}	1.553	1.343
abs coeff, mm^{-1}	2.856	5.508
F(000)	1054	2704
θ range, deg	2.50−24.96	2.87−55.03
index ranges	$-12 \le h \le 12$	$-10 \le h \le 10$
	$-15 \le k \le 14$	$0 \le k \le 17$
	$0 \le l \le 19$	$0 \le l \le 39$
reflcns collcd	6802	7556
indepdt reflcns	6524 ($R_{int} = 0.0257$)	7429 ($R_{int} = 0.0183$)
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
data/constraints/ params	6522/0/572	7423/0/259
goodness-of-fit on F^2	1.447	1.045
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0336$	$R1 = 0.0648$
	w$R2 = 0.0852$	w$R2 = 0.1616$
R indices (all data)	$R1 = 0.0508$	$R1 = 0.0668$
	w$R2 = 0.0901$	w$R2 = 0.1665$
largest diff peak, e Å^3	1.814	1.697
largest diff hole, e Å^{-3}	−0.937	−0.879

200 workstation using the programs SHELX76,[11] SHELX93,[12] ORTEP,[13] and ZORTEP.[14] Final atomic coordinates of all atoms and structure factors are available as Supporting Information.

[(triphos)Re(CO)$_2${C=C(H)Ph}]BF$_4$ (3-BF$_4$). Deep-violet crystals of the compound were grown under nitrogen from a diluted dichloromethane/ethanol solution. A parallelepiped crystal with dimension 0.225 × 0.200 × 0.075 mm was used for the data collection. The structure was solved via Patterson methods. Refinement was done by full-matrix least-squares calculations, initially with isotropic thermal parameters and then with anisotropic thermal parameters for all non-F and non-H atoms. The phenyl rings were treated as rigid bodies with D_{6h} symmetry with C−C bond distances fixed at 1.39 Å. The hydrogen atoms were introduced in calculated positions ($d_{C-H} = 0.96$ Å for sp^3 carbon atoms and $d_{C-H} = 0.92$ Å for sp^2 carbon atoms).

[(triphos)Re(CO)$_2${C(OEt)(CH$_3$)}]BPh$_4$·0.5CH$_2$Cl$_2$ (8-BPh$_4$·0.5 CH$_2$Cl$_2$). Light yellow crystals of the compound were grown from slow concentration in the air of a dichloromethane solution layered with ethanol. A parallelepiped crystal with dimension 0.25 × 0.25 × 0.50 mm was used for the data collection. The structure was solved by using the heavy-atom technique and all of the non-hydrogen atoms were found through a series of F_0 Fourier maps. Full-matrix least-squares refinement were carried out initially with isotropic thermal parameters and then with anisotropic thermal parameters only for Re, P, and the C atoms of the ligand triphos backbone. The phenyl rings were treated as rigid bodies with D_{6h} symmetry with C−C bond distances fixed at 1.39 Å, and the hydrogen atoms were introduced in calculated positions ($d_{C-H} = 0.95$ Å). The final difference maps revealed the presence of a disordered molecule of dichloromethane which was attributed a population factor of 0.5.

Results and Discussion

The preparations and the principal reactions of the complexes described in this paper are illustrated in Schemes 1−4. Selected NMR spectral data for the metal complexes are collected in Table 1 (IR and ^{31}P{^{1}H} NMR) and Table 2 (^{1}H and ^{13}C{^{1}H} NMR) or are provided in the Experimental Section. ^{1}H{^{31}P}, ^{13}C-DEPT, ^{13}C−^{1}H-2D HETCOR, ^{1}H−^{13}C-2D HETCOR, and ^{1}H−^{1}H 2D COSY NMR spectra allowed the total and unequivocal assignment of all hydrogen and carbon resonances for all metal complexes.

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[11] Sheldrick, G. M. *SHELX-76. A Program for Crystal Structure Determination*; University of Cambridge: Cambridge, U.K., 1976.

[12] Sheldrick, G. M. *SHELX-93. Program for Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993.

[13] Johnson, C. K. *Report ORNL-5138*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

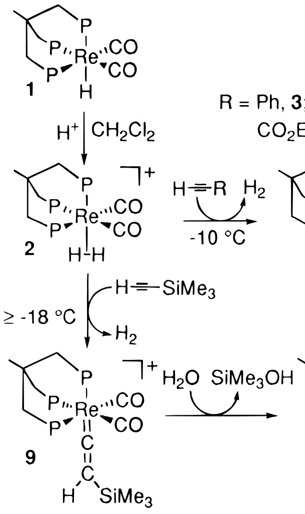
[14] Zsolnai, L.; Pritzkow, H. *ZORTEP. Ortep Original Program Modified for PC*; University of Heidelberg: Heidelberg, Germany, 1994.

[15] The literature of vinylidene complexes is extensive. Some comprehensive reviews are as follows: (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.

[16] Recent leading references of transition metal vinylidene complexes: (a) Ara, I.; Berenguer, J. R.; Forniés, J.; Lalinde, E.; Tomas, M. *Organometallics* **1996**, *15*, 1014. (b) Beddoes, R. L.; Bitcon, C.; Grime, R. W.; Ricalton, A.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1995**, 2873. (c) O'Connor, J. M.; Hübner, K.; Merwin, R.; Pu, L. *J. Am. Chem. Soc.* **1995**, *117*, 8861. (d) Bianchini, C.; Innocenti, P.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Organometallics* **1996**, *15*, 272. (e) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Valero, C.; Zeier, B. *J. Am. Chem. Soc.* **1995**, *117*, 7935. (f) Wiedemann, R.; Wolf, J.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1244. (g) Werner, H. *J. Organomet. Chem.* **1994**, *475*, 45. (h) Touchard, D.; Haquette, P.; Pirio, N.; Toupet, L.; Dixneuf, P. H. *Organometallics* **1993**, *12*, 3132. (i) Bianchini, C.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Organometallics* **1995**, *14*, 3152. (j) Bianchini, C.; Glendenning, L.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *J. Chem. Soc., Chem. Commun.* **1994**, 2219.

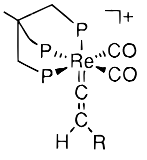
[17] For leading references on the alkyne to vinylidene tautomerization, see: (a) Fryzuk, M. D.; Huang, L.; McManus, N. T.; Paglia, P.; Rettig, S. J.; White, G. S. *Organometallics* **1992**, *11*, 2979. (b) Lumphrey, J. R.; Selegue, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 5518. (c) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1077. (d) Bianchini, C.; Peruzzini, M.; Vacca, A.; Zanobini, F. *Organometallics* **1991**, *10*, 3697. (e) Xiao, J.; Cowie, M. *Organometallics* **1993**, *12*, 463. (f) Davies, S. G.; McNally, J. P.; Smallridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 30. (g) Bullock, R. M. *J. Chem. Soc., Chem. Commun.* **1989**, 165.

Scheme 1

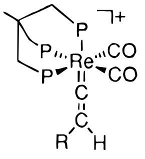


Synthesis and Characterization of the Vinylidene Complexes [(triphos)Re(CO)$_2${C=C(H)R}]Y. (Y = BF$_4$, BPh$_4$; R = Ph (3), *p*-tolyl (4), COOEt (5), *n*-C$_6$H$_{13}$ (6), H (7)). Scheme 1 illustrates the one-pot reaction which converts the Re(I) hydride complex [(triphos)Re(CO)$_2$H] (**1**) to the vinylidene derivatives [(triphos)Re(CO)$_2${C=C(H)R}]Y (Y = BF$_4$, BPh$_4$; R = Ph (**3**), *p*-tolyl (**4**), COOEt (**5**), *n*-C$_6$H$_{13}$ (**6**)) by sequential action of a protic acid and a terminal alkyne. The reactions proceed via the intermediacy of the isolable complex [(triphos)Re(CO)$_2$(η^2-H$_2$)]$^+$,[4] which undergoes displacement of the η^2-H$_2$ ligand by the terminal alkynes. The latter molecules most likely form π-adducts prior to tautomerism to vinylidene ligands by 1,2-hydrogen shift which is the mechanism generally followed by d^6 metal systems.[15−17] In actuality, a π-alkyne intermediate has been intercepted at low temperature with ethyne (*vide infra*).

Despite the different electronic properties of the vinylidene substituents, compounds **3**−**6** exhibit very similar NMR characteristics. All ^{31}P{^{1}H} NMR spectra show first-order AM$_2$ spin systems with chemical shifts and coupling constants, which are in line with those of Re(I) phosphine complexes.[4] The substantial negligibility of coordination chemical shift [$\Delta\delta(^{31}\mathrm{P}) = \delta(^{31}\mathrm{P}_{\mathrm{coord}}) - \delta(^{31}\mathrm{P}_{\mathrm{free\ ligand}}) \leq 20$ ppm][18] well accounts for the deshielding effect of coordinated ^{31}P nuclei observed for 5d-block metal phosphine complexes.[19] The ^{31}P{^{1}H} NMR spectra of the vinylidene complexes are temperature invariant down to −90 °C, consistent with a low-energy rotational barrier separating the different rotamers **I** and **II**.



I



II

A rapid rotation of the vinylidene group about the M−C axis characterizes most of the known metal complexes and has also been rationalized by means of theoretical studies.[20] However, some examples of restricted rotation have been reported, *i.e.* the rhenium compounds [(η^5-Cp)Re(NO)(PPh$_3$)(C=CHR)]$^+$ described by Gladysz for which the existence of a mixture of rotamers at room temperature has been demonstrated by NMR spectroscopy.[21]

The presence of vinylidene ligands in **3**−**6** is unambiguously shown by ^{1}H NMR resonances at ca. 4 ppm due to the vinylidene hydrogen[15−17] and by ^{13}C NMR resonances at *ca.* 350 ppm (C$_\alpha$) and *ca.* 110 ppm (C$_\beta$), which appear as doublets of triplets due to coupling of both vinylidene carbon atoms to the phosphorus nuclei.[15,16,22] Two phosphorus nuclei are trans to the carbonyl ligands which are thus magnetically inequivalent (AXX′Y multiplets at *ca.* 190 ppm). Analogous spin systems have been reported by Baird and co-workers for the isoelectronic ruthenium complexes [(triphos)Ru(CO)$_2$X]$^{n+}$ (X = halide or organyl).[23] Finally, medium-intensity IR absorptions in the region 1600−1660 cm^{-1} [16,22] and a pair of strong bands near 2000 cm^{-1} characterize the vinylidene C=C bond and the terminal carbonyls, respectively.

The molecular structure of the phenylvinylidene complex **3**-BF$_4$ has been determined by an X-ray diffraction analysis. The crystal structure consists of [(triphos)Re(CO)$_2${C=C(H)Ph}]$^+$ cations and tetrafluoroborate anions in a 1:1 ratio. A selected list of bond angles and distances is given in Table 3, while an ORTEP view of the complex cation is shown in Figure 1 with the atomic labeling scheme.

The coordination geometry around rhenium can be described as a slightly distorted octahedron with the metal atom surrounded by the three P donor atoms of triphos, by two mutually *cis* carbonyl ligands, and by a σ-bonded phenylvinylidene group. The most relevant distortions from the idealized geometry are related to the structural constraints imposed by the tripodal phosphine. This is confirmed by the bending of the three P−Re−P angles which are significantly smaller than 90° (average value 85.1°).[4,24] The overall donor-atom set around rhenium is quite symmetrical with a negligible displacement [0.001(3) Å] of the metal from the orthogonal planes P1−P2−C6−C7 and P3−P2−C8−C7, while a slightly larger displacement [0.0045(3)] Å is observed with respect to the P3−P1−C8−C6 plane. The Re−P bond lengths [$d_{(\mathrm{Re-P})\mathrm{av}} = 2.49$ Å] are signifi-

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(18) The chemical shift of triphos phosphorus atoms in dichloromethane-*d*$_2$ is −25.2 ppm.

(19) See, for example: (a) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complxes*; Diehl, P., Fluck, E., Konsfeld, R., Eds.; Springer-Verlag: Berlin, Heidelberg, New York, 1979. (b) Crumbliss, A. L.; Topping, R. J. *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.: VCH Publ. Inc.: Deerfield Beach, FL, 1987.

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(22) See, for example: (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Zanobini, F.; Zanello, P. *Organometallics* **1990**, *9*, 241. (b) Gamasa, M. P.; Gimeno, J.; Mártin-Vaca, B. M.; Borge, J.; Gárcia-Granda, S.; Perez-Carreño, E. *Organometallics* **1994**, *13*, 4045. (c) Wolf, J.; Lass, R. W.; Manger, M.; Werner, H. *Organometallics* **1995**, *14*, 2649 and references therein.

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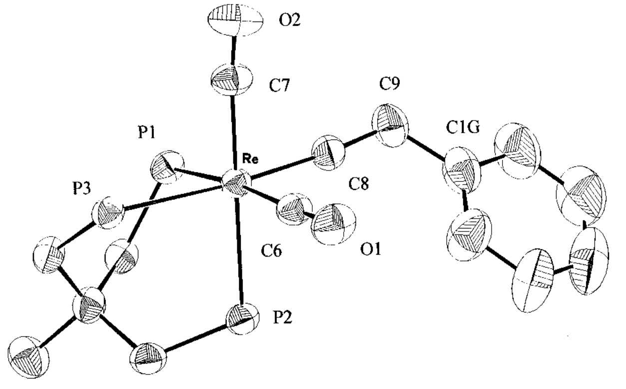
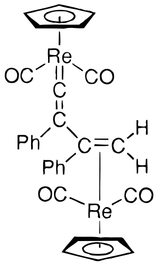


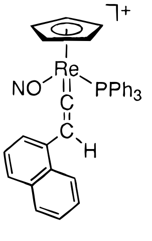
Figure 1. ORTEP drawing of the complex cation [(triphos)-Re(CO)$_2${C=C(H)Ph}]$^+$ in **3**-BF$_4$. All of the phenyl rings of the triphos ligand are omitted for clarity.

catively longer than those found in the monohydride (triphos)Re(CO)$_2$H [$d_{(Re-P)av}$ = 2.42 Å][4,24] but compare well with the analogous distances in [(triphos)Re(CO)$_2$-{C(OEt)Me}]BPh$_4$ [$d_{(Re-P)av}$ = 2.48 Å] (*vide infra*). The Re−P1 and Re−P2 distances are similar [2.469(2) and 2.480(2) Å, respectively] and shorter than the Re−P3 separation [2.523(2) Å], which is consistent with the smaller *trans* influence of the vinylidene ligand.

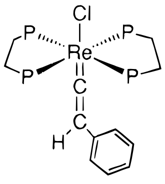
The phenylvinylidene ligand shows the typical geometrical features of this organyl moiety[17d,25] with metrical data which are consistent with sp and sp^2 hybridizations of the C8 and C9 carbon atoms, respectively. Accordingly, the angle at the C$_\beta$ carbon, C8−C9−C1G, measures 122.3(7)°. The Re−C8 bond distance [1.925(6) Å] is considerably shorter than those found in Re−C single bond compounds[26] and is close to the separation found in [Cp(CO)$_2$Re{C=CPhCPh=CH$_2$}][(CO)$_2$ReCp][27] [1.90(2) Å] (**III**). As a consequence of the *trans* influence of the P3 phosphorus atom, the C8−C9 bond length [1.289(9) Å] is slightly shorter than those found in other X-ray-authenticated Re(I) vinylidenes without *trans* phosphine ligands, **III** [1.33(3) Å],[27] [CpRe(NO)(PPh$_3$)-{C=CH(1-C$_{10}$H$_7$)}]BPh$_4$ (**IV**) [1.387(17) Å],[21b] and *trans*-[ReCl{C=CH(Ph)}(dppe)$_2$] (**V**) [1.31(2) Å] [dppe = 1,2-bis(diphenylphosphino)ethane].[25e,f]



III



IV



V

Finally, the crystal packing appears to be dictated by van der Waals interactions with no anomalous intermolecular contacts.

Unlike all the other vinylidene complexes, the one obtained by reaction of **2** in CH$_2$Cl$_2$ with ethynyltrimethylsilane is highly reactive toward moisture. In fact, the complex [(triphos)Re(CO)$_2${C=C(H)SiMe$_3$}]BF$_4$ (**9**) is seen only as a transient species, which quite rapidly transforms into the parent vinylidene derivative [(triphos)Re(CO)$_2$(C=CH$_2$)]BPh$_4$ (**7**-BPh$_4$) and HOSiMe$_3$ even at −18 °C (Scheme 1). Consistently, in the presence of stoichiometric water, **9** is not intercepted even at low temperature (NMR experiment). The facile hydrolysis of C(sp^2)-Si bonds in metal complexes is well documented in the literature.[28] Despite its transient nature which does not allow one to record ^{13}C NMR spectra, **9** can unequivocally be assigned the same structure of the previously described vinylidene complexes in which the metal center is octahedrally coordinated by a *fac* triphos ligand, by two *cis* disposed carbonyls group, and by a vinylidene ligand *trans* to a phosphorus atom. In particular, the resonance of the vinylidene hydrogen in **9** appears as a doublet of triplets at 3.14 ppm ($J_{HPtrans}$ 4.3 Hz, J_{HPcis} 1.9 Hz) and collapses to a singlet in the broad-band phosphorus-decoupled ^{1}H spectrum. Identical primary geometry is adopted by the parent vinylidene complex [(triphos)Re(CO)$_2$(C=CH$_2$)]-BF$_4$ (**7**-BF$_4$), whose geminal vinylidene protons appear in the ^{1}H NMR spectrum as a quartet (3.09 ppm, J_{HP} 2.8 Hz) which, in a 2D-NMR H,C-HETCOR experiment, correlates with a doublet of triplets at 95.8 ppm (C=*C*H$_2$). Consistent with its methylenic nature, this signal is antiphased in the ^{13}C-DEPT spectrum.

In addition to hydrolysis of **9**, the parent vinylidene complex can straightforwardly be prepared by treatment of **2** in CH$_2$Cl$_2$ with ethyne (Scheme 2).

A variable-temperature NMR study of the reaction between **2** and ethyne has provided valuable mechanistic information on the formation of the vinylidene complex. At −18 °C, the formation of the vinylidene complex **7** is preceded by that of the kinetic η^2-alkyne product [(triphos)Re(CO)$_2$(π-HC≡CH)]BF$_4$ (**10**), which spontaneously transforms into the vinylidene complex **7** within 1 h.

Although it was not possible to record a ^{13}C NMR spectrum of the kinetic product, **10**, there is little doubt that this complex contains a π-bonded ethyne molecule. In fact, the ^{31}P NMR resonance of the phosphorus donor *trans* to the ethyne ligand in **10** (P$_A$) is shifted downfield as compared to the analogous resonance in the vinylidenes **3**−**7** due to the higher π acidity of the vinylidene ligands.[15,16] Moreover, the ^{1}H NMR spectrum contains a resonance at δ 5.27 (td, J_{HPM} 3.3 Hz, J_{HPA} 2.2 Hz) which fall in the proper region for two-electron donor π-HC≡CH ligands;[17b,29] see for example [CpRe(CO)$_2$(η^2-C$_2$H$_2$)] (δ_{CH} 5.61)[30] and [CpRu(PMe$_2$Ph)$_2$-

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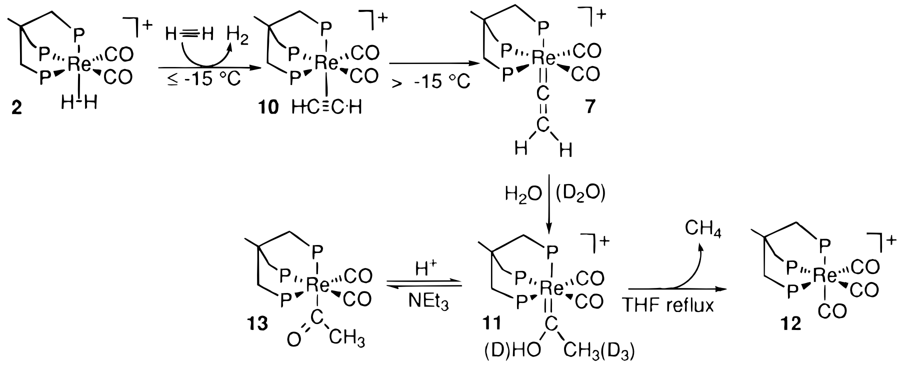
Scheme 2

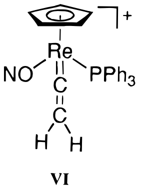


(η^2-C_2H_2)] (δ_{CH} 5.27).[17b] Like **10**, the ruthenium complex rearranges to its vinylidene tautomer above 60 °C.

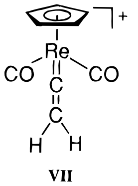
In an attempt to isolate **10**, cold *n*-hexane was added to a solution of **2** and HC≡CH thermostated at −15 °C until precipitation of a yellowish solid occurred. This solid contains **10** and **7**-BF_4 in a 1:4 ratio (^{31}P NMR integration). More importantly, the IR spectrum shows a band at 1740 cm^{-1} which may tentatively be assigned to the C≡C stretching frequency of the π-coordinated ethyne ligand.[17b,29]

The interception of the kinetic product **10** suggests that the present Re-assisted 1-alkyne to vinylidene tautomerization reactions proceed via the 1,2-H shift mechanism proposed in 1985 by Jerome and Hoffmann[31] on the basis of EHMO calculations and recently supported by *ab initio* studies on the conversion of $RuCl_2(PH_3)_2(HC{\equiv}CH)$ to $RuCl_2(PH_3)_2(C{=}CH_2)$.[32] In actuality, the alternative intramolecular 1,3-H shift mechanism would hardly be accessible to the present [(triphos)Re$(CO)_2$]$^+$ fragment, which is not sufficiently electron-rich to undergo the oxidative addition of the alkyne C−H bond. As a matter of fact, the only known d^6 metal system which has been found capable of tautomerizing a terminal alkyne to vinylidene via a 1,3-H shift mechanism is the very electron-rich Ru system [(C_5Me_5)RuCl(dippe)] reported by Puerta and co-workers (dippe = 1,2-bis(diisopropylphosphino)ethane).[33]

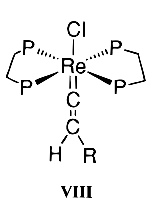
Complex **7** is the first parent Re vinylidene complex directly accessible by displacement of a labile ligand by ethyne. Moreover, unlike the Gladysz derivative [(η^5-Cp)Re(NO)(PPh_3)($C{=}CH_2$)]OSO_2CF_3[21b] (**VI**), which requires rigorous anaerobic and moisture-free conditions for its preparation, and the Geoffrey compound (η^5-Cp)Re$(CO)_2(C{=}CH_2)$[34] (**VII**), which decomposes in solution at room temperature, **7** is sufficiently air- and moisture-stable in the solid state to be handled in a laboratory with no particular care.



VI



VII



VIII

With the exception of **9**, excellent stability in both the solid state and solution characterizes all the members of the present family of vinylidene complexes. This feature and the general synthetic methodology herein described provide facile access to a large variety of Re(I) vinylidene complexes, the chemistry of which still is at an early stage of development. Moreover, with the exception of the neutral complexes *trans*-ReCl{C=C(H)R}$(dppe)_2$ (**VIII**) (R = Ph, Et, ^{t}Bu, $SiMe_3$, COOMe, COOEt, $C_6H_{10}OH$) described by Pombeiro *et al.*,[25f] all the other known Re vinylidene complexes, reported by Gladysz,[21] Casey,[35] Geoffroy,[34] and Kolobova,[27] contain as ancillary ligands either cyclopentadienyl or substituted cyclopentadienyl rings, which are less thermally and chemically stable than triphos.

Reactions of the Vinylidene Complexes. The following sections describe selected examples of chemical transformations occurring at the vinylidene ligands bound to the [(triphos)Re$(CO)_2$]$^+$ auxiliary.

Synthesis, Characterization, and Reactivity of the Secondary Hydroxycarbene Complex [(triphos)Re$(CO)_2${C(OH)CH_3}]BF_4 (11). Treatment of the parent vinylidene complex **7**-BF_4 in THF with an excess of water at ≥0 °C results in the transformation of the starting compound into the secondary hydroxycarbene complex [(triphos)Re$(CO)_2${C(OH)CH_3}]BF_4 (**11**) (Scheme 2). *In situ* NMR experiments show that the addition of water to **7**-BF_4 (see trace "B" in Figure 2) is a selective reaction.[36−39] In contrast, **11**, isolated by removal of the solvent in vacuo, is invariably contaminated by some acetyl derivative (triphos)Re$(CO)_2$($COCH_3$) (**13**) (≤10%) whose formation, however, is an indirect evidence of the nature of **11** (*vide infra*).

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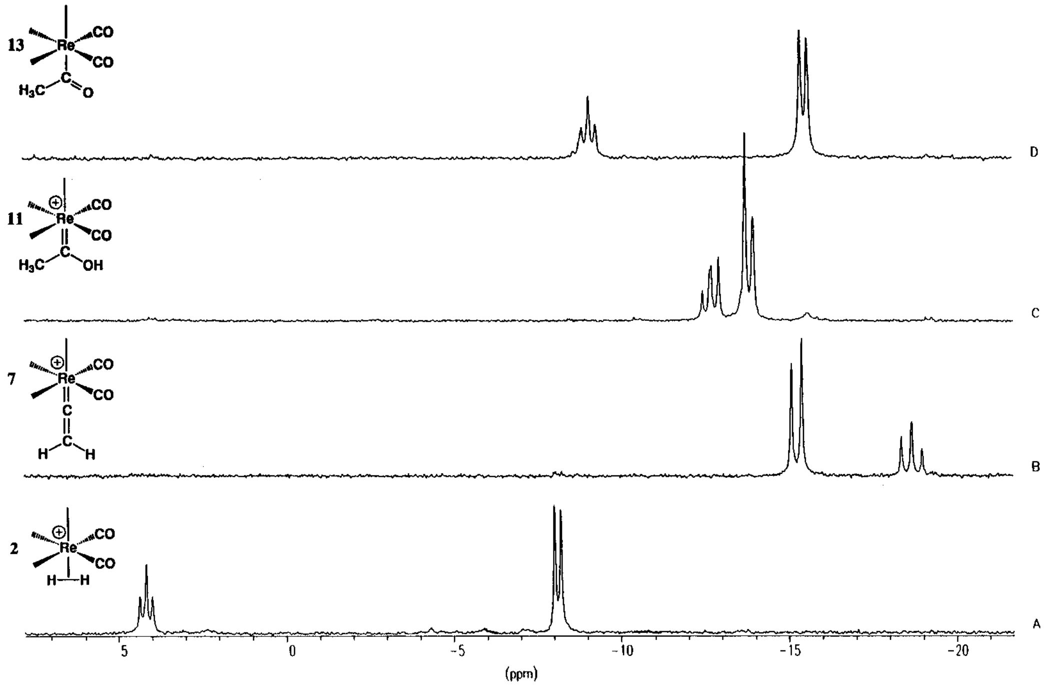

Figure 2. $^{31}P\{^1H\}$ NMR spectra of the stepwise reaction $\mathbf{2} \xrightarrow{i} \mathbf{7} \xrightarrow{ii} \mathbf{11} \xrightarrow{iii} \mathbf{13}$ carried out by sequential addition to **2** of C_2H_2 (i), H_2O (ii), and NEt_3 (iii) (5-mm screw-cap NMR tube, THF-d_8, 21 °C, 81.01 MHz, 85% H_3PO_4 reference).

The presence of a hydroxycarbene ligand in **11** is unequivocally demonstrated by a ^{13}C NMR resonance at 296.3 ppm (dt, $^2J_{CPtrans}$ 32.1 Hz, $^2J_{CPcis}$ 10.3 Hz) that can readily be assigned to the carbene carbon atom,[2f,36,37] which couples to the triphos phosphorus nuclei (slightly second-order ^{31}P NMR AB_2 pattern; see trace "C" in Figure 2). In the ^1H NMR spectrum, the resonance due to the carbene CH_3 substituent appears as a singlet at 2.82 ppm,[36,38] which, in fact, disappears in the spectrum of the perdeuterated isotopomer [(triphos)Re(CO)$_2$-{C(OD)CD$_3$}]BF$_4$ (**7**-d_4) obtained by reacting **7**-BF$_4$ with D_2O (exchange of the vinylidene hydrogens with deuterium[40] evidently occurs prior to interaction of water with the Re=C=C moiety). The hydroxycarbene OH resonance was not detected in the ^1H NMR spectrum of **11**. However, the compound shows a broad absorption at *ca.* 3500 cm^{-1} in its IR spectrum, which we assign as ν_{OH}.[36−38]

Compound **11** is fairly stable in solution at room temperature. On long standing, however, it decomposes to the know tricarbonyl complex [(triphos)Re(CO)$_3$]BF$_4$ (**12**)[5] and methane (detected by ^1H NMR) (23% conversion in 72 h). In refluxing THF, this transformation quantitatively occurs in a few minutes (Scheme 2).

Deprotonation of **11** in THF to the acetyl complex **13** rapidly and selectively occurs by treatment with mild bases such as NEt_3 (see trace "D" in Figure 2). Compound **13**, isolated as yellow crystals, is reversibly protonated by strong acids ($HBF_4{\cdot}OMe_2$) in THF to regenerate the hydroxycarbene precursor.[39l] The main spectroscopic properties of **13** are similar to those of all the present neutral complexes containing the [(triphos)-Re(CO)$_2$]$^+$ auxiliary. The acetyl ligand is readily recognized by a ^{13}C NMR resonance at 265.5 ppm (dt, $^2J_{CPtrans}$ 30.1 Hz, $^2J_{CPcis}$ 9.0 Hz) due to the *C*OCH$_3$ carbon atom, by a ^1H NMR singlet at 2.53 ppm due to the Re−COCH$_3$ acetyl protons, and by an IR $\nu_{C=O}$ absorption at 1621 cm^{-1}.[36] The facile deprotonation of **11** accounts for the observed formation of some **13** in any attempt to isolate **11** from its solutions.

Hydroxycarbene metal complexes are still rare species.[36−39] With the exception of (η^5-C$_5$Me$_5$)Fe(CO)$_2$-(CHOH), prepared by hydride abstraction from a hydroxymethyl ligand,[39c] all the known, authentic, hydroxycarbene complexes have been generated by reaction of either η^1-formyl or η^1-acyl precursors with strong protic acids.[36−39] Compound **11** thus represents *the first example of generation of a stable hydroxycarbene ligand by direct addition of water to a vinylidene ligand.*

The evident interconnection of vinylidene and hydroxycarbene ligands is quite interesting as both these species are believed to play a key role in the hydrogenation of CO catalyzed by iron-group metals to give a variety of organic products.[41,42] In particular, surface-bound secondary hydroxycarbene ligands have been postulated in forming the initial C−H bonds in Fischer−Tropsch reactions.[43,44] Accordingly, in light of our discovery, one cannot disregard the possibility that water (produced in the Fischer−Tropsch process)[45] interacts with vinylidene intermediates to give hydroxycarbene species, which ultimately may generate either hydrocarbons and CO or other oxygenated products such as aldehydes and ketones. As a matter of fact, we have found that the hydroxycarbene ligand in **11** is selectively transformed into CO and methane by thermolysis in THF.

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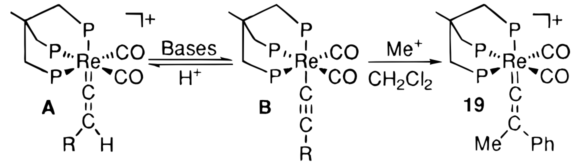
The cleavage of the C−C bond in vinylidene ligands by water has a few precedents in the literature.[40,46,47] A mechanistic study has recently been carried out on the reaction which converts the Ru vinylidene complex *fac,cis*-(PNP)RuCl$_2${C=C(H)Ph} to the carbonyl complex *fac,cis*-(PNP)RuCl$_2$(CO) and toluene by treatment with water [PNP = CH$_3$CH$_2$CH$_2$N(CH$_2$CH$_2$PPh$_2$)$_2$].[40] A number of key intermediates were intercepted, including σ-acyl and alkylcarbonyl species, but the intermediacy of a hydroxycarbene complex was only postulated. The present discovery thus confirms that hydroxycarbene species can be precursors to the C−C bond cleavage step.

As for the mechanism of the thermal degradation of **11** to the tricarbonyl complex **12** and methane, we can safely exclude an intramolecular rearrangement of the hydroxycarbene ligand to acetaldehyde,[31a,f,48] followed by decarbonylation of the latter ligand.[43,49] In fact, the [(triphos)Re(CO)$_2$]$^+$ fragment binds acetaldehyde to form a mixture of both η^1-*O*-CH$_3$CHO and η^2-*C,O*-CH$_3$CHO complexes,[50] which do not degrade to the tricarbonyl complex **12** and methane upon thermolysis in THF.

Following the thermolysis of **11** in THF-d_8 by variable-temperature NMR spectroscopy in a sealed tube, we had no evidence of intermediate species prior to formation of the tricarbonyl complex. Accordingly, no reliable mechanism can be forwarded for the thermal conversion of **11** to **12** and methane. Like the above mentioned Ru-PNP vinylidene complex reaction,[40] also the transformation of **11** into **12** might proceed via the intermediacy of an Re η^2-triphos acyl species which would degrade to the tricarbonyl complex and methane by CO deinsertion, followed by protonolysis of the Re−CH$_3$ bond. However, no experimental evidence of an arm-off mechanism was provided by a variable-temperature NMR study of the acetyl complex **13** in THF. Arm-off mechanisms have frequently been observed or proposed for metal triphos complexes, particularly in CO and alkyl insertion/deinsertion reactions.[51] Examples of Re η^2-triphos complexes have also been described.[3] In the absence of experimental evidence, however, this remains only speculation and we cannot exclude the occurrence of different types of either intramolecular or intermolecular mechanisms.

Scheme 3



A: R = Ph, **3**; *p*-tolyl, **4**;
CO$_2$Et, **5**; *n*-C$_6$H$_{13}$, **6**; H, **7**.

B: R = Ph, **14**; *p*-tolyl, **15**;
CO$_2$Et, **16**; *n*-C$_6$H$_{13}$, **17**; H, **18**.

Synthesis and Characterization of the Alkynyl Complexes (triphos)Re(CO)$_2$(C≡CR) (R = Ph (14), *p*-tolyl (15), COOEt (16), *n*-C$_6$H$_{13}$ (17), H (18)]. The monosubstituted vinylidene complexes **3**−**7** are readily deprotonated by bases (KO^{t}Bu, NEt$_3$, LiC≡CPh, LiHBEt$_3$) to give σ-alkynyl derivatives of the general formula (triphos)Re(CO)$_2$(C≡CR) [R = Ph (**14**), *p*-tolyl (**15**), COOEt (**16**), *n*-C$_6$H$_{13}$ (**17**), H (**18**)] (Scheme 3).

All the alkynyl complexes show a strong IR $\nu_{C\equiv C}$ absorption between 2062 and 2101 cm^{-1}. The parent ethynyl complex **18** displays C−H and C≡C stretching modes at 3280 and 1954 cm^{-1}, respectively. The red-shift observed for the $\nu_{C\equiv C}$ frequency in **18** is due to the less electron-rich character of the unsubstituted alkynyl ligand. In accord with the lack of charge as well as the major basicity of the alkynyl ligands, the $\nu_{C\equiv O}$ stretching frequencies of the carbonyl ligands are shifted to lower energy as compared to the corresponding vinylidene precursors [$\Delta\nu = \nu_{(C\equiv O)\text{vinylidene}} - \nu_{(C\equiv O)\text{alkynyl}} > 70$ cm^{-1}]. The ^{31}P NMR spectra display the expected AM$_2$ patterns in which the triplet resonance of the phosphorus donor trans to the σ-organyl ligand is shifted to lower field as compared to the vinylidene precursors, most likely due to the greater trans influence of the σ-alkynyl groups.[52]

Reactions of the σ-Alkynyl Complexes with Electrophiles. The alkynyl complexes **14**−**18** regenerate the vinylidene precursors by reaction with protic acids which regioselectively attack the C$_\beta$ carbon atom (Scheme 3). In a similar way, the reaction of the alkynyl complexes with carbon electrophiles provides a simple and convenient route to the synthesis of disubstituted vinylidene derivatives. As an example, the reaction of **14** with different methylating reagents, such as MeOSO$_2$CF$_3$, Me$_3$OBF$_4$, or MeI, gives the cationic methylphenylvinylidene species [(triphos)Re(CO)$_2${C=C(Me)Ph}]Y (**19**) (Y = OSO$_2$CF$_3$, BF$_4$, I) which can be isolated as deep violet crystals. Compound **19** exhibit IR and NMR spectral properties which are quite comparable with those of the monosubstituted Re(I) vinylidenes **3**−**7**.

Synthesis and Characterization of the Ethoxycarbene Complexes [(triphos)Re(CO)$_2${C(OEt)CH$_2$R}]BPh$_4$ (R = H, 8; R = COOEt, 20). In keeping with the well-known proclivity of vinylidene complexes to undergo nucleophilic additions across the C=C double bond,[15] the less electron-rich vinylidene complexes **5** and **7** react with ethanol at room temperature to give the ethoxycarbene complexes [(triphos)Re(CO)$_2${C(OEt)CH$_2$R}]BPh$_4$ (R = H, **8**; R = COOEt, **20**) (Scheme 4). Consistent with previous reports,[22b] the less activated vinylidene complexes, **3**, **4**, and **6**, do not react with either methanol or ethanol even under drastic reaction conditions.

The IR spectra of the ethoxycarbene complexes exhibit ν_{COC} bands at *ca.* 1260−1290 cm^{-1}. The NMR data

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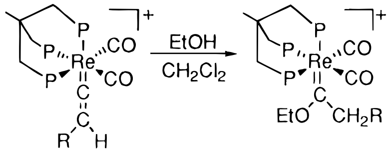
Scheme 4



R = CO_2Et, **5**; H, **7** R = H, **8**; CO_2Et, **20**

unequivocally point to the presence of an ethoxycarbene ligand. In particular, the $^{31}P\{^1H\}$ NMR spectra display the typical AM_2 patterns which are temperature invariant down to −90 °C consistent with a rapid rotation of the carbene moiety arbout the Re−C bond. In the $^{13}C\{^1H\}$ NMR spectra, the carbene carbon atoms appear as a doublet of triplets in the expected down-field region of the spectrum (ca. 300 ppm).[22b,36,39l]

Since the preparation of alkoxycarbene complexes from vinylidene precursors and alcohols has been known for many years,[15,53] it is thus surprising that none of the relatively few Re alkoxycarbene complexes so far reported has been synthesized through the direct addition of alcohols to vinylidene complexes. Alkylation of neutral metal acyls has been used by Fischer,[54] Gladysz,[36] and Gibson,[39l] while Geoffroy has reported that Re alkoxycarbene complexes can be prepared by reaction of cationic rhenium carbyne derivatives with epoxides.[55]

The molecular structure of the ethoxycarbene complex **8**-BPh_4·$0.5CH_2Cl_2$ has been determined by an X-ray diffraction analysis. The crystal structure consists of $[(triphos)Re(CO)_2\{C(OEt)CH_3\}]^+$ cations, tetraphenylborate anions, and interspersed dichloromethane solvent molecules in a ratio of 1:1:0.5. An ORTEP drawing of the complex cation is shown in Figure 3, while a list of selected bond distances and angles is presented in Table 3.

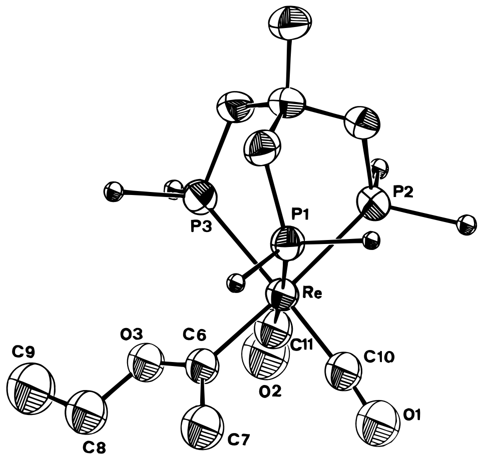


Figure 3. ORTEP drawing of the complex cation $[(triphos)Re(CO)_2\{C(OEt)(CH_3)\}]^+$ in **8**-BPh_4·$0.5CH_2Cl_2$. Only the *ipso* carbon of the phenyl rings of the triphos ligand are shown for the sake of clarity.

Like the vinylidene derivative **3**-BF_4 (*vide supra*), the coordination geometry around the rhenium atom can be described as a slightly distorted octahedron with comparable distortions with respect to the idealized geometry. A salient structural feature is the length of the Re−P3 bond opposite to the carbene ligand [2.482(2) Å], which is practically identical with the other two Re−P separations [2.478(2) Å] but is significatively shorter than the analogous distance in **3**-BF_4 [2.523(2) Å]. We assign this finding to the higher electron-withdrawing character of the vinylidene ligand as compared to the alcoxycarbene group. In keeping with this hypothesis, we notice also a significative Re═C bond elongation [2.071(8) Å] *vs* [1.925(6) Å] in **3**-BF_4 as well as shorter Re−CO distances [$d_{(Re-CO)av}$ is 1.898(9) Å in **8**-BPh_4 and 1.946(7) Å in **3**-BF_4]. On the other hand, also the trend of $\nu_{C\equiv O}$ observed in the IR spectra of the vinylidene and alkylidene complexes points to a higher π-acceptor character of the vinylidene ligand (see Table 1). The other metrical parameters exhibited by the carbene complex **8**-BPh_4 are in good agreement with those reported for authenticated rhenium ethoxycarbene complexes and do not deserve additional comments.[54,56]

Conclusions

A family of stable Re(I) vinylidene complexes has been prepared by tautomerism of ethyne and various 1-alkynes at the unsaturated metal center in $[(triphos)Re(CO)_2]^+$. All the vinylidene complexes exhibit a rich reactivity toward nucleophiles. In particular, they are excellent precursors to either other types of Re−C multiple bond compounds, such as disubstituted vinylidene, secondary hydroxycarbene, and alkoxycarbene complexes, or Re−C single bond compounds, such as σ-alkynyl and σ-acyl complexes. For the first time, experimental evidence has been provided of the key role of hydroxycarbene species in the metal-assisted hydration of alkynes leading to C−C bond cleavage.[40,46,47]

Acknowledgment. Thanks are due to Mr. Dante Masi for technical assistance in the X-ray structure determinations. Thanks are also expressed to the EC for financial support (Contract No. ERBCHRXCT930147).

Supporting Information Available: Tables of final positional parameters and isotropic and anisotropic displacement parameters for all atoms and bond lengths and angles for **3**-BF_4 and **8**-BPh_4·$0.5CH_2Cl_2$ (18 pages). Ordering information is given on any current masthead page.

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