First Examples of Rhenium-Assisted Activation of Propargyl Alcohols: Allenylidene, Carbene, and Vinylidene Rhenium(I) Complexes

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The complex [(triphos)$(CO)_2$Re(OTf)] (**1**) reacts with disubstituted propargyl alcohols HC≡CCR(R′)OH in CH_2Cl_2 at room temperature (R = R′ = Ph, Me; R = Ph, R′ = Me), to give either allenylidene derivatives [(triphos)$(CO)_2$Re{C=C=C(R)Ph}]OTf (R = Ph, **2**; R = Me, **3**) or the dinuclear vinylidene−carbene complex [{(triphos)$(CO)_2$Re}$_2${μ-($C_{10}H_{12}$)}](OTf)$_2$ (**5**) (R = R′ = Me) (triphos = MeC(CH_2PPh_2)$_3$; OTf = $CF_3SO_3^-$). The secondary propargyl alcohol HC≡CCH(Me)OH reacts with **1** in the presence of methanol to give the methoxy-alkenyl Fischer-type carbene [(triphos)$(CO)_2$Re{C(OMe)-CH=CHMe}]OTf (**11**). Compound **11** has been authenticated by an X-ray diffraction analysis. The structure of this complex shows the metal center to be surrounded by a *fac* triphos ligand, by two mutually *cis* carbonyl groups, and by the organyl ligand in a slightly distorted octahedral geometry. The reaction with HC≡CCH_2OH results in the double addition of methanol to give the carbene complex [(triphos)$(CO)_2$Re{C(OMe)(CH_2CH_2OMe)}]OTf **(9)**. When the reaction between **1** and propargyl alcohol is carried out in the dichloromethane dinuclear vinylidene−carbene complex, [{(triphos)$(CO)_2$Re}$_2${μ-(C_6H_6O)}](OTf)$_2$ (**10**) is obtained.

Introduction

The dehydration of propargyl alcohols by transition metal fragments, discovered in 1982 by Selegue,[1] provides a general method for the synthesis of compounds containing multiple metal−carbon bonds and, in particular, of allenylidene complexes.[2] Like the carbene and vinylidene homologous compounds, metal allenylidenes are useful reagents in both organic synthesis and homogeneous catalysis, especially in ring-closure reactions of α,ω-dienes or ene-ynes, as recently shown by Hill, Fürstner, and Dixneuf.[3−5]

Despite the ubiquitous character of metal allenylidenes,[2] no example of a mononuclear rhenium complex has been reported so far,[6] which is quite surprising given the propensity of rhenium to form M−C double bonds.[7] Aimed at filling in this gap, we report here that rhenium(I), in a proper environment of ligands, is capable of effectively dehydrating propargyl alcohols, leading to a wide range of known and new metallacumulene structural motifs depending on the 1-alkynol substituents.

Results and Discussion

Synthesis and Characterization of the Rhenium Allenylidene Complexes [(triphos)$(CO)_2$Re{C=C=C(R)Ph}]OTf (R = Ph, 2; R = Me, 3). The allenylidene complexes [(triphos)$(CO)_2$Re{C=C=C(R)Ph}]OTf (R = Ph, **2**; R = Me, **3**; triphos = MeC(CH_2PPh_2)$_3$; OTf = $CF_3SO_3^-$) were straightforwardly obtained by reaction of [(triphos)$(CO)_2$Re(OTf)][8] (**1**) with a slight excess of HC≡CCPh(R)OH (R = Ph, Me) in CH_2Cl_2 at room temperature (Scheme 1). Compounds **2** and **3** are air-stable in the solid state but slowly decompose in solution. They exhibit spectroscopic features in line with the presence of a C_3 disubstituted allenylidene (e.g., $^{13}C\{^1H\}$ NMR resonances at ca. 290, 208, and 163 ppm due to the α, β, and γ carbons of the Re=C=C=C moiety, respectively).[2] The $^{31}P\{^1H\}$ NMR spectra consist of strongly second-order AXX′ spin systems in line with the magnetically inequivalence of the two phosphorus atoms *trans* to the carbonyl groups. The IR spectra show

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(1) Selegue, J. P. *Organometallics* **1982**, *1*, 217.
(2) Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797.
(3) Fürstner, A.; Picquet, M.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun.* **1998**, 1315.
(4) Fürstner, A.; Hill, A. F.; Liebl, M.; Wilton-Ely, J. D. E. T. *Chem. Commun.* **1999**, 601.
(5) Picquet, M.; Touchard, D.; Bruneau, C.; Dixneuf, P. H. *New J. Chem.* **1999**, 141.
(6) A dinuclear complex of the formula $(CO)_9Re_2(C{=}C{=}CBu^t_2)$ has been reported: Berke, H.; Harter, P.; Huttner, G.; Zsolnai, L. *Chem. Ber.* **1984**, *117*, 3423.
(7) See for example: (a) Bianchini C.; Marchi A.; Marvelli L.; Peruzzini M.; Romerosa A.; Rossi R. *Organometallics* **1996**, *15*, 3804. (b) Bianchini C.; Marchi A.; Marvelli L.; Peruzzini M.; Romerosa A.; Rossi R.; Vacca A. *Organometallics* **1995**, *14*, 3203.
(8) Bergamini, P.; Fabrizi De Biani, F.; Marvelli, L.; Mascellani, N.; Peruzzini, M.; Rossi, R.; Zanello, P. *New J. Chem.* **1999**, 207.

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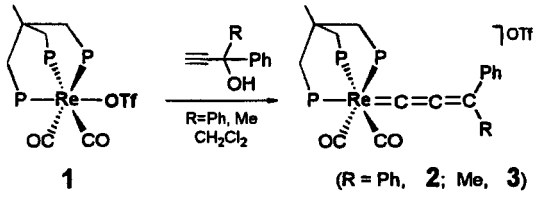
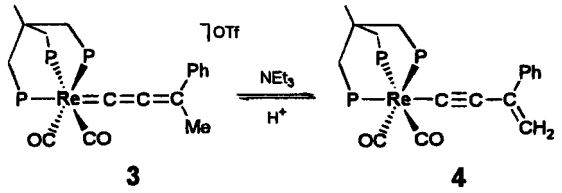
Scheme 1



Scheme 2



two ν(CO) bands in the range 2000−1920 cm^{-1}, while no ν(C═C═C) band of the allenylidene ligand[1,9] is visible, most likely because of overlapping with the intense low-frequency carbonyl band.

In keeping with previous reports,[10] the methyl substituent of **3** can readily be deprotonated by NEt_3 to yield the enynyl derivative [(triphos)$(CO)_2$Re{C≡C−C(Ph)═CH_2}] (**4**) (Scheme 2). The IR spectrum of **4** contains a ν(C≡C) band at 2074 cm^{-1}, while the ν(CO) bands are shifted to lower frequencies (1944−1885 cm^{-1}) as compared to the allenylidene precursor. This findings accounts for the weaker π-acceptor properties of the alkynyl ligand as well as the neutral nature of **4**. The $^{31}P\{^1H\}$ NMR spectrum shows the expected AM_2 pattern with chemical shifts and coupling constants similar to other σ-alkynylrhenium phosphine compounds.[7] The $^{13}C\{^1H\}$ NMR spectrum exhibits two doublet of triplets for the alkynyl C_α and C_β carbons,[7,11] while the CH_2 end of the enynyl ligand appears as a singlet at 111.8 ppm (DEPT-assigned).

Synthesis and Characterization of the Dinuclear Complexes [{(triphos)$(CO)_2$Re}$_2${μ-($C_{10}H_{12}$)}](OTf)$_2$ (5) and [{(triphos)$(CO)_2$Re}$_2${μ-C_6H_6O)}](OTf)$_2$ (10). Under identical experimental conditions, **1** reacts with either HC≡$CCMe_2OH$ or HC≡CCH_2OH, yielding the dinuclear carbene−vinylidene complexes [{(triphos)$(CO)_2$Re}$_2${μ-($C_{10}H_{12}$)}](OTf)$_2$ (**5**) and [{(triphos)-$(CO)_2$Re}$_2${μ-C_6H_6O)}](OTf)$_2$ (**10**), respectively (Schemes 3 and 4).

Although we were unable to grow crystals suitable for an X-ray analysis, both **5** and **10** have unambiguously been authenticated in solution by multinuclear and multidimensional NMR spectroscopy. The structure of **5** is quite similar to that of the complex [Ru_2{μ-($C_{10}H_{12}$)}(PPh_3)$_4$(Cp)$_2$][PF_6]$_2$ previously reported by Selegue.[12] Two [(triphos)$(CO)_2$Re]$^+$ fragments are held together by a six-membered carbon ring resulting from the intermolecular condensation of allenylidene, Re═C═C═CMe_2, and alkenylvinylidene, Re═C═C(H)CCMe═CH_2, intermediates (Scheme 5a). The cyclohexene bridging unit binds one rhenium atom in a carbenoid fashion (δ_{C_3} 294.5) and is connected to the other rhenium using the C_β atom of a Re−vinylidene moiety (δ_{C_b} 120.9).

The dimer **10**, resulting from the activation of HC≡CCH_2OH, is the coupling product of the allenylidene [(triphos)$(CO)_2$Re(C═C═CH_2)] (nonisolated) with the hydroxyvinylidene [(triphos)$(CO)_2$Re{C═C(H)CH_2OH}]$^+$ (**7**) (intercepted, see below) (Scheme 5b). The bridging unit in **10** may be described as a tetrahydropirane ring in which the bridgehead C_5 and C_4 carbon atoms are the C_β atom of a vinylidene ligand (δ_{C_b} 111.9) and the carbon atom of a carbene ligand (δ_{C_4} 302.4), respectively. To the best of our knowledge, no compound exhibiting the structure of **10** has ever been reported.

The two cyclic derivatives **5** and **10** share many relevant spectroscopic features. In particular, the ^{31}P NMR spectra of both compounds show two AM_2 patterns displaying chemical shifts and coupling constants that are characteristic of [(triphos)$(CO)_2$Re−*vinylidene*] and [(triphos)$(CO)_2$Re−*carbene*] moieties.[7]

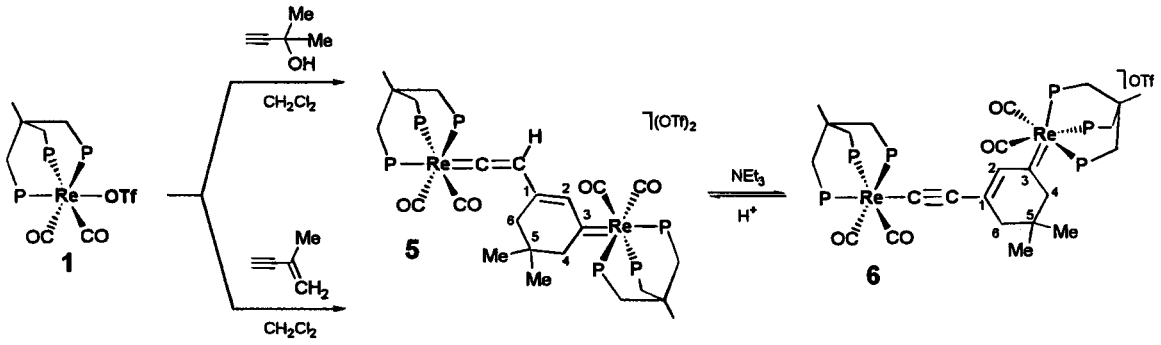
The structures of both **5** and **10** were unequivocally determined by a combination of $^{13}C\{^1H\}$, ^{13}C-DEPT, ^1H,^{13}C-HMQC, and ^1H,^1H-COSY NMR experiments. Crucial spectroscopic features for compound **5** were (i) two doublets of triplets at 340.4 and 294.5 ppm in the ^{13}C NMR spectrum, which are typical of the α carbon of vinylidene and carbene groups, respectively, (ii) a quartet at 3.26 ppm in the proton spectrum ^1J-coupled with the vinylidene C_β resonance (δ 120.9), and (iii) two vinylic carbon resonances at 147.8 and 148.7 ppm assigned to the *C*═*C*H carbon atoms of the cyclohexene bridging unit. Key NMR features for **10** were (i) the presence of typical vinylidene and carbene resonances in the ^{13}C NMR spectrum, (ii) the absence of any vinylidene proton, and (iii) the observation of three inverted CH_2 singlets in the DEPT-135 spectrum, two of which, the C_2 and C_6 atoms close to the oxygen atom of the pyrane ring, show a significant high-field shift.

In keeping with the presence of a secondary vinylidene ligand in **5**, the treatment of a dichloromethane solution of this compound with weak nucleophiles resulted in the deprotonation of the C_β atom to give the alkynyl−carbene complex [{(triphos)$(CO)_2$Re}$_2${μ-(C_{10}-H_{11})}](OTf) (**6**) (Scheme 3). Such a process is reversible, and **5** was regenerated upon addition of HBF_4 (NMR experiment). As expected no deprotonation occurs when **10** was reacted with different bases.

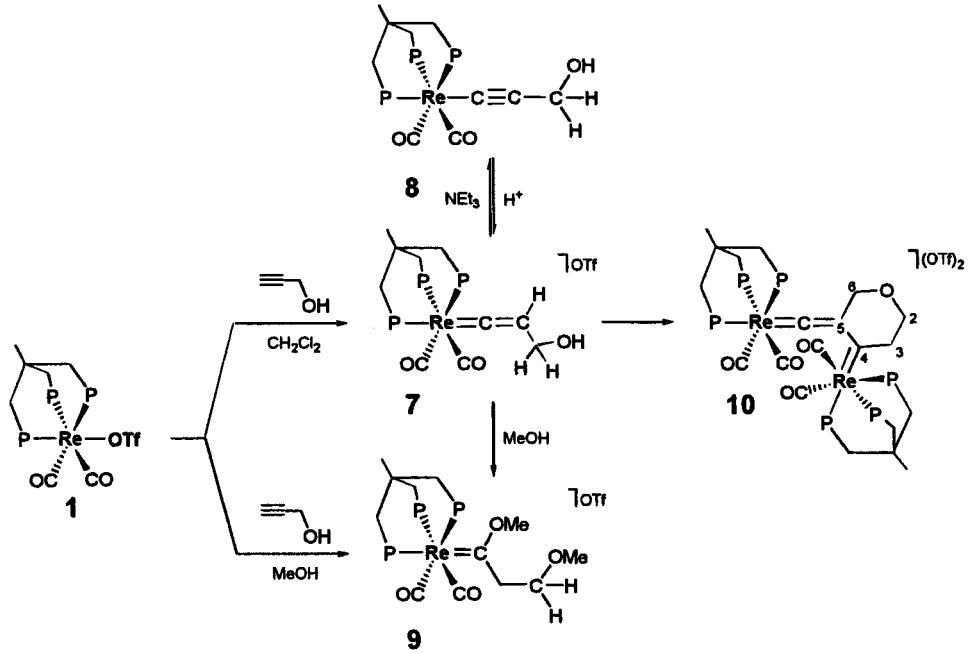
Mechanism of the Reaction of 1 with Propargylic Alcohols. The mechanisms by which alkyldisubstituted alkynols are transformed, by interaction with metal complexes, into either allenylidene ligands (as in **2** and **3**) or μ-cyclic ligands (as in **5**) are well-known.[2] The first step, e.g., 1-alkynol to hydroxyvinylidene (**A**) tautomerization, is common to both processes (Scheme 5). Depending on the number and size of the substituent(s) in the 1-alkynol, the eventual elimination of water from hydroxyvinylidene intermediates may involve the vinylidene hydrogen atom, a hydrogen from an alkyl substituent, or both.[2] In the first case, an allenylidene complex (**B**) is formed which either may be stable (as in **2** and **3**) or may react with the hydroxyvinylidene precursor, leading to the formation of dimers of type **E** (as in **10**). When the two ways of water elimination become equally possible, allenylidene

(9) Selegue; J. P.; Young, B. A.; Logan, S. L. *Organometallics* **1991**, *10*, 1972.
(10) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Gonzales-Cueva, M.; Lastra, E.; Borge, J.; Garcia-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137.
(11) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: New York, 1981; pp 133−143.
(12) Selegue, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 5921.

Scheme 3



Scheme 4



(**B**) and alkenylvinylidene (**C**) species are contemporaneously formed and may react with each other, yielding dimers of type **D** (as in **5**).

The proposed mechanism for the formation of **5** is indirectly supported by the fact that this compound can also be formed by reacting **1** with 2-methyl-1-buten-3-yne, $HC{\equiv}CC(CH_3){=}CH_2$. Indeed, this result suggests that the vinylvinylidene intermediate $[(triphos)(CO)_2Re\{{=}C{=}C(H)C(CH_3){=}CH_2\}]^+$ can tautomerize to the allenylidene species $[(triphos)(CO)_2Re\{{=}C{=}C{=}CMe_2\}]^+$ (Scheme 5a).[13,14] Although the vinylvinylidene intermediate was not observed, its formation is highly probable in light of a previous report by Casey and co-workers, who showed that $Cp^*(CO)_2Re(THF)$ reacts with $HC{\equiv}CC(CH_3){=}CH_2$ to give the vinylvinylidene $Cp^*(CO)_2Re\{C{=}C(H)\text{-}C(CH_3){=}CH_2\}$ via thermal rearrangement of a π-alkyne precursor $Cp^*(CO)_2Re\{\eta^2\text{-}HC{\equiv}C{-}C(CH_3){=}CH_2\}$.[15]

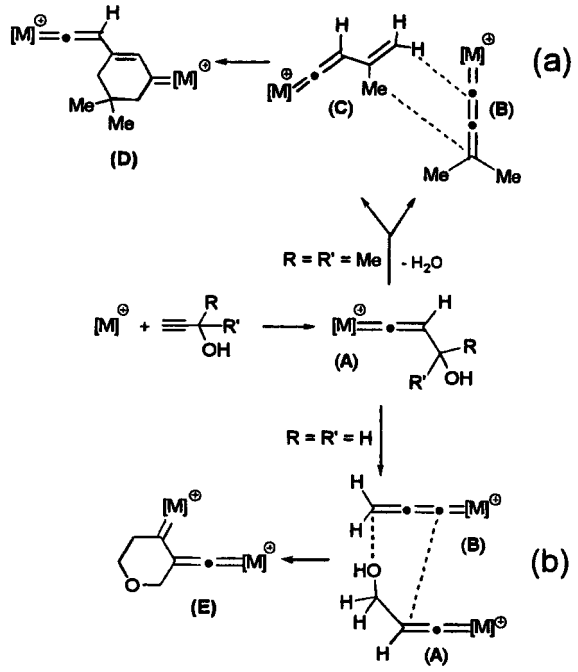
Monitoring by variable-temperature ^{31}P NMR spectroscopy the reactions of **1** in CD_2Cl_2 with every 1-alkynol investigated did not allow us to detect any intermediate species except for the reaction of **1** with $HC{\equiv}CCH_2OH$. At ca. −15 °C, the lilac hydroxyvinylidene complex $[(triphos)(CO)_2Re\{C{=}C(H)CH_2OH\}]^+$ (**7**) was detected, and this complex was the only Re product visible after 15 min at −8 °C.[14] Heating the NMR sample to room temperature quickly and selectively transformed **7** into **10**, which is consistent with the elimination of a molecule of water from **7** to give the highly reactive primary allenylidene $[(triphos)(CO)_2Re\{C{=}C{=}CH_2\}]^+$. The subsequent reaction of this intermediate with intact **7** would give the indigo dimer **10** (Scheme 4).

All our attempts to isolate the parent hydroxyvinylidene complex **7** in the solid state were unsuccessful, as extensive decomposition of this compound invariably took place to give a mixture of **1** and the dimer **10** together with other unidentified products. However, the structure of **7** was also indirectly supported by the isolation of the hydroxymethylalkynyl derivative $[(triphos)(CO)_2Re\{C{\equiv}CCH_2OH\}]$ (**8**) by treatment of a solution of **7** with different weak bases (Scheme 4).

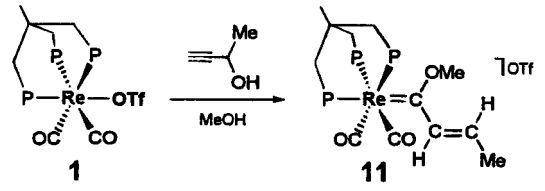
Synthesis and Characterization of the Rhenium Methoxycarbene Complexes $[(triphos)(CO)_2Re\{C(OMe)CH_2CH_2OMe\}]OTf$ (9) and $[(triphos)(CO)_2Re\{C(OMe)CH{=}CHMe\}]OTf$ (11). The methoxy(methoxyethyl)carbene complex $[(triphos)(CO)_2Re\{C(OMe)$-

(13) Dussel, R.; Pilette, D.; Dixneuf, P. H.; Fehlhammer, W. P. *Organometallics* **1991**, *10*, 3287.
(14) Devanne, D.; Dixneuf, P. H. *Chem. Commun.* **1990**, 641.
(15) Casey, C. P.; Ha, Y.; Powell, D. R. *J. Organomet. Chem.* **1994**, *472*, 185.

Scheme 5



Scheme 6



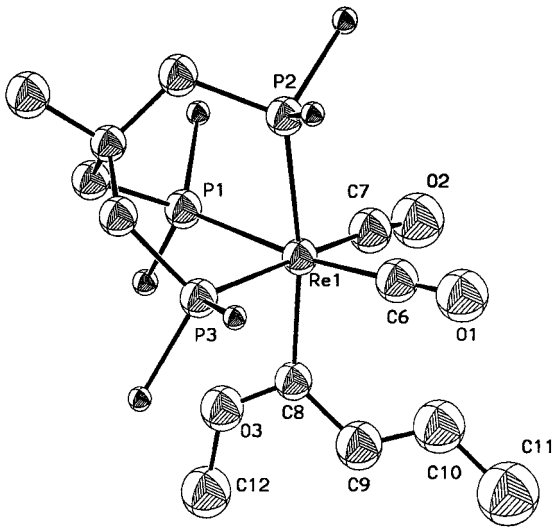


Figure 1. ORTEP drawing of the complex cation [(triphos)$(CO)_2$Re{C(OMe)CH=C(H)Me}]$^+$ in **11**·C_6H_6. For the sake of clarity only the *ipso* carbon atoms of the phenyl substituents in the triphos ligand are shown.

CH_2CH_2OMe}]$^+$ (**9**) has straightforwardly been prepared in situ by adding MeOH to a CD_2Cl_2 solution of **7** into an NMR tube. Complex **9** was isolated in the solid state as pale pink microcrystals by reacting **1** with HC≡CCH_2OH in the presence of MeOH. The formation of the methoxy(methoxyethyl)carbene complex, as suggested by Dixneuf,[16] formally proceeds via a concerted dehydration of the coordinated propargyl alcohol, followed by a double addition of methanol to the C_α and C_γ carbon atoms of an allenylidene intermediate.

The reaction between **1** and HC≡CCH(Me)OH has also been investigated in CD_2Cl_2. Even at low temperature a dark blue solution was immediately obtained that $^{31}P\{^1H\}$ NMR spectroscopy showed to contain several products. Only when the reaction was carried out in the presence of methanol was a single complex formed, namely, the methoxyalkenylcarbene [(triphos)-$(CO)_2$Re{C(OMe)CH=CHMe}]OTf (**11**), which was isolated as pale green crystals (Scheme 6). The formation of **11** apparently involves the addition of a molecule of methanol to the transient allenylidene compound [(triphos)$(CO)_2$Re{C=C=C(H)Me}]$^+$ before it spontaneously degrades to a Fischer-type carbene. Indeed, although the complexity of the mixture containing **1** and HC≡CCH(Me)OH denied first-order analysis, the low-temperature $^{31}P\{^1H\}$ NMR spectrum showed the presence of resonances attributable to both types of dimers (**D** and **E** in Scheme 5) as well as a hydroxyvinylidene intermediate.

X-ray Crystal Structure of [(triphos)$(CO)_2$Re-{C(OMe)CH=CHMe}]OTf (11). An ORTEP[17] drawing of the complex cation of **11** is reported in Figure 1 with the atomic labeling scheme, while selected bond lengths and angles are given in Table 2. The structure consists of [(triphos)$(CO)_2$Re{C(OMe)CH=CHMe}]$^+$ complex cations and triflate anions in a 1:1 ratio with interspersed benzene molecules. The metal atom is surrounded by three P donor atoms from a *facial* triphos ligand, by two mutually *cis* carbonyl groups, and by a methoxyalkenyl carbene ligand in a slightly distorted octahedral geometry. This distortion is a consequence of the structural constraints imposed by the tripodal phosphine which subtends three P−Re−P angles with an average value of 84.8°. The Re−P, Re−CO, and Re−$C_{carbene}$ bond lengths [$d_{(Re-P)av}$ = 2.48 Å; $d_{(Re-CO)av}$ = 1.89 Å; $d_{Re=C}$ = 2.078(10) Å] are in good agreement with those reported for the ethoxycarbene complex [(triphos)$(CO)_2$Re{=C(OEt)Me}]$^+$ [$d_{(Re-P)av}$ = 2.48 Å; $d_{(Re-CO)av}$ = 1.90 Å; $d_{Re=C}$ = 2.071(8) Å][7a] and for the rhenium oxacyclopentylidene complex [(triphos)$(CO)_2$Re{=CCH_2CH_2CH-(Me)O}]$^+$ [$d_{(Re-P)av}$ = 2.48 Å; $d_{(Re-CO)av}$ = 1.87 Å; $d_{Re=C}$ = 2.02(2) Å].[18] The methoxyalkenyl carbene ligand shows bond lengths and angles similar to those found in other octahedral transition metal compexes.[16]

Experimental Section

All reactions and manipulations were routinely performed under a dry nitrogen atmosphere by using standard Schlenk techniques. Tetrahydrofuran (THF) was freshly distilled over $LiAlH_4$; dichloromethane and methanol were purified by distillation over CaH_2 before use; *n*-hexane was stored over molecular sieves and purged with nitrogen prior to use. All the other reagents and chemicals were commercial products and were used as received without further purification. The ligand 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) and the complex [(triphos)Re$(CO)_2$(OTf)][8] (**1**) were prepared

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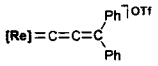
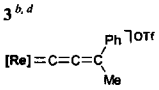
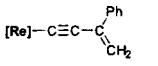
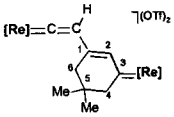
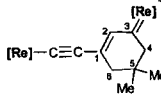
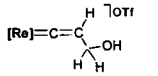
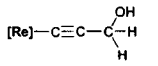
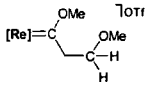
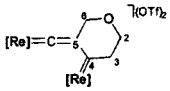
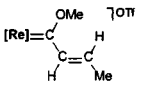
(18) Bianchini, C.; Marchi, A.; Mantovani, N.; Marvelli, L.; Masi, D.; Peruzzini, M.; Rossi, R. *Eur. J. Inorg. Chem.* **1998**, 211.

Table 1. Selected ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR Spectral Data and IR Absorptions for the Complexes

Complexes	^1H δ (ppm), *J* (Hz)	$^{13}C\{^1H\}$ δ (ppm), *J* (Hz)	$^{31}P\{^1H\}$ δ (ppm), *J* (Hz) / IR (KBr, cm^{-1})
2 [b, d] 		290.7 (m, Re=*C*=C=C) 208.1 (m, Re=C=*C*=C) 192.3 (m, CO) 163.3 (s, Re=C=C=*C*)	δ_A -17.82 $J_{AB} = J_{AB'}$ 24.4 $\delta_B = \delta_{B'}$ -17.63 $J_{BB'}$ -25.0 --- $\nu(CO)_{sym}$ 2000 $\nu(CO)_{antisym}$ + ν(C=C=C) 1921 ν(OTf) 1273
3 [b, d] 	1.78 (s, 3H, CH_3)	292.8 (dt, $J_{CPtrans}$ 30.0, J_{CPcis} 11.1, Re=*C*=C=C) 202.8 (d, $J_{CPtrans}$ 15.7, Re=C=*C*=C) 192.0 (m, *C*O) 162.9 (s, Re=C=C=*C*) 32.0 (s, $CH_{3(cumulene)}$)	δ_A -18.19 $J_{AB} = J_{AB'}$ 24.0 $\delta_B = \delta_{B'}$ -17.70 $J_{BB'}$ 9.9 --- $\nu(CO)_{sym}$ 2002 $\nu(CO)_{antisym}$ + ν(C=C=C) 1933 ν(OTf) 1271
4 [a] 	4.98 (d, J_{HH} 2.4, 1H, =CH_2) 5.40 (d, J_{HH} 2.4, 1H, =CH_2)	198.8 (m, CO) 115.3 (d, $J_{CPtrans}$ 12.9, Re-C≡*C*) 110.3 (dt, $J_{CPtrans}$ 23.9, J_{CPcis} 10.7, Re-*C*≡C) 111.8[h] (s, C=*C*H_2) 73.2[h] (s, *C*=CH_2)	δ_A -6.46 J_{AM} 17.1 δ_M -19.31 --- ν(C≡C) 2074 ν(CO) 1944, 1885 ν(C=C) not observed
5 [a, e, f] 	0.82 (s, 6H, $CH_{3(ring)}$) 1.83 (m, 2H, $CH_{2(C6, ring)}$) 2.98 (s, 2H, $CH_{2(C4, ring)}$) 3.26 (q, J_{HP} 2.8, 1H, Re=C=CH)	340.4 (dt, $J_{CPtrans}$ 35.6, J_{CPcis} 10.2, Re=*C*=C) 294.5 (dt, $J_{CPtrans}$ 28.0, J_{CPcis} 7.6, C3) 199.6 (m, *C*O) 189.4 (m, *C*O) 148.7 (q, J_{CP} 3.8 C2) 147.8 (q, J_{CP} 2.2, C1) 120.9 (dt, $J_{CPtrans}$ 14.0, J_{CPcis} 2.0, Re=C=*C*) 72.1, (s, C4) 44.1, 34.1(all s, C7, C6) 28.2[h] (s, 2C, $CH_{3\ ring}$)	δ_A -22.30 J_{AM} 20.3 δ_M -12.00 $\delta_{A'}$ -24.40 $J_{A'M'}$ 26.2 $\delta_{M'}$ -16.60 --- ν(CO) 2008, 1946, 1894 ν(C=C)$_{vinylidene}$ 1662 ν(C=C)$_{ring}$ 1551 ν(OTf) 1271
6 [a] 	0.68 (s, 6H, $CH_{3(ring)}$) 1.40 (s, 2H, $CH_{2(C6, ring)}$) 2.68 (s, 2H, $CH_{2(C4, ring)}$) 6.9-7.5 (aromatic + $CH_{(C2, ring)}$)	272.8 (dt, $J_{CPtrans}$ 28.1, J_{CPcis} 8.5, C3) 199.2 (m, *C*O) 196.6 (m, *C*O) 156.2 (s, C2) 148.8 (s, C1) 117.9 (s, Re-C≡*C*) 71.0 (s, C4) 50.0 (s, C6) 33.7 (s, C5) 28.2[h] (s, 2C, $CH_{3\ ring}$) Re-*C*≡C not observed	δ_A -10.44 J_{AM} 20.3 δ_M -18.39 $\delta_{A'}$ -19.03 $J_{A'M'}$ 18.7 $\delta_{M'}$ -15.42 --- ν(C≡C) 2010 ν(CO) 1952, 1930, 1892 ν(OTf) 1289 ν(C=C) not observed
7 [a] 	4.39 (br d, J_{HH} 7.9, 2H, CH_2) 3.62 (m, 1H, Re=C=CH) 2.35 (br s, 1H, OH)	340.3 (dt, $J_{CPtrans}$ 31.7, J_{CPcis} 10.4, Re=*C*=C) 191.3 (m, CO) 108.3 (dt, $J_{CPtrans}$ 13.4, J_{CPcis} 3.6, Re=C=*C*) 59.0 (s, CH_2OH)	δ_A -20.50 J_{AM} 25.3 δ_M -15.88 --- ν(CO) 2000, 1949 ν(C=C) 1634 ν(OTf) 1267
8 [a] 	4.21 (d, J_{HH} 2.4, 2H, CH_2)		δ_A - 6.69 J_{AM} 17.9 δ_M -19.23 --- ν(C≡C) 2095 ν(CO) 1940, 1878 ν(OH) 3440
9 [a] 	3.93, 3.58 (t, J_{HH} 7.0, 2H each, CH_2) 3.33. 2.83 (s, 3H each, OCH_3)	306.2 (dt, $J_{CPtrans}$ 38.5, J_{CPcis} 9.6, Re=*C*) 190.2 (m, CO) 69.0[h] (s, CH_2-*C*H_2) 63.6[h] (d, J_{CP} 3.2, OCH_3) 57.0[h] (d, J_{CP} 4.8, =C-*C*H_2) 41.5[h] (s, CH_2-O*C*H_3)	δ_A -17.06 J_{AM} 20.7 δ_M -9.87 --- ν(CO) 1958, 1888 ν(OTf) 1271
10 [a, e] 	4.51 (s, 2H, $CH_{2(C3\ ring)}$) 3.14 (t, J_{HH} 7.1, 2H, $CH_{2(C3\ ring)}$) 2.82 (t, J_{HH} 7.1, 2H, $CH_{2(C1\ ring)}$)	332.5 (dt, $J_{CPtrans}$ 33.5, J_{CPcis} 11.1, Re=*C*=C) 196.4; 190.5 (m, CO) 302.4 (dt, $J_{CPtrans}$ 37.0, J_{CPcis} 8.6, Re=C4) 111.9 (dt, $J_{CPtrans}$ 14.4, J_{CPcis} 2.9, Re=C=*C*) 63.8 (s, C6)[i] 54.9 (s, C2)[i] 32.3 (s, C3)[i]	δ_A -18.30 J_{AM} 21.6 δ_M -12.37 δ_A -21.60 $J_{A'M'}$ 25.3 δ_M -14.54 --- ν(CO) 2018, 1964, 1906 ν(C=C) 1665 ν(OTf) 1267
11 [a] 	2.07 (d, J_{HH} 6.7, 3H, CH_3) 2.65 (s, 3H, OCH_3) 6.26 (d, J_{HH} 15.4, *H*C=CHMe) 7.16 (d, J_{HH} 15.4, CH=C*H*Me)	290.0 (dt, $J_{CPtrans}$ 37.8, J_{CPcis} 8.5, Re=*C*) 199.9 (dt, $J_{CPtrans}$ 29.91, J_{CPcis} 6.72, CO) 151.5 (s, *C*H=C(H)CH_3) 141.8 (s, CH=*C*(H)CH_3) 62.8 (br s, O*C*H_3) 16.0 (s, CH=C(H)*C*H_3)	δ_A -16.50 J_{AM} 20.9 δ_M - 9.19 --- ν(CO) 1946, 1890 ν(C=C) 1628 ν(OTf) 1269

The NMR spectra were recorded in CD_2Cl_2 or for complex **11**, in $CDCl_3$ at room temperature using: ([a]) Bruker AC200, ([b])Varian VXR300, or ([c]) Bruker Avance DRX500 instruments. Only the ^1H and ^{13}C resonances due to the rhenium coordinated organyl ligand are reported in the table; the triphos skeleton resonances and the CO signals are given in the Experimental Section. Key: s, singlet; d, doublet; t, triplet, q, quartet; m, multiplet; br, broad. All $^{31}P\{^1H\}$ NMR spectra exhibit an AM_2 splitting pattern. ([d]) ABB' spin system. ([e]) AA'$M_2M'_2$ spin system. ([f]) $CH_{(C2\ ring)}$ not observed, likely masked by the aromatic resonaces. ([h]) Assigned by DEPT-135 experiment. ([i]) Assigned by ^1H,^{13}C-HMQC NMR experiment.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex [(triphos)(CO)$_2$Re-{C(OMe)CH=C(H)Me}]OTf·C$_6$H$_6$ (11·C$_6$H$_6$)

Re(1)−C(7)	1.887(12)	C(7)−O(2)	1.176(13)
Re(1)−C(6)	1.901(12)	C(8)−O(3)	1.289(12)
Re(1)−C(8)	2.078(10)	C(8)−C(9)	1.462(15)
Re(1)−P(2)	2.464(3)	C(9)−C(10)	1.299(17)
Re(1)−P(1)	2.483(3)	C(10)−C(11)	1.50(2)
Re(1)−P(3)	2.492(3)	C(12)−O(3)	1.449(14)
C(6)−O(1)	1.182(13)		
C(7)−Re(1)−C(6)	85.3(5)	C(6)−Re(1)−P(3)	97.9(4)
C(7)−Re(1)−C(8)	87.4(4)	C(8)−Re(1)−P(3)	88.7(3)
C(6)−Re(1)−C(8)	91.6(4)	P(2)−Re(1)−P(3)	81.03(9)
C(7)−Re(1)−P(2)	102.8(3)	P(1)−Re(1)−P(3)	88.46(9)
C(6)−Re(1)−P(2)	92.1(3)	O(1)−C(6)−Re(1)	172.7(10)
C(8)−Re(1)−P(2)	169.4(3)	O(2)−C(7)−Re(1)	175.7(10)
C(7)−Re(1)−P(1)	88.7(4)	O(3)−C(8)−C(9)	115.1(9)
C(6)−Re(1)−P(1)	172.6(3)	O(3)−C(8)−Re(1)	116.9(7)
C(8)−Re(1)−P(1)	92.5(3)	C(9)−C(8)−Re(1)	127.7(8)
P(2)−Re(1)−P(1)	84.97(9)	C(10)−C(9)−C(8)	125.2(13)
C(7)−Re(1)−P(3)	175.0(4)	C(9)−C(10)−C(11)	127.0(15)
		C(8)−O(3)−C(12)	124.9(9)

as previously reported. The propargylic alcohols HC≡CCH(Me)OH, HC≡CCMe$_2$OH, HC≡CCPh$_2$OH, HC≡CC(Me)(Ph)OH, and 2-methyl-1-buten-3-yne were purchased from Aldrich or Lancaster and used as received. 1-Propyn-2-ol, HC≡CCH$_2$OH, was distilled at atmospheric pressure just 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 either light diethyl ether or *n*-hexane before being dried in a stream of nitrogen unless otherwise stated. IR spectra were obtained in KBr using a Nicolet 510P FT-IR (4000−200 cm^{-1}) spectrophotometer. Deuterated solvents for NMR measurements (Aldrich and Merck) were dried over molecular sieves (4 Å). ^{1}H and ^{13}C-{^{1}H}NMR spectra were recorded on Bruker AC200, Varian VXR300, and Bruker DRX 500 spectrometers operating at 200.13, 299.94, and 500.13 MHz and 50.32, 75.42 and 125.75 MHz, respectively. Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (^{1}H) or the deuterated solvent multiplet (^{13}C). ^{31}P-{^{1}H}NMR spectra were recorded on the same instruments operating at 81.01, 121.42, and 202.46 MHz, respectively. Chemical shifts were measured relative to external 85% H_3PO_4 with downfield values taken as positive. The computer simulation of the second-order NMR spectra was carried out with a locally developed package containing the programs LAOCN3[19] and DAVINS.[20] 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 being less than 1% in all cases. Elemental analyses (C, H, S) were performed using a Carlo Erba model 1106 elemental analyzer. MS-FAB spectra were acquired with a Hewlett Packard MS Engine HP 5989A mass spectrometer (8 kV, 10 μA, probe temperature 50 °C) using nitrobenzyl alcohol as matrix.

Reaction of 1 with HC≡CCPh$_2$OH: Synthesis of [(triphos)(CO)$_2$Re{C=C=CPh$_2$}]OTf (2). To a suspension of **1** (200.0 mg, 0.20 mmol) in dichloromethane (5 mL) was added a slight excess (47 mg, 0.22 mmol) of 1,1-diphenyl-2-propyn-1-ol, HC≡CCPh$_2$OH. Immediately the color turned from pale yellow to deep red-violet. The reaction was completed after stirring 2 h at room temperature. The solution was concentrated under reduced pressure. Addition of *n*-hexane gave **2** as dark violet microcrystals. Yield: 81%. Anal. Calcd for $C_{59}H_{49}F_3O_5P_3SRe$: C, 58.75; H, 4.09; S, 2.66. Found: C, 58.68; H, 4.01; S, 2.57. ^{1}H NMR (CD_2Cl_2, 22 °C, 299.94 MHz): δ 1.68 (br s, 3H, $CH_{3(triphos)}$), 2.62 (m, 6H, $CH_{2(triphos)}$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 22 °C, 75.42 MHz): 40.0 (q, J_{CP}10.0 Hz, $CH_{3(triphos)}$), 39.8 (q, J_{CP}3.3 Hz, $CH_3C_{(triphos)}$), 34.3 (m, CH_2-$P_{ax(triphos)}$), 33.5 (m, $CH_2P_{eq(triphos)}$). UV−vis (CH_2Cl_2): λ_{max} (log ε) 545 nm (4.08). FAB$^+$-MS: *m/z* 1058 (M^+), 1030 [(triphos)-(CO)Re(C=C=CPh$_2$)]$^+$, 1000 [(triphos)Re(C=C=CPh$_2$)]$^+$.

Reaction of 1 with HC≡CCPh(Me)OH: Synthesis of [(triphos)(CO)$_2$Re{C=C=C(Ph)Me}]OTf (3). Complex **3** was obtained as dark red microcrystals following the same procedure for **2**. Yield: 77%. Anal. Calcd for $C_{54}H_{47}F_3O_5P_3SRe$: C, 56.69; H, 4.14; S, 2.80. Found: C, 57.01; H, 4.23; S, 2.76.^{1}H NMR (CD_2Cl_2, 22 °C, 299.94 MHz): δ 1.63 (s, 3H, $CH_{3\ triphos}$), 2.4−2.8 (m, 6H, $CH_{2\ triphos}$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 22 °C, 75.42 MHz): δ 39.4 (br s, $CH_{3\ triphos}$, $CH_3-C_{triphos}$), 33.4 (m, $CH_{2\ triphos}$). UV−vis (CH_2Cl_2): λ_{max} (log ε) 482 nm (5.322). FAB$^+$-MS: *m/z* 995 (M^+), 967 [(triphos)(CO)Re{C=C=C(Ph)-Me}]$^+$, 937 [(triphos)Re{C=C=C(Ph)Me}]$^+$, 867 [(triphos)-(CO)$_2$Re]$^+$.

In Situ NMR Studies of the Reaction between 1 and HC≡CCPh(R)OH (R = Ph, Me). A solution of **1** (30.0 mg, 0.03 mmol) in CD_2Cl_2 (0.8 mL) was prepared in a 5 mm screw-cap NMR tube and frozen at −196 °C, and 1 equiv of the appropriate alkynol, HC≡CCPh(R)OH (R = Ph, Me), was introduced through the serum cap. The tube was inserted into the NMR probe precooled at −70 °C. The progress of the reaction was followed by variable-temperature ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. No reaction occurred until the temperature was raised to about −5 °C. At this temperature **1** started to convert to the allenylidene **2** (or **3**), which was the only detectable product. Further heating to 15 °C completed the transformation within 1 h.

Reaction of 3 with Triethylamine: Synthesis of [(triphos)(CO)$_2$Re{C≡CC(Ph)=CH$_2$}] (4). To a solution of **3** (200.0 mg, 0.17 mmol) in dichloromethane (5 mL) was added a 2-fold excess of NEt$_3$ (48 μL, 0.34 mmol) at room temperature with stirring. After 3 h, a brown-green solution was obtained. Addition of *n*-hexane and concentration under nitrogen yielded a pale brown solid; yield 82%. Anal. Calcd for $C_{53}H_{46}O_2P_3Re$: C, 64.04; H, 4.66. Found: C, 64.12; H, 4.59. ^{1}H NMR (CD_2Cl_2, 22 °C, 200.13 MHz): δ 1.43 (br s, 3H, $CH_{3\ triphos}$), 2.42 (m, 6H, $CH_{2\ triphos}$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 22 °C, 50.32 MHz): 40.4 (q, J_{CP} 9.78 Hz, $CH_{3\ triphos}$), 39.9 (q, J_{CP} 4.31 Hz, $CH_3-C_{\ triphos}$), 35.6 (br d, J_{CPax} 22.69 Hz, $CH_2-P_{ax\ triphos}$), 34.2 (m, $CH_2-P_{eq\ triphos}$).

Reaction of 4 with HBF$_4$·OMe$_2$. One equivalent of HBF$_4$·OMe$_2$ (3.6 μl, 0.03 mmol) was syringed into a CD_2Cl_2 solution (0.8 mL) of **6** (30.0 mg, 0.03 mmol) in a 5 mm screw-cap NMR tube. ^{31}P{^{1}H} NMR analysis showed the complete transformation of **4** into **3**.

Synthesis of [{(triphos)(CO)$_2$Re}$_2${μ-(C$_{10}$H$_{12}$)}](OTf)$_2$ (5). Method A: Reaction of 1 with HC≡CCMe$_2$OH. A slight excess of 2-methyl-3-butyn-2-ol, HC≡CCMe$_2$OH, (21 μL, 0.22 mmol) was syringed into a suspension of **1** (200.0 mg, 0.20 mmol) in dichloromethane (6 mL) under stirring. The initial pale yellow color quickly disappeared to produce a deep violet solution, which was stirred additionally for 1 h at room temperature. Concentration of the solution under nitrogen to ca. half volume and addition of diethyl ether (3 mL) gave **5** as violet microcrystals, which were filtered off and dried under nitrogen. Yield: 68%. Anal. Calcd for $C_{98}H_{90}F_6O_{10}P_6S_2Re_2$: C, 54.39; H, 4.19; S, 2.96. Found: C, 54.45; H, 4.27; S, 2.81. ^{1}H NMR (CD_2Cl_2, 22 °C, 200.13 MHz): δ 1.66 (q, J_{HP} 2.8 Hz, 3H, $CH_{3\ triphos}$), 1.82 (q, J_{HP} 3.3 Hz, 3H, $CH_{3\ triphos}$), 2.9−2.4 (m, 12H, $CH_{2\ triphos}$).^{13}C{^{1}H} NMR (CD_2Cl_2, 22 °C, 50.32 MHz): δ 40.1−38.8 (m, $CH_{3\ triphos}$, $CH_3-C_{\ triphos}$), 36.1 (td, $N = (J_{CPeq} + J_{CPax}$ 14.6 Hz, J_{CPax} 4.8 Hz), $CH_2-P_{ax\ triphos}$), 33.1−31.0 (m, CH_2-

(19) Castellano, S.; Bothner-By, A. A. *J. Chem. Phys.* **1964**, *41*, 3863.
(20) Stephenson, D. S.; Binsch, G. A. *J. Magn. Reson.* **1980**, *37*, 395; **1980**, *37*, 409.

$P_{ax\ triphos}$, $CH_2-P_{eq\ triphos}$). FAB$^+$-MS: *m*/*z* 895 [(triphos)-$(CO)_3Re]^+$, 867 [(triphos)$(CO)_2Re]^+$, 839 [(triphos)$(CO)Re]^+$.

Method B: Reaction of 1 with HC≡CC(Me)=CH$_2$. Compound **5** was prepared in similar yield by replacing HC≡$CCMe_2OH$ with 2-methyl-1-buten-3-yne, HC≡CC(Me)=CH_2 (21 μL, 0.22 mmol), in the above procedure.

In Situ NMR Studies of the Reaction of 1 with HC≡CCMe$_2$OH. A solution of **1** (30.0 mg, 0.03 mmol) in CD_2Cl_2 (0.8 mL) was prepared in a 5 mm screw-cap NMR tube and cooled at −78 °C with a dry ice/acetone bath before adding 1 equiv of HC≡$CCMe_2OH$ through the serum cap. The tube was inserted into the NMR probe precooled at −70 °C. The progress of the reaction was followed by variable-temperature ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy. No reaction product was observed until the temperature was raised to about −5 °C. At this temperature **1** started to convert to the dinuclear complex **5**, which remains the only detectable product until the transformation was complete.

Replacing HC≡$CCMe_2OH$ with HC≡CC(Me)=CH_2 in the above in situ NMR test did not reveal the formation of any intermediate along the transformation of **1** into **5**.

Reaction of 5 with Amines: Synthesis of [{(triphos)-(CO)$_2$Re}$_2${μ-(C$_{10}$H$_{11}$)}]OTf (6). Addition of a double proportion of either NEt_3 (26 μL, 0.18 mmol) or NH_2Bu^t (20 μL, 0.18 mmol) to a dichloromethane solution of **5** (200.0 mg, 0.09 mmol) caused an immediate color change from dark violet to blue ink. After 30 min stirring, the solvent was removed under reduced presssure to leave **6** as a blue ink solid. Yield: 78%. Anal. Calcd for $C_{97}H_{89}F_3O_7P_6SRe_2$: C, 57.85; H, 4.45; S, 1.59. Found: C, 56.98; H, 4.37; S, 1.73. ^{1}H NMR (CD_2Cl_2, 22 °C, 200.13 MHz): δ 1.57 (br s, 3H, $CH_{3\ triphos}$), 1.49 (br s, 3H, $CH_{3\ triphos}$), 2.8−2.3 (m, 12H, $CH_{2\ triphos}$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C, 50.32 MHz): δ 40.3 (m, 2C, $CH_{3\ triphos}$), 39.4 (m, 2C, $CH_3-C_{triphos}$), 34.0−36.5 (m, $CH_{2\ triphos}$).

Reaction of 6 with HBF$_4$·OMe$_2$. Addition of $HBF_4{\cdot}OMe_2$ (2 μL) to a CD_2Cl_2 solution (0.8 mL) of **6** (30.0 mg, 0.015 mmol) in a 5 mm screw-cap NMR tube immediately regenerated the dark violet coloration of **5** (^{31}P NMR analysis).

Reaction of 1 with HC≡CCH$_2$OH: Synthesis of [{(triphos)(CO)$_2$Re}$_2$(μ-C$_6$H$_6$O)](OTf)$_2$ (10). To a suspension of **1** (200.0 mg, 0.20 mmol) in 5 mL of dichloromethane was added propargyl alcohol (13 μL, 0.22 mmol), changing immediately the color of the solution from pale yellow to indigo. After stirring 2 h at room temperature, the solution was evaporated to dryness to leave a blue-gray solid, which was washed with *n*-hexane (3 × 2 mL) and dried under reduced pressure. Yield: 88%. Anal. Calcd for $C_{94}H_{84}F_6O_{11}P_6S_2Re_2$: C, 53.11; H, 3.98; S, 3.01. Found: C, 53.45; H, 4.32; S, 3.19. ^{1}H NMR (CD_2Cl_2, 22 °C, 200.13 MHz): δ 1.61 (br s, 3H, $CH_{3\ triphos}$), 1.72 (br s, 3H, $CH_{3\ triphos}$), 2.63 (m, 14H, $CH_{2\ triphos} + CH_{2\ ring}$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C, 50.32 MHz): δ 39.3 (m, $CH_{3\ triphos} + CH_3-C_{triphos}$), 34.9 (m, $CH_2-P_{ax\ triphos}$), 32.2 (m, $CH_2-P_{eq\ triphos}$). FAB$^+$-MS: *m*/*z* 895 [(triphos)$(CO)_3Re]^+$, 867 [(triphos)-$(CO)_2Re]^+$, 839 [(triphos)$(CO)Re]^+$.

In Situ NMR Studies of the Reaction of 1 with HC≡CCH$_2$OH. A solution of **1** (30.0 mg, 0.03 mmol) in CD_2Cl_2 (0.8 mL) was prepared in a 5 mm screw-cap NMR tube and cooled at −78 °C with a dry ice/acetone bath before adding 1 equiv of HC≡CCH_2OH through the serum cap. The tube was inserted into the NMR probe precooled at −70 °C. The progress of the reaction was followed by variable-temperature ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy. At −15 °C the hydroxyvinylidene [(triphos)-$(CO)_2Re\{C{=}C(H)CH_2OH\}]OTf$ (**7**) began to form. This lilac intermediate was obtained in quantitative NMR yield after standing 15 min at −8 °C. Further heating of the NMR sample to 5 °C slowly transformed **7** into the dinuclear complex **10**. Within 2 h at room temperature, **10** became the only detectable rhenium species.

Reaction of 7 with Triethylamine: Synthesis of [(triphos)(CO)$_2$Re {C≡CCH$_2$OH}] (8). An excess of neat NEt_3 (110 μL, 0.80 mmol) was syringed into a solution of **7** prepared in situ by mixing 20 mg of **1** and 1 equiv of HC≡CCH_2OH in CD_2Cl_2 (0.8 mL) into a 5 mm screw-cap NMR tube, maintained at −15 °C. Immediately the lilac color disappeared to afford a yellow solution of the hydroxymethylethynyl complex **8**. ^{1}H NMR (CD_2Cl_2, 22 °C, 200.13 MHz): δ 1.43 (br s, 3H, $CH_{3\ triphos}$), 2.5 (m, 6H, $CH_{2\ triphos}$).

Treatment of this solution with $HBF_4{\cdot}OMe_2$ at −15 °C regenerates quantitatively **7**.

Synthesis of [(triphos)(CO)$_2$Re{C(OMe)CH$_2$CH$_2$OMe}]-OTf (9). Method A: Reaction of 7 with Methanol. Addition of methanol (9 μL) into a NMR tube containing a freshly generated solution of **7** (ca. 0.03 mmol) caused a fast color change from lilac to yellow. ^{31}P NMR analysis confirmed the quantitative formation of **9**. Anal. Calcd for $C_{49}H_{49}F_3O_7P_3SRe$: C, 52.64; H, 4.42; S, 2.86. Found: C, 53.22; H, 4.57; S, 2.91. ^{1}H NMR (CD_2Cl_2, 22 °C, 200.13 MHz): δ 1.82 (br s, 3H, $CH_{3\ triphos}$), 2.4−3.1 (m, 6H, $CH_{2\ triphos}$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C, 50.32 MHz): δ 40.3 (q, J_{CP} 9.64 Hz, $CH_{3\ triphos}$), 39.7 (q, J_{CP} 3.22 Hz, $CH_{2\ triphos}$), 34.9 (td, J_{CPax} 13.65 Hz, J_{CPeq} 3.22 Hz, $CH_2-P_{ax\ triphos}$), 32.6 (dt, J_{CPeq} 24.09 Hz, J_{CPax} 4.0 Hz, $CH_2-P_{eq\ triphos}$). FAB$^+$-MS: *m*/*z* 970 (M^+), 895 [(triphos)$(CO)_3Re]^+$, 867 [(triphos)$(CO)_2Re]^+$, 839 [(triphos)$(CO)Re]^+$.

Method B: Reaction of 1 with HC≡CCH$_2$OH in the Presence of Methanol. 1 (200.0 mg, 0.20 mmol), suspended in a 5 mL of a 3:1 dichloromethane/methanol mixture, was treated with propargyl alcohol (15 μL, 0.24 mmol) at room temperature. The resulting pale red solution was stirred at room temperature for 1 day, and the solvent was removed in vacuo to leave a pink residue, which was washed with *n*-hexane and diethyl ether. Yield: 68%.

[(triphos)(CO)$_2$Re{C(OMe)CH=C(H)Me}OTf (11). A slight excess of 3-butyn-2-ol, HC≡CC(Me)HOH (17 μL, 0.22 mmol), was syringed into a solution of **1** (200.0 g, 0.20 mmol) in a 3:1 dichloromethane/methanol mixture (5 mL). After stirring at room temperature for 3 h, the solvent was removed in vacuo to yield a pale green residue, which washed with diethyl ether and dried at the pump. Yield: 73%. Anal. Calcd for $C_{49}H_{47}F_3O_6P_3SRe$: C, 53.5; H, 4.31; S, 2.91. Found: C, 52.98; H, 4.53; S, 2.97. ^{1}H NMR ($CDCl_3$, 22 °C, 200.13 MHz): δ 1.82 (br s, 3H, $CH_{3\ triphos}$), 2.55 (m, 4H, $CH_2-P_{eq\ triphos}$), 3.01

Table 3. Crystal Data and Structure Refinement for [(triphos)(CO)$_2$Re{C(OMe)CH=C(H)Me}]OTf·C$_6$H$_6$ (11·CC$_6$H$_6$)

empirical formula	$C_{55}H_{53}F_3O_6P_3ReS$
fw	1178.21
temperature	293(2) K
wavelength	0.71069 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	a = 15.129(2) Å
	b = 15.834(5) Å
	c = 11.763(5) Å
	α = 97.78(3)°
	β = 93.06(2)°
	γ = 70.02(2)°
volume	2623.8(16) Å^3
Z	1
density (calcd)	1.498 Mg/m^3
abs coeff	2.506 mm^{-1}
F(000)	1198
cryst size	0.25 × 0.12 × 0.10 mm
θ range for data collection	1.38−25.00°
index ranges	$-17 \le h \le 17$, $-18 \le k \le 18$, $0 \le l \le 13$
no. of reflns collected	9202
no. of indep reflns	9202 [R(int) = 0.0000]
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	9202/0/243
goodness-of-fit on F^2	1.025
final R indices [$I > 2\sigma(I)$]	R1 = 0.0659, wR2 = 0.1450
R indices (all data)	R1 = 0.1259, wR2 = 0.1666
largest difference peak and hole	1.348 and −1.230 e Å^{-3}

(m, 2H, CH_2−$P_{ax\ triphos}$).^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C, 50.32 MHz): δ 40.6 (q, J_{CP} 10.37 Hz, $CH_{3\ triphos}$), 39.9 (q, J_{CP} 3.66 Hz, CH_3−$C_{\ triphos}$), 35.4 (td, J_{CPax} 13.43, J_{CPeq} 3.27, CH_2−$P_{ax\ triphos}$), 32.2 (dt, J_{CPeq} 23.8 Hz, J_{CPax} 3.27 Hz, CH_2−$P_{eq\ triphos}$).

X-ray Diffraction Study of [(triphos)(CO)$_2$Re{C(OMe)CH=C(H)Me}]OTf·C$_6$H$_6$ (11·C$_6$H$_6$). Pale green crystals (0.25 × 0.12 × 0.10 mm) of **11·C$_6$H$_6$** were grown by slow evaporation in air of a diluted dichloromethane/benzene solution of **11**. A summary of crystal and intensity data for the compound is presented in Table 3. Experimental data were recorded at room temperature on a Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. A set of 25 carefully centered reflections in the range 7.5° ≤ θ ≤ 10° was used for determining the lattice constants. As a general procedure, the intensity of three standard reflections was measured periodically every 2 h for orientation and intensity control. This procedure did not reveal any decay of intensities. The data were corrected for Lorentz and polarization effects. Atomic scattering factors were those tabulated by Cromer and Waber,[21] with anomalous dispersion corrections taken from ref 22. An empirical absorption correction was applied using the program XABS[23] with transmission factors in the range 0.53−1.36. The computational work was performed with a Pentium-II personal computer using the programs SHELX93[24] and ZORTEP.[25] Final atomic coordinates with equivalent isotropic thermal parameters of all atoms and structure factors are available as Supporting Information.

The structure was solved via the heavy atom technique, and all the non-hydrogen atoms were found through a series of F_o Fourier maps. Refinement was done by full-matrix least-squares calculations, initially with isotropic thermal parameters, and then, in the last least-squares cycle, with anisotropic thermal parameters for rhenium, phosphorus, and the carbon atoms of the triphos skeleton. All of the phenyl rings were treated as rigid bodies with D_{6h} symmetry and C−C distances fixed at 1.39 Å. Hydrogen atoms were introduced in calculated positions, but not refined. At an advanced stage of refinement, a solvent molecule of benzene was found and successfully refined.

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Supporting Information Available: Tables of crystallographic data for **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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