2-Oxacyclopentylidene, 2-Oxacyclohexylidene, and 2-Oxacycloheptylidene Rhenium Complexes by Reaction of ω-Alkynols with the $[\{MeC(CH_2PPh_2)_3\}Re(CO)_2]^+$ Auxiliary

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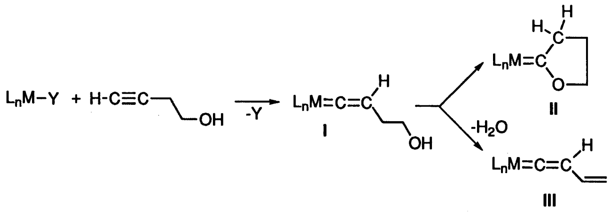
Various β-, γ-, and δ-alkynols have been reacted with the $16e^-$ fragment $[(triphos)Re(CO)_2]^+$ generated in situ by H_2 elimination from $[(triphos)Re(CO)_2(\eta^2\text{-}H_2)]BF_4$ [triphos = $MeC(CH_2PPh_2)_3$]. Irrespective of the length of the alkyl chain between the C≡C and OH functional groups in the ω-alkynol, 2-oxacyclocarbene complexes are obtained. These include the 2-oxacyclopentylidene derivatives $[(triphos)Re(CO)_2\{=CCH_2CH_2CH_2O\}]BF_4$ and $[(triphos)Re(CO)_2\{=CCH_2CH_2CH(Me)O\}]BF_4$, the 2-oxacyclohexylidene derivatives $[(triphos)Re(CO)_2\{=CCH_2CH_2CH_2CH_2O\}]BF_4$ and $[(triphos)Re(CO)_2\{=CCH_2CH_2CH_2CH(Me)O\}]BF_4$, and the 2-oxacycloheptylidene complex $[(triphos)Re(CO)_2\{=CCH_2CH_2CH_2CH_2CH_2O\}]BF_4$. The latter compound contains a unprecedented seven-membered oxacarbene ring. The rhenium-assisted δ-alkynol to 2-oxacyloheptylidene rearrangement proceeds via the hydroxybutylvinylidene kinetic intermediate $[(triphos)Re(CO)_2\{C=C(H)CH_2CH_2CH_2CH_2OH\}]BF_4$, which has been characterized in both the solid state and solution. An X-ray analysis has been carried out on a single crystal of $[(triphos)Re(CO)_2\{=CCH_2CH_2CH(Me)O\}]BF_4$. The structure of this complex consists of $[(triphos)Re(CO)_2\{=CCH_2CH_2CH(Me)O\}]^+$ cations and tetrafluoroborate anions with no interspersed solvent molecules. A *facial* triphos ligand, two *cis*-disposed carbonyl groups and a 2-oxacyclopentylidene ligand coordinate the Re centre in a slightly distorted octahedral environment.

Introduction

The reaction of alkynols with unsaturated metal fragments provides a convenient synthetic route to 2-oxacyclocarbene complexes,[1] that are receiving increasing attention as organometallic synthons in several catalytic and stoichiometric elaborations.[2][3] The most widely studied of these, are the reactions of β-alkynols to give 2-oxacyclopentylidene derivatives, and various complexes with ruthenium,[4][5][6][7] osmium,[8] manganese,[9] rhenium,[9a] and metals of the chromium group[1][10] have recently been described. The β-alkynol to oxacyclocarbene rearrangement has been shown to proceed via preliminary metal-assisted 1-alkyne to vinylidene tautomerization.[1][10b][11] For β-alkynols, the formation of cyclic Fischer carbene implies the generation of hydroxyethylvinylidene derivatives (**I**), which have been intercepted spectroscopically in a few cases (Scheme 1).[5] Vinylidenes are highly polarized C_2 ligands and both experimental[12][13] and theoretical studies[14] show the C_α atom to be an electrophilic centre susceptible to attack by almost any sort of nucleophile (alcohols, water, amines, thiols, phosphanes, etc.).[12] In case of β-hydroxyethylvinylidene ligands, the oxacarbene ring forms via intramolecular attack by the OH group of the dangling hydroxyalkyl substituent at the C_α atom. When this happens it is implicit that the ring-closure reaction affording the Fischer carbene (**II**) is favored over the equally possible elimination of water to give the vinylvinylidene derivative (**III**).[15]

Scheme 1. Reactions of 3-butyn-1-ol with metal-ligand systems



It has been observed experimentally that the intramolecular attack by the hydroxy group is increasingly disfavored as the number of CH_2 spacers between the triple bond and the OH group in the alkynol increases. Indeed, 2-oxacyclohexylidene complexes derived from metal-assisted rearrangements of γ-alkynols are quite rare compounds,[1][8a][10b] while no example involving δ-alkynols has yet been reported.[16][17] In actuality, δ-alkynols are still reactive substrates towards transition metal fragments. Due to the length of the pendant hydroxyalkyl tail, however, their activation results in the preferential formation of stable hydroxybutylvinylidene complexes.[8][18] In no case was the hydroxybutylvinylidene intermediate seen to convert to the 2-oxacycloheptylidene isomer.

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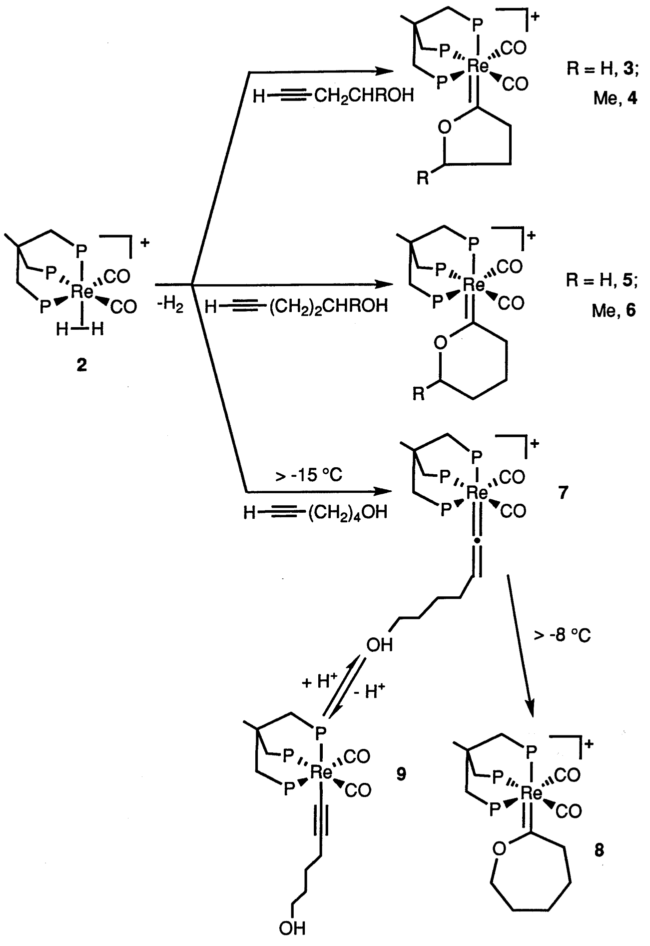
Stimulated by the idea that a comparative study involving the reaction of a unique metal fragment with different ω-alkynols could have provided additional information on the mechanism of formation of 2-oxacarbene complexes as well as their chemistry, we decided to examine the reactions of various β-, γ-, and δ-alkynols with the kinetically inert organometallic support $[\{MeC(CH_2PPh_2)_3\}Re(CO)_2]^+$.[19] We were gratified to find that Fischer carbene complexes are selectively formed, via kinetic hydroxyvinylidene intermediates, irrespective of the number of CH_2 spacers. The hydroxyvinylidene complex has exclusively been intercepted with the δ-alkynol 5-hexyn-1-ol and its conversion to the thermodynamic 2-oxacycloheptylidene product has been studied.

Results and Discussion

The preparations and principal reactions reported in this article are summarized in Scheme 2. Selected spectroscopic data (IR and NMR) are collected in Table 1, or are provided in the Experimental Section. The total and unambiguous assignment of all the hydrogen and carbon resonances for all rhenium complexes was obtained by a combination of 1D- and 2D-NMR spectroscopy including $^1H\{^{31}P\}$, DEPT-135, $^1H,^1H$-COSY, $^1H,^1H$-NOESY, and $^1H,^{13}C$-HETCOR experiments.

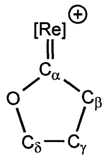
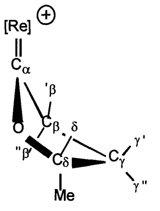
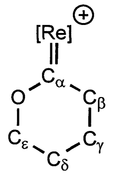
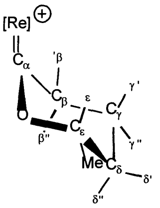
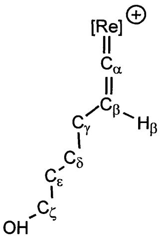
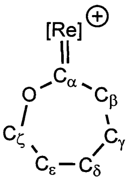
Scheme 2. Reactions of $[(triphos)Re(CO)_2]^+$ auxiliary with ω-alkynols



Synthesis and Characterization of 2-Oxacycloalkylidene Complexes: In earlier work,[19] we have shown that $[(triphos)Re(CO)_2H]$ (**1**) reacts with $HBF_4{\cdot}OMe_2$ in CH_2Cl_2 to give $[(triphos)Re(CO)_2(\eta^2\text{-}H_2)]BF_4$ (**2**) which contains a weakly bound dihydrogen ligand.[19] We have now found that **2** in CH_2Cl_2 reacts with 3-butyn-1-ol yielding the 2-oxacyclopentylidene complex $[(triphos)Re(CO)_2\{=CCH_2CH_2CH_2O\}]BF_4$ (**3**). The selective formation of this Fischer carbene complex takes place already at −10°C, and proceeds with no detectable intermediate on the NMR timescale. The room-temperature $^{31}P\{^1H\}$-NMR spectrum consists of an AM_2 pattern with chemical shifts and coupling constants in line with those reported for other cationic carbene complexes of the general formula $[(triphos)Re(CO)_2\{CRR'\}]Y$.[20] The magnetic equivalence of the two phosphorus atoms lying *trans* to the two carbonyl ligands is consistent with a rapid rotation of the oxacyclopentylidene group about the Re=C bond. The oxacarbene ligand continues to rotate freely even at −80°C. A very low-energy barrier to rotation is typical of carbene and vinylidene groups bonded to the $[(triphos)Re(CO)_2]^+$ fragment,[19][20] and it is also commonly encountered in carbene complexes with other transition metals.[9b][21] The most direct spectroscopic evidence of the presence of a carbene ligand in **3** is provided by the $^{13}C\{^1H\}$-NMR spectrum which contains a doublet of triplets centred at $\delta = 293.4$ ($J_{CPtrans} = 35.0$ Hz, $J_{CPcis} = 8.9$ Hz).[12][13] The other oxacyclopentylidene carbon atoms resonate at $\delta = 85.3$, 62.7, and 22.8, consistent with this type of ligand, while the two carbonyl carbon atoms appear as a second-order multiplet at $\delta = 197.0$. This may properly be computed using an AXX′Y spin system (A: carbonyl C atom, X and X′: P atoms *trans* to the CO ligands, Y: P atom *trans* to the carbene ligand; see Table 1).[19][20][22] The proton NMR spectrum correlates well with the spectra of various 2-oxacyclocarbene metal complexes containing three methylene groups in the ring.[4] A cyclic oxacarbene ligand in **3** is finally supported by the IR spectrum displaying a medium intensity ν(COC) band at 1194 cm^{-1} and two strong ν(CO) absorptions at wavenumbers (1962 and 1912 cm^{-1}) that are typical of $[(triphos)Re(CO)_2\{=CRR'\}]Y$ carbene compounds.[20]

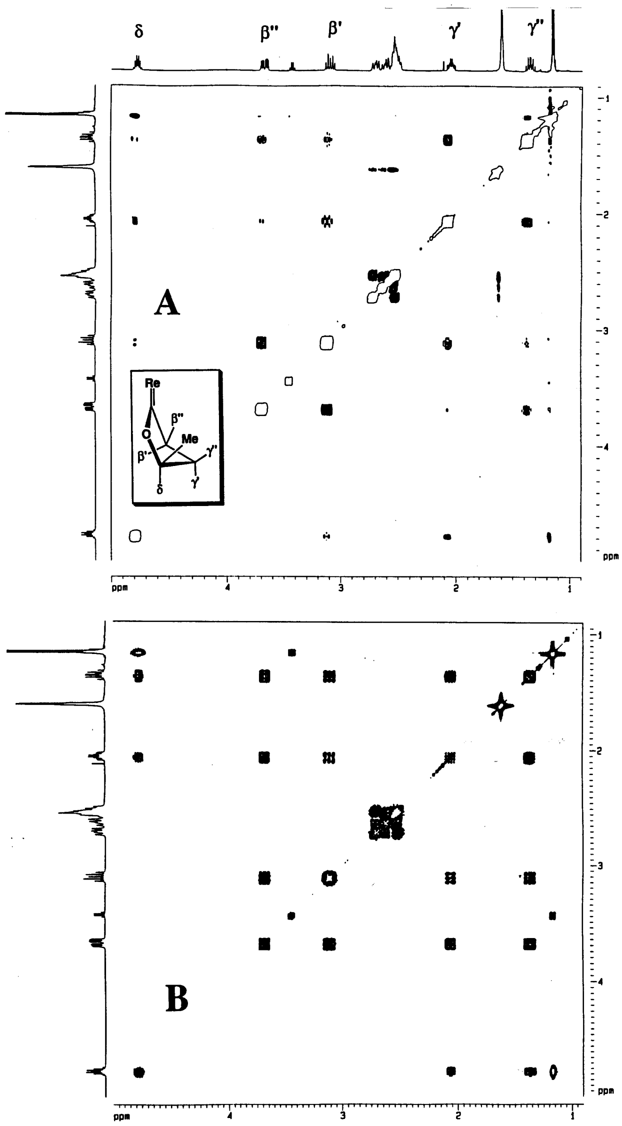
Replacing 3-butyn-1-ol with (±)-4-pentyn-2-ol in the reaction with **2** affords the substituted 2-oxa-3-methyl-cyclopentylidene complex $[(triphos)Re(CO)_2\{=CCH_2CH_2CH(Me)O\}]BF_4$ (**4**) as air-stable orange crystals. As expected, the presence of a stereogenic carbon atom in the oxacarbene ring differentiates the spectroscopic characteristics of **4** from those of **3**. For example, the $^{31}P\{^1H\}$-NMR spectrum of **4** consists of an AMQ spin system, while the carbonyl carbons appear in the $^{13}C\{^1H\}$-NMR spectrum as a well-resolved doublet of triplets ($\delta = 198.6$, $J_{CPtrans} = 45.5$ Hz, $J_{CPcis} = 5.7$ Hz). The stereocenter in the 2-oxacyclopentylidene ring also leads to the chemical and magnetic nonequivalence of the methylene protons. For this reason, the resonances of the oxacarbene-ring protons could only be unambiguously assigned by means of 2D-COSY and 2D-phase sensitive NOESY NMR spectra. In particular, the

Table 1. Selected ^{1}H-, ^{13}C{^{1}H}-, and ^{31}P{^{1}H}-NMR spectral data and IR absorptions for the complexes

Complex	^{1}**H** δ (mult, J, assignt)^{b,c}	^{13}**C**{^{1}**H**} δ (mult, J, assignt)^{b,c}	^{31}**P** {^{1}**H**} δ^{c,d} **IR** (KBr) cm^{-1}
 **3**	1.73 (qu, J_{HH} 7.8, H_{γ}, 2H) 3.28 (td, J_{HH} 7.7, J_{HP} 0.6, H_{β}, 2H) 4.06 (t, J_{HH} 7.6, H_{δ}, 2H)	293.4 (dt, $J_{CPtrans}$ 35.0, J_{CPcis} 8.9, C_{α}) 197.0 (m, CO) 85.3 (d, J_{CP} 3.2, C_{δ}) 62.7 (d, J_{CP} 5.7, C_{β}) 22.8 (s, C_{γ})	δ_{A} -15.90, J_{AM} 22.1 δ_{M} -11.86 ν(CO) 1962; 1912 ν(COC) 1194
 **4**	1.15 (d, $J_{MeH\delta}$ 6.3Hz, $CH_{3\,carbene}$, 3H) 1.35 (dddd, $J_{H\gamma''H\gamma'}$ 12.8, $J_{H\gamma''H\beta'}$ 9.2, $J_{H\gamma''H\delta}$ 6.3, $J_{H\gamma''H\beta''}$ 3.6, $H_{\gamma''}$, 1H) 2.05 (dddd, $J_{H\gamma'H\gamma''}$ 12.8, $J_{H\gamma'H\beta''}$ 8.8, $J_{H\gamma'H\delta}$ 6.7, $J_{H\gamma'H\beta'}$ 3.6, $H_{\gamma'}$, 1H) 3.10 (ddd, $J_{H\beta''H\beta'}$ 19.8, $J_{H\beta'H\gamma''}$ 9.2, $J_{H\beta'H\gamma'}$ 3.6, $H_{\beta'}$, 1H) 3.68 (ddd, $J_{H\beta'H\beta''}$ 19.8, $J_{H\beta''H\gamma'}$ 8.8, $J_{H\beta''H\gamma''}$ 3.6, $H_{\beta''}$, 1H) 4.77 (dpsqu, $J_{H\delta H\gamma'}$ 6.7, $J_{H\delta Me} \cong J_{H\delta H\gamma''}$ 6.3, H_{δ}, 1H)	294.5 (dt, $J_{CPtrans}$ 35.6, J_{CPcis} 9.2, C_{α}) 198.6 (dt, $J_{CPtrans}$ 45.5, J_{CPcis} 5.7, CO) 98.5 (d, J_{CP} 3.2, C_{δ}) 65.5 (d, J_{CP} 5.0, C_{β}) 32.5 (s, C_{γ}) 22.4 (s, $CH_{3\,carbene}$)	δ_{A} -13.10, J_{AM} 26.7 δ_{M} -14.73, δ_{Q} -16.63, $J_{AQ} \approx J_{MQ}$ 21.3 ν(CO) 1958, 1906 ν(COC) 1223
 **5**	1.50 (m, H_{γ}+ H_{δ}, 4H) 3.28 (t, $J_{H\beta H\gamma}$ 6.8, H_{β}, 2H) 3.44 (t, $J_{H\varepsilon H\delta}$ 6.0, H_{ε}, 2H)	303.0 (dt, $J_{CPtrans}$ 36.8, J_{CPcis} 9.5, Cα) 198.0 (m, CO) 75.0 (d, J_{CP} 2.5, C_{ε}) 55.6 (d, J_{CP} 3.8, C_{β}) 21.1 (s, C_{δ}) 16.7 (s, C_{γ})	δ_{A} -16.71, J_{AM} 21.4 δ_{M} -10.70 ν(CO) 1956, 1902 ν(COC) 1273
 **6**	1.01 (d, $J_{MeH\varepsilon}$ 6.3, $CH_{3\,carbene}$, 3H) 1.35 (m, $H_{\beta'}$ + $H_{\delta''}$, 2H) 1.60 (m, $H_{\gamma'}$+$CH_{3\,triphos}$, 4H) 1.96 (m, $H_{\delta'}$,1H) 2.40-2.70 (m, Hγ″+ $CH_{2\,triphos}$, 7H) 3.92 (ddd, $J_{H\beta''H\beta'}$ 17.1, $J_{H\beta''H\gamma'}$ 5.8, $J_{H\beta''H\gamma''}$ 3.6, $H_{\beta''}$, 1H) 4.14 (m, H_{ε}, 1H)	305.3 (dt, $J_{CPtrans}$ 36.9, J_{CPcis} 8.6, C_{α}) 197.1 (dt, $J_{CPtrans}$ 44.5, J_{CPcis} 7.6, CO) 83.9 (d, J_{CP} 2.2, C_{ε}) 55.8 (dt, $J_{CPaxial}$ 4.5, J_{CPeq} 1.3, C_{β}) 28.7 (s, C_{δ}) 20.3 (s, $CH_{3\,carbene}$) 16.9 (s, C_{γ})	δ_{A} -12.80, J_{AM} 20.1 δ_{M} -14.00, J_{AQ} 23.5 δ_{Q} -16.56, J_{MQ} 20.7 ν(CO) 1962, 1896 ν(COC) 1252
 **7**	1.43 (psqu, $J_{H\delta H\gamma} \approx J_{H\delta H\varepsilon}$ 7.4 H_{δ} 2H) 1.61 (m, H_{ε}, 2H) 2.38 (psq, $J_{H\gamma H\beta}$ 8.3, $J_{H\gamma H\delta}$ 7.4, H_{γ} 2H) 3.53 (tpsq $J_{H\beta H\gamma}$ 8.3,$J_{HPA} \approx J_{HPM}$ 2.8, $H_{\beta\,vinylidene}$, 1H) 3.64 (br t, $J_{H\zeta\,H\varepsilon}$ 6.1, H_{ζ}, 2H)	343.9 (dt, $J_{CPtrans}$ 32.1, J_{CPcis}11.6, C_{α}) 191.7 (m, CO) 111.0 (dt, $J_{CPtrans}$ 12.7, J_{CPcis} 2.5, C_{β}) 52.1 (s, C_{ζ}) 31.5 (s), 27.6 (s) (C_{δ} e C_{ε}) 19.8 (s, Cγ)	δ_{A} -19.41, J_{AM} 23.2 δ_{M} -15.82 ν(CO) 2008, 1946 ν(C=C) 1663 ν(OH) 3550
 **8**	1.41 (m, H_{ε}, 2H) 1.70 (m, H_{γ}+ Hδ, 4H) 3.57 (m, H_{β}, 2H) 3.91 (t, $J_{H\zeta H\varepsilon}$ 4.6, H_{ζ}, 2H)	310.8 (dt, $J_{CPtrans}$ 38.4, J_{CPcis} 8.6, C_{α}) 198.1 (AXX’Y $_{spin\ sistem}$, J_{AX} 7.0, J_{AY} 5.8, $J_{AX'}$ -8.2, $J_{XX'}$ 26.8, CO) 78.6 (d, J_{CP} 2.9 C_{ζ}) 60.1 (d, J_{CP} 5.2, C_{β}) 29.1, 28.2, 21.5 (all s, C_{γ}, C_{δ}, C_{ε})	δ_{A} -17.14, J_{AM} 20.9 δ_{M} -11.49 ν(CO) 1956, 1890

latter experiment allowed us to establish the spatial relationships between the H_{δ} proton at $\delta = 4.77$ (which correlates with the CH carbon at $\delta = 98.5$ in the 2D-^{1}H,^{13}C-HMQC NMR experiment) and the signal at $\delta = 2.05$ of the opposite $H_{\gamma'}$ proton. Following this assignment, the remaining proton and carbon resonances were readily and reliably identified. Significant sections of the NOESY and COSY spectra are presented in Figure 1.

Figure 1. (**A**) Section ($\delta = 5.00 - 0.90$) of the phase-sensitive 2D-^{1}H NOESY spectrum of **4** (500.13 MHz, CD_2Cl_2, 25°C, τ_{mix} 800 ms) showing the negative cross-peaks between the protons of the 2-oxa-3-methyl-cyclopentylidene ring. (**B**) Contour plot of a section ($\delta = 5.00-0.90$) of the 2D-^{1}H COSY spectrum of **4** (500.13 MHz, CD_2Cl_2, 25°C) showing the scalar couplings for the protons of the 2-oxa-3-methyl-cyclopentylidene ring



The solid-state structure of the 2-oxa-3-methyl-cyclopentylidene complex (**4**) has been determined by a single-crystal X-ray analysis. A view of the complex cation is shown in Figure 2, while selected bond lengths and angles are given in Table 2.

Figure 2. ORTEP Drawing of the complex cation $[(triphos)Re(CO)_2\{=CCH_2CH_2CH(Me)O\}]^+$ in **4-BF$_4$**. Only the *ipso* carbons of the phenyl rings of the triphos ligand are shown for the sake of clarity

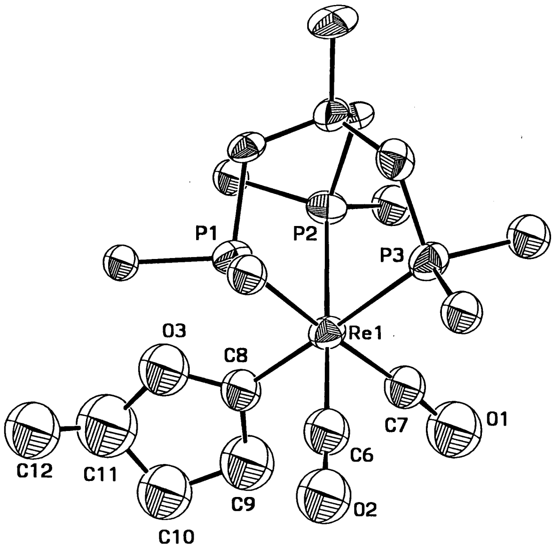


Table 2. Selected bond distances and angles for **4-BF$_4$**

Re−P1	2.488(4)	C7−O1	1.21(2)
Re−P2	2.490(4)	C8−O3	1.31(2)
Re−P3	2.466(4)	C8−C9	1.51(2)
Re−C6	1.89(2)	C9−C10	1.47(2)
Re−C7	1.85(2)	C10−C11	1.47(2)
Re−C8	2.02(2)	C11−C12	1.36(2)
C6−O2	1.16(2)	C11−O3	1.56(2)
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−C10	122.3(7)

The structure of **4** consists of $[(triphos)Re(CO)_2\{=CCH_2CH_2CH(Me)O\}]^+$ cations and tetrafluoroborate anions with no interspersed solvent molecules. A *facial* triphos ligand, two *cis* disposed carbonyl groups and an oxacyclopentylidene ligand co-ordinate the Re center in a slightly distorted octahedral environment. The $Re-C_{carbene}$ bond length [$d_{Re=C} = 2.02(2)$ Å] is shorter than that found in the alkoxycarbene complex $[(triphos)Re(CO)_2\{=C(OEt)CH_3\}]BF_4$ [$d_{Re=C} = 2.071(8)$ Å],[20] but longer than that reported for the vinylidene complex $[(triphos)Re(CO)_2\{=C=C(H)Ph\}]BPh_4$ [$d_{Re=C} = 1.925(6)$ Å].[20] Noticeably, the present $Re-C_{carbene}$ distance is also shorter than that found in $(CO)_5Re=CCH_2CH_2CH_2O$ [$d_{Re=C} = 2.125$ Å][9a] and in $Br(CO)_4Re=COCH_2CH_2O$ [$d_{Re=C} = 2.135$ Å].[23] The oxacyclopentylidene ring adopts an "envelope" conformation with small deviations from the mean plane defined by the rhenium atom, and by the O3 and C8 to C12 atoms. The largest deviation affects the C10 atom (−0.0201 Å) in β-position with respect to O3. Deviations from planarity are often encountered in this class of oxacyclocarbene complexes and deformations ranging from practically planar systems to significantly distorted rings have been reported.[24][25] A comparable distortion has been reported for the molybdenum complex $[MoI(CO)_2\{=COCH_2CH_2CH_2\}(\eta^5-C_5H_5)]$.[26] The C8−O3 distance and the other metrical parameters pertaining to the carbene ligand fall into the range determined for related complexes.[5][9][23][24][25][26]

Reactions of **2** *with γ- and δ-Alkynols:* When either 4-pentyn-1-ol or (±)-5-hexyn-2-ol are allowed to react with a CH_2Cl_2 solution of **2** at room temperature, the Fischer carbene complexes $[(triphos)Re(CO)_2\{=CCH_2CH_2CH_2CH(R)O\}]BF_4$ (R = H, **5**; R = Me, **6**) are obtained in good yields (Scheme 2). To the best of our knowledge, known examples of oxacyclohexylidene metal complexes are limited to the chromium complex $(CO)_5Cr\{=CCH_2CH_2CH_2CH_2O\}$ described by Dötz,[1] the manganese compound $Cp(CO)(PPh_3)Mn=C\{OCH_2C(Me)_2CH_2CH(Me)\}$ synthesized by Geoffroy and coworkers,[9b] the molybdenum derivative $[Mo\{=CH_2(CH_2)_2CH_2O\}(dppe)(\eta-C_7H_7)]PF_6$ (dppe = $Ph_2PCH_2CH_2PPh_2$) reported by Whiteley and co-workers,[10b] and the indenyl osmium complex $[(\eta^5-C_9H_7)Os\{=CCH_2CH_2CH_2CH_2O\}(PPh_3)_2]$ described by Gimeno.[8a]

The presence of oxacyclohexylidene rings in **5** and **6** is shown by the $^{13}C\{^1H\}$-NMR spectra which exhibit four different methylene resonances (singlets at δ = 16.7, 21.6, 55.6, and 75.0), while the carbene carbon atoms resonate at δ = 303.0 (**5**: dt, $J_{CPtrans}$ = 36.8 Hz, J_{CPcis} = 9.5 Hz) and at δ = 305.3 (**6**: dt, $J_{CPtrans}$ = 36.9 Hz, J_{CPcis} = 8.6 Hz). As expected the NMR properties of **6** are similar to those of **4**, which analogously contains a stereogenic carbon atom in the ring.[27]

Monitoring the reactions between **2** and 4-pentyn-1-ol [or (±)-5-hexyn-2-ol] by multinuclear NMR spectroscopy in the temperature range from −50 to +20°C showed no intermediate species in the course of the conversion of **2** to **5** (or **6**). In contrast, V. T. NMR spectroscopy has revealed that the hydroxybutylvinylidene complex $[(triphos)Re(CO)_2\{=C=C(H)CH_2CH_2CH_2CH_2OH\}]BF_4$ (**7**) is an intermediate to the oxacarbene thermodynamic product $[(triphos)Re(CO)_2\{=CCH_2CH_2CH_2CH_2CH_2O\}]BF_4$ (**8**) when **2** is reacted with a δ-alkynol such as $HC{\equiv}CCH_2(CH_2)_2CH_2OH$. The hydroxyvinylidene complex is stable in solution below −10°C. Above this temperature it slowly but selectively transforms into the 2-oxacycloheptylidene isomer **8** (Scheme 2). The conversion is fast at room temperature. Nonetheless, the stability at low temperature allows **7** to be unambiguously characterized in solution and isolated in the solid state as well.

Bands in the IR spectrum of **7** at 1663 (C=C) and ca. 3550 cm^{-1} (OH), diagnose the presence of a hydroxyvinylidene ligand. These absorptions are not present in the IR spectrum of **8**, in which the stretching frequencies of the two CO′s are at lower energy (1960 and 1900 cm^{-1}) compared to those of **7** (2008 and 1946 cm^{-1}) due to the greater π-acceptor character of the hydroxyvinylidene ligand.[14][20] In keeping with this electronic effect, the phosphorus resonances of **8** (δ_A = −17.14, δ_M = −11.49, J_{AM} = 20.9 Hz) are shifted to low field with respect to those of **7** (δ_A = −19.41, δ_M = −15.82, J_{AM} = 23.2 Hz). The $^{13}C\{^1H\}$-NMR spectrum of **7** displays the characteristic low-field resonance of the vinylidene C_α atom (δ = 343.9), while the resonance of the C_β atom appears at higher field (doublet of triplets at δ = 111.0).[12][13][21] Four signals, spanning from δ = 52.1 (C_ζ) to δ = 19.8 (C_γ) are assigned to the CH_2 carbon atoms of the δ-hydroxybutyl substituent in the vinylidene ligand. In the proton NMR spectrum of **7**, the vinylidene hydrogen resonance appears as a well-resolved triplet of pseudoquartets at δ = 3.53 which collapses into a triplet of 8.3 Hz in the broad-band phosphorus-decoupled spectrum.

Further experimental evidence of the vinylidene nature of the organyl ligand in **7** is provided by the reaction of the latter compound with Brønsted bases, such as NEt_3, which remove the vinylidene hydrogen atom, leading to the clean formation of the σ-alkynyl complex $[(triphos)Re(CO)_2\{C{\equiv}CCH_2CH_2CH_2CH_2OH\}]$ (**9**).[12][20] This reaction is reversible and **9** re-generates **7** by treatment with protic acids. The alkynyl derivative **9** has been isolated and authenticated spectroscopically by comparison with several Re^I alkynyls of the formula $[(triphos)Re(CO)_2(C{\equiv}CR)]$.[20]

A careful and complete analysis of the $^{13}C\{^1H\}$-NMR spectrum was carried out for the unambiguous identification of **8**. Key features are a doublet of triplets at δ = 310.8, assigned to the carbene carbon atom, and five methylene resonances assigned to the five CH_2 groups of the 2-oxacycloheptylidene ring. The presence of five methylene resonances was of crucial importance for ruling out a vinylvinylidene structure which might have been formed via the alternative water-elimination pathway (Scheme 1). Of the five methylene resonances, only those of the C_ζ (δ = 78.6) and C_β (δ = 60.1) carbons, proximal to the oxygen and to the carbene carbon atoms, respectively, appear as doublets with small phosphorus-carbon couplings. The remaining CH_2 resonances (between δ = 29.1 and 21.5) are singlets with no discernible coupling.

Fischer carbene complexes containing oxacycloheptylidene rings are extremely rare. To the best of our knowledge, the only example reported in the literature is the dinuclear dimanganese complex $[(CO)_5Mn-Mn(CO)_4\{=COCH_2CH_2CH_2CH_2CH_2\}]$.[16] This, however, was prepared by the alternative reaction of the bistriflate $TfOCH_2CH_2CH_2CH_2CH_2OTf$ with the carbonyl metalate salt $K[Mn(CO)_5]$ in THF, and not by δ-alkynol activation.[16][17]

Conclusions

Our study of the reactions of the $16e^-$ $[(triphos)Re(CO)_2]^+$ support with different β-, γ-, and δ-alkynols has shown that cyclic carbenes are formed irrespective of the separation between the triple bond and the hydroxy functional group. We have also demonstrated that this cyclization reaction occurs via the hydroxyalkylvinylidene complexes. For the particular case of the δ-alkynol 5-hexyn-1-ol the kinetic hydroxybutylvinylidene intermediate has been intercepted in solution and isolated in the solid state. Its thermal rearrangement to the thermodynamic 2-oxacycloheptylidene product has been observed, showing that the intramolecular nucleophilic attack by the OH group at the vinylidene C_α atom may still be favored over H_2O elimination to give vinylvinylidene products. The same should be true for long-chain ω-alkynols. Studies are currently in progress to scrutiny the chemistry of this new family of rhenium 2-oxacarbenes.

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Experimental Section

General Procedure: Tetrahydrofuran (THF), *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. The ligand $CH_3C(CH_2PPh_2)_3$ (triphos)[28] and the complexes [(triphos)Re(CO)$_2$H] (**1**)[19] and [(triphos)Re(CO)$_2$(η^2-H$_2$)]BF$_4$ (**2**)[20] were prepared as described in the literature. All the alkynols were purchased from Aldrich except for (±)-5-hexyn-2-ol which was provided by Prof. A. Medici (Department of Chemistry, University of Ferrara). The purity of all alkynols was checked by ^{1}H-NMR spectroscopy, and, when necessary, they were distilled under inert atmosphere prior to use. All the other reagents and chemicals were reagent grade and, unless otherwise stated, were used as received from commercial suppliers. All reactions and manipulations were routinely performed under a dry nitrogen atmosphere by using standard Schlenk-tube techniques. CD_2Cl_2 for NMR measurements (Merck and Aldrich) was 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. The ^{1}H,^{1}H-2D COSY NMR experiments on the racemate complexes **4** and **6** were acquired on the AVANCE DRX 500 Bruker spectrometer using the phase-sensitive TPPI mode with double quantum filter. ^{1}H,^{1}H-2D NOESY NMR experiments were conducted on the same instrument in the phase-sensitive TPPI mode in order to discriminate between positive and negative cross peaks. – ^{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 broad-band phosphorus decoupling were recorded on the Bruker AC200 instrument equipped with a 5-mm inverse probe and a BFX-5 amplifier device using the wideband phosphorus decoupling sequence GARP.[29] – Computer simulations of NMR spectra were carried out with a locally developed package containing the programs LAOCN3[30] and DAVINS.[31] 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. $1 \cdot 10^{-3}$ M in nitroethane solutions at room temperature (21 °C). – Elemental analyses were performed with a Carlo Erba model 1106 elemental analyzer.

Synthesis of [(triphos)Re(CO)$_2${=CCH$_2$CH$_2$CH$_2$O}]BF$_4$ (**3**): A dichloromethane (5 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 treating [(triphos)Re(CO)$_2$H] (**1**) (0.25 g, 0.26 mmol) with HBF$_4$.OMe$_2$ (33 µl, 0.27 mmol) at −20°C under nitrogen.[19] To this solution, a slight excess of 3-butyn-1-ol (23 µl, 0.30 mmol) was added with stirring, and the solution was slowly brought to room temperature. During this time, the color of the resulting solution changed from pale yellow to orange. After the reaction mixture was allowed to reach room temperature, stirring was continued for additional 30 min. The solvent was removed under reduced pressure and the solid residue washed with 2 × 2 ml of ethanol and 2 × 3 ml of diethyl ether. The crude reaction product was recrystallized from dichloromethane/diethyl ether (1:1, v/v) to yield orange crystals of [(triphos)Re(CO)$_2${=CCH$_2$CH$_2$CH$_2$O}]BF$_4$ (**3**). Yield 80%. – $C_{47}H_{45}BF_4O_3P_3Re$: calcd. C 55.14, H 4.45; found C 55.20, H 4.55.– ^{1}H NMR (CD_2Cl_2, 22°C, 200.13 MHz): (the numbering scheme for the hydrogen and carbon resonances of this complex as well as all the other new complexes described in this paper is given in Table 1) $\delta = 1.62$ (q, $J_{HP} = 3.1$ Hz, $CH_{3(triphos)}$, 3 H), 1.73 (quint, $J_{HH} = 7.8$ Hz, H_γ, 2 H), 2.54 (d, $J_{HP\mathit{axial}} = 8.8$ Hz, CH_2P_{axial}, 2 H), 2.70 (m, CH_2P_{equat}, 4 H), 3.28 (td, $J_{HH} = 7.7$ Hz, $J_{HP} = 0.6$ Hz, H_β, 2 H), 4.06 (t, $J_{HH} = 7.6$ Hz, H_δ, 2 H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 22°C, 50.32 MHz): $\delta = 293.4$ (dt, $J_{CP\mathit{trans}} = 35.0$ Hz, $J_{CP\mathit{cis}} = 8.9$ Hz, C_α), 197.0 (m, CO), 85.3 (d, $J_{CP} = 3.2$ Hz, C_δ), 62.7 (d, $J_{CP} = 5.7$ Hz, C_β), 40.3 (q, $J_{CP} = 9.9$ Hz, $CH_{3(triphos)}$), 39.7 (q, $J_{CP} = 3.5$ Hz, $MeC_{(triphos)}$), 35.1 (td, $N = J_{CP\mathit{equat}'} + J_{CP\mathit{equat}''} = 14.0$ Hz, $J_{CP\mathit{axial}} = 4.5$ Hz, CH_2P_{equat}), 32.4 (dt, $J_{CP\mathit{axial}} = 23.5$ Hz, $J_{CP\mathit{equat}} = 4.4$ Hz, CH_2P_{axial}), 22.8 (s, C_γ).– ^{31}P{^{1}H} NMR (CD_2Cl_2, 22°C, 81.01 MHz): AM$_2$ spin system, $\delta_A = -15.90$, $\delta_M = -11.86$, $J_{AM} = 22.1$ Hz. $-\Lambda_{M(nitroethane)} = 80\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Recrystallization of **3** from dichloromethane/ethanol in the presence of 2 equiv of NaBPh$_4$, yielded the corresponding tetraphenylborate salt (**3′**) in ca. 90% yield. – [(triphos)Re(CO)$_2$-{=CCH$_2$CH$_2$CH$_2$O}]BPh$_4$ (**3′**, $C_{71}H_{65}BO_3P_3Re$): calcd. C 67.89, H 5.21; found C 67.19, H 5.01. – $\Lambda_{M(nitroethane)} = 53\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Synthesis of [(triphos)Re(CO)$_2${=CCH$_2$CH$_2$CH(Me)O}]BF$_4$ (**4**): The methyl-substituted oxycarbene complex **4**, was obtained as described above for **3** using (±)-4-pentyn-2-ol (24 µl, 0.26 mmol) instead of 3-butyn-1-ol. The reaction was complete after stirring the mixture at room temperature for 1 h. Work-up as above gave [(triphos)Re(CO)$_2${=CCH$_2$CH$_2$CH(Me)O}]BF$_4$ (**4**) as orange microcrystals. Yield 85%. – $C_{48}H_{47}BF_4O_3P_3Re$: calcd. C 55.55, H, 4.56; found C 54.99, H 4.38. – ^{1}H NMR (CD_2Cl_2, 25°C, 500.13 MHz): $\delta = 1.15$ (d, $J_{MeH\delta} = 6.3$ Hz, $CH_{3(carbene)}$, 3 H), 1.35 (dddd, $J_{H\gamma''H\gamma'} = 12.8$ Hz, $J_{H\gamma''H\beta'} = 9.2$ Hz, $J_{H\gamma''H\delta} = 6.3$ Hz, $J_{H\gamma''H\beta''} = 3.6$ Hz, $H_{\gamma''}$, 1H), 1.62 (q, $J_{HP} = 3.0$ Hz, $CH_{3(triphos)}$, 3 H), 2.05 (dddd, $J_{H\gamma'H\gamma''} = 12.8$ Hz, $J_{H\gamma'H\beta''} = 8.8$ Hz, $J_{H\gamma'H\delta} = 6.7$ Hz,

$J_{H\gamma'H\beta'} = 3.6$ Hz, $H_{\gamma'}$, 1 H), 2.60 (m, $CH_{2(triphos)}$, 6 H), 3.10 (ddd, $J_{H\beta''H\beta'} = 19.8$ Hz, $J_{H\beta'H\gamma''} = 9.2$ Hz, $J_{H\beta'H\gamma'} = 3.6$ Hz, $H_{\beta'}$, 1 H), 3.68 (ddd, $J_{H\beta'H\beta''} = 19.8$ Hz, $J_{H\beta''H\gamma'} = 8.8$ Hz, $J_{H\beta''H\gamma''} = 3.6$ Hz, $H_{\beta''}$, 1 H), 4.77 (dpsquint, $J_{H\delta H\gamma'} = 6.7$ Hz, $J_{H\delta Me} \approx J_{H\delta H\gamma''} = 6.3$ Hz, H_δ, 1 H). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22°C, 50.32 MHz): $\delta = 294.5$ (dt, $J_{CPtrans} = 35.6$ Hz, $J_{CPcis} = 9.2$ Hz, C_α), 198.6 (dt, $J_{CPtrans} = 45.5$ Hz, $J_{CPcis} = 5.7$ Hz, CO), 98.5 (d, $J_{CP} = 3.2$ Hz, C_δ), 65.5 (d, $J_{CP} = 5.0$ Hz, C_β), 42.1 (q, $J_{CP} = 10.1$ Hz, $CH_{3(triphos)}$), 41.6 (q, $J_{CP} = 3.6$ Hz, $MeC_{(triphos)}$), 37.3 (d, $J_{CPequat} = 25.7$ Hz, CH_2P_{equat}), 36.6 (dt, $J_{CPaxial} = 22.2$ Hz, $J_{CPequat} = 4.7$ Hz, CH_2P_{axial}), 32.5 (s, C_γ), 22.5 (s, $CH_{3(carbene)}$). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22°C, 81.01 MHz): AMQ spin system, $\delta_A = -13.10$, $\delta_M = -14.73$, $\delta_Q = -16.63$, $J_{AM} = 26.7$ Hz, $J_{AQ} = 21.3$ Hz, $J_{MQ} = 21.3$ Hz. − $\Lambda_{M(nitroethane)} = 81\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Synthesis of $[(triphos)Re(CO)_2\{=CCH_2CH_2CH_2CH_2O\}]BF_4$ (**5**): A slight excess of 4-pentyn-1-ol (40 µl, 0.37 mmol) was added with stirring to a solution of **2** (0.26 mmol) prepared as described above. Usual work-up gave pale orange crystals of $[(triphos)Re(CO)_2\{=CCH_2CH_2CH_2CH_2O\}]BF_4$ (**5**). Yield 80%. − $C_{48}H_{47}BF_4O_3P_3Re$: calcd. C 55.55, H 4.56; found C 55.49, H 4.50. − ^1H NMR (CD_2Cl_2, 25°C, 500.13 MHz): $\delta = 1.50$ (m, $H_\gamma + H_\delta$, 4 H), 1.68 (q, $J_{HP} = 3.0$ Hz, $CH_{3(triphos)}$, 3 H), 2.48 (d, $J_{HPaxial} = 8.8$ Hz, CH_2P_{axial}, 2 H), 2.70 (m, CH_2P_{equat}, 4 H), 3.28 (t, $J_{H\beta H\gamma} = 6.8$ Hz, H_β, 2 H), 3.44 (t, $J_{H\varepsilon H\delta} = 6.0$ Hz, H_ε, 2 H). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22°C, 50.32 MHz): $\delta = 303.0$ (dt, $J_{CPtrans} = 36.8$ Hz, $J_{CPcis} = 9.5$ Hz, C_α), 198.0 (m, CO), 75.0 (d, $J_{CP} = 2.5$ Hz, C_ε), 55.6 (d, $J_{CP} = 3.8$ Hz, C_β), 40.3 (q, $J_{CP} = 10.4$ Hz, $CH_{3(triphos)}$), 39.7 (q, $J_{CP} = 3.8$ Hz, $MeC_{(triphos)}$), 32.5 (td, $N = J_{CPequat'} + J_{CPequat''} = 14.0$ Hz, $J_{CPaxial} = 4.4$ Hz, CH_2P_{equat}), 32.5 (dt, $J_{CPaxial} = 22.9$ Hz, $J_{CPequat} = 4.3$ Hz, CH_2P_{axial}), 21.1 (s, C_δ), 16.7 (s, C_γ). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22°C, 81.01 MHz): AM_2 spin system, $\delta_A = -16.71$, $\delta_M = -10.70$, $J_{AM} = 21.4$ Hz. − $\Lambda_{M(nitroethane)} = 82\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Synthesis of $[(triphos)Re(CO)_2\{=CCH_2CH_2CH_2CH(Me)O\}]BF_4$ (**6**): A two-fold excess of (±)-5-hexyn-2-ol (54 µl, 0.55 mmol) was syringed into a dichloromethane solution of **2** (0.026 mmol) prepared as described above. Orange microcrystals of $[(triphos)Re(CO)_2\{=CCH_2CH_2CH_2CH(Me)O\}]BF_4$ (**6**) were obtained in ca. 65% yield after usual work up. − $C_{49}H_{49}BF_4O_3P_3Re$: calcd. C 55.88, H 4.69; found C 55.90, H 4.72. − ^1H NMR (CD_2Cl_2, 25°C, 200.13 MHz): $\delta = 1.01$ (d, $J_{MeH\varepsilon} = 6.3$ Hz, $CH_{3(carbene)}$, 3 H), 1.35 (m, $H_{\beta'} + H_{\delta''}$, 2 H), 1.60 (m, $H_{\gamma'} + CH_{3(triphos)}$, 4 H), 1.96 (m, $H_{\delta'}$, 1H), 2.40 − 2.70 (m, $H_{\gamma''} + CH_{2(triphos)}$, 7H), 3.92 (ddd, $J_{H\beta''H\beta'} = 17.1$ Hz, $J_{H\beta''H\gamma'} = 5.8$ Hz, $J_{H\beta''H\gamma''} = 3.6$ Hz, $H_{\beta''}$, 1 H), 4.14 (m, H_ε, 1H). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20°C, 50.32 MHz): $\delta = 305.3$ (dt, $J_{CPtrans} = 36.9$ Hz, $J_{CPcis} = 8.6$ Hz, C_α), 197.1 (dt, $J_{CPtrans} = 44.5$ Hz, $J_{CPcis} = 7.6$ Hz, CO), 83.9 (d, $J_{CP} = 2.2$ Hz, C_ε), 55.8 (dt, $J_{CPaxial} = 4.5$ Hz, $J_{CPequat} = 1.3$ Hz, C_β), 39.7 (q, $J_{CP} = 10.1$ Hz, $CH_{3(triphos)}$), 39.5 (q, $J_{CP} = 3.2$ Hz, $MeC_{(triphos)}$), 35.7 (td, $N = J_{CPequat'} + J_{CPequat''} = 5.0$ Hz, $J_{CPaxial} = 2.5$ Hz, CH_2P_{equat}), 35.1 (td, $N = J_{CPequat'} + J_{CPequat''} = 5.0$ Hz, $J_{CPaxial} = 2.4$ Hz, CH_2P_{equat}), 32.8 (dt, $J_{CPaxial} = 22.2$ Hz, $J_{CPequat} = 4.8$ Hz, CH_2P_{axial}), 28.7 (s, C_δ), 20.3 (s, $CH_{3(carbene)}$), 16.9 (s, C_γ). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22°C, 81.01 MHz): AMQ spin system, $\delta_A = -12.80$, $\delta_M = -14.00$, $\delta_Q = -16.56$, $J_{AM} = 20.1$ Hz, $J_{AQ} = 23.5$ Hz, $J_{MQ} = 20.7$ Hz. − $\Lambda_{M(nitroethane)} = 85\ \Omega^{-1}\ cm^2\ mol^{-1}$.

In Situ NMR Studies: Reactions of $[(triphos)Re(CO)_2(\eta^2\text{-}H_2)]BF_4$ (**2**) *with 3-Butyn-1-ol, (±)-4-Pentyn-2-ol, or 4-Pentyn-1-ol:* Deoxygenated 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). The addition of 3.3 µl of HBF4·OMe2 dissolved the monohydride **1** within a few minutes to give a solution of **2** which was cooled down to −78°C. After 2.3 µl (0.030 mmol) of 3-butyn-1-ol was syringed into the tube, this was flame-sealed under nitrogen at −78°C and then introduced into the NMR probe of the spectrometer precooled to −50°C. The progress of the reaction was followed by variable-temperature (V.T.) $^{31}P\{^1H\}$- and ^1H-NMR spectroscopy. No reaction occurred until the temperature was raised to about −10°C. At this temperature, the molecular hydrogen complex started converting to the oxycarbene derivative **3.** Within 1 h at −10°C, **3** was the only product detectable by ^{31}P-NMR spectroscopy.

In analogous experiments, (±)-4-pentyn-2-ol or 4-pentyn-1-ol were substituted for 3-butyn-1-ol. Monitoring the reaction by V.T.-NMR spectroscopy showed no intermediate species for the transformation of **2** into **4** or **5**.

In Situ NMR Studies: Reaction of $[(triphos)Re(CO)_2(\eta^2\text{-}H_2)]BF_4$ (**2**) *with 5-Hexyn-1-ol:* To a dry-ice/acetone cooled solution of **2** (0.050 mmol) in CD_2Cl_2 (0.8 ml), prepared in a 5-mm NMR tube from **1** and $HBF_4\cdot OMe_2$, was added 6.3 µl (0.055 mmol) of 5-hexyn-1-ol. The tube was flame-sealed and the reaction progress was monitored by V.T.-NMR spectroscopy. A reaction between **2** and the alkynol already occurred at −15°C to give the vinylidene complex $[(triphos)Re(CO)_2\{=C=C(H)CH_2CH_2CH_2CH_2OH\}]BF_4$ (**7**) as the only new rhenium-containing product. A complete transformation of **2** into **7** was observed after 6 h at −15°C. Heating the NMR tube to room temperature caused the transformation of **7** into the carbene $[(triphos)Re(CO)_2\{=CCH_2CH_2CH_2CH_2CH_2O\}]BF_4$ (**8**) at ca. −8°C. The formation of **8** was complete after the sample was heated to 20°C for 1 h.

NMR Data for **7**: ^1H NMR (CD_2Cl_2, −16°C, 500.13 MHz): $\delta = 1.43$ (psquint, $J_{H\delta H\gamma} \approx J_{H\delta H\varepsilon} = 7.4$ Hz, H_δ, 2 H), 1.61 (m, H_ε, 2 H), 1.67 (q, $J_{HP} = 3.0$ Hz, $CH_{3(triphos)}$, 3 H), 2.38 (psq, $J_{H\gamma H\beta} = 8.3$ Hz, $J_{H\gamma H\delta} = 7.4$ Hz, H_γ, 2 H), 2.46 (d, $J_{HPaxial} = 9.3$ Hz, CH_2P_{axial}, 2 H), 2.54 (m, CH_2P_{equat}, 2 H), 2.73 (m, CH_2P_{equat}, 2 H), 3.53 (tpsq, transforms into a triplet in the $^1H\{^{31}P\}$-NMR spectrum, $J_{H\beta H\gamma} = 8.3$ Hz, $J_{HPA} \approx J_{HPM} = 2.8$ Hz, $H_{\beta(vinylidene)}$, 1 H), 3.64 (br t, $J_{H\zeta H\varepsilon} = 6.1$ Hz, H_ζ, 2 H); the resonance of the OH proton was not observed. − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −16°C, 50.32 MHz): $\delta = 343.9$ (dt, $J_{CPtrans} = 32.1$ Hz, $J_{CPcis} = 11.6$ Hz, C_α), 191.7 (m, CO), 111.0 (dt, $J_{CPtrans} = 12.7$ Hz, $J_{CPcis} = 2.5$ Hz, C_β), 52.1 (s, C_ζ), 39.7 (q, $J_{CP} = 10.2$ Hz, $CH_{3(triphos)}$), 39.2 (br s, $MeC_{(triphos)}$), 36.9 (m, CH_2P_{axial}), 32.4 (m, CH_2P_{equat}), 31.5 (s) and 27.6 (s) (C_δ and C_ε), 19.8 (s, C_γ). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −16°C, 81.01 MHz): AM_2 spin system, $\delta_A = -19.41$, $\delta_M = -15.82$, $J_{AM} = 23.2$ Hz.

NMR Data for **8**: ^1H NMR (CD_2Cl_2, 22°C, 200.13 MHz): $\delta = 1.41$ (m, H_ε, 2 H), 1.66 (q, $J_{HP} = 2.9$ Hz, $CH_{3(triphos)}$, 3 H), 1.7 (m, partially masked by triphos CH_3 resonance, assigned by 2D-^1H,^1H-COSY NMR experiment, $H_\gamma + H_\delta$, 4 H), 2.53 (d, $J_{HPaxial} = 8.7$ Hz, CH_2P_{axial}, 2 H), 3.57 (m, H_β, 2 H), 3.91 (t, $J_{H\zeta H\varepsilon} = 4.6$ Hz, H_ζ, 2 H). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22°C, 75.42 MHz): $\delta = 310.8$ (dt, $J_{CPtrans} = 38.4$ Hz, $J_{CPcis} = 8.6$ Hz, C_α), 198.1 (AXX'Y spin system, $J_{AX} = 7.0$ Hz, $J_{AY} = 5.8$ Hz, $J_{AX'} = -8.2$ Hz, $J_{XX'} = 26.8$ Hz, CO), 78.6 (d, $J_{CP} = 2.9$ Hz, C_ζ), 60.1 (d, $J_{CP} = 5.2$ Hz, C_β), 40.2 (q, $J_{CP} = 10.1$ Hz, $CH_{3(triphos)}$), 39.7 (q, $J_{CP} = 4.1$ Hz, $MeC_{(triphos)}$), 35.6 (td, $N = J_{CPequat} + J_{CPequat'} = 14.0$ Hz, $J_{CPaxial} = 4.4$ Hz, CH_2P_{equat}), 32.7 (dt, $J_{CPaxial} = 22.3$ Hz, $J_{CPequat} = 4.8$ Hz, CH_2P_{axial}), 29.1 (s), 28.2 (s), and 21.5 (s), (C_γ, C_δ and C_ε). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25°C, 81.01 MHz): AM_2 spin system, $\delta_A = -17.14$, $\delta_M = -11.49$, $J_{AM} = 20.9$ Hz. − $\Lambda_{M(nitroethane)} = 80\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Synthesis of $[(triphos)Re(CO)_2\{=C=C(H)CH_2CH_2CH_2CH_2OH\}]BF_4$ (**7**): A slight excess of 5-hexyn-1-ol (60 µl, 0.55 mmol) was added to a stirred solution of **2** (0.26 mmol) prepared as described above and maintained at −15°C. The resulting solution was stirred for 15 min, then the solvent was removed under reduced pressure to give a raspberry-colored powder. The solid residue was washed with diethyl ether before being dried under vacuum. NMR spectroscopy showed it to contain **7**, occasionally contaminated by some **8** (usually less than 10%). − $C_{49}H_{49}BF_4O_3P_3Re$: calcd. C 55.88, H 4.69; found C 55.70, H 4.74.

Synthesis of $[(triphos)Re(CO)_2\{=CCH_2CH_2CH_2CH_2CH_2O\}]BF_4$ (**8**): A solution of **7** obtained by reacting **2** with 5-hexyn-1-ol as described above, was slowly warmed to room temperature with stirring. Within 30 min, the reaction mixture became pale yellow. Evaporation of the solvent under reduced pressure gave **8** as yellow microcrystals. Yield 90%. − $C_{49}H_{49}BF_4O_3P_3Re$: calcd. C 55.88, H 4.69; found C 55.92, H 4.75.

Synthesis of $[(triphos)Re(CO)_2\{C{\equiv}CCH_2CH_2CH_2CH_2OH\}]$ (**9**): To a Schlenk-tube charged with the vinylidene complex **7** (0.19 g, 0.20 mmol) in CH_2Cl_2 (5 ml) at −15°C, a three-fold excess of neat NEt_3 (85 µl, 0.60 mmol) was added with stirring. An immediate reaction took place to give a pale yellow solution. The reaction mixture was stirred for 1 h at room temperature. After the solvent was removed in vacuo, the pale yellow residue was washed with water (2 × 1 ml), ethanol (2 × 1 ml) and diethyl ether (2 × 2 ml) before being dried under vacuum. Yield 80%. − $C_{49}H_{48}O_3P_3Re$: calcd. C 60.98, H 5.02; found C 60.70, H 5.1. − ^1H NMR (CD_2Cl_2, 25°C, 200.13 MHz): $\delta = 1.3 - 1.6$ (m, $H_\delta + H_\gamma$, 4 H), 1.77 (q, $J_{HP} = 3.4$ Hz, $CH_{3(triphos)}$, 3 H), 2.3 − 2.7 (m, $CH_{2(triphos)} + H_\gamma$, 8 H), 3.60 (t, $J_{H\zeta H\varepsilon} = 6.5$ Hz, 2 H); the resonance of the OH proton was not observed. − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22°C, 81.01 MHz): AM_2 spin system, $\delta_A = -6.55$, $\delta_M = -20.30$, $J_{AM} = 17.2$ Hz.

Reaction of **9** *with* $HBF\cdot OMe_2$*:* A 5-mm NMR tube was charged with a CD_2Cl_2 solution (0.8 ml) of **9** (0.020 g, 0.02 mmol), and cooled to −78°C. Addition of one equiv of HBF4·OMe2 (25 µl, 0.20 mmol) selectively regenerated **7** as shown by $^{31}P\{^1H\}$-NMR analysis at −20°C.

X-ray Diffraction Study of $[(triphos)Re(CO)_2\{=CCH_2CH_2CH(Me)O\}]BF_4$ (**4**): A summary of crystal and intensity data is presented in Table 3. Experimental data were recorded at room temperature (20°C) on an Enraf-Nonius CAD4. A set of 25 carefully centered reflections in the range 6.5° < θ < 8.5° was used for determining the lattice constants. As a general procedure, the intensity 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,[32] with anomalous dispersion corrections taken from ref.[33]. An empirical absorptions correction was applied by using the program XABS2[34] with transmission factors in the range 0.631−1.425. The computational work was carried out by intensively using the program SHELX93.[35] Final atomic co-ordinates of all atoms and structure factors are available on request from the authors and are provided as supplementary material.

Pale orange crystals of **4** were grown in air from a dilute dichloromethane/ethanol solution. A parallelepiped crystal with dimension 0.25 × 0.20 × 0.11 mm was used for the data collection. The structure was solved by direct methods using the SIR92 program.[36] Refinement was done by full-matrix least-squares calculations, initially with isotropic thermal parameters then with anisotropic thermal parameters for Re, P, and C atoms of the triphos skeleton. The phenyl rings were treated as rigid bodies with D_{6h} symmetry, and the hydrogen atoms were allowed to ride on the attached carbon atoms. Crystallographic disorder was detected in the region of the tetrafluoroborate anion resulting in a double image of the four fluorine atoms. The two sets of fluorines were assigned a population factor of 0.6 and 0.4 respectively.

Table 3. Summary of crystal data and structure refinement for **4-BF$_4$**

Formula	$C_{48}H_{47}BF_4O_3P_3Re$		
Formula weight	1038.23	Crystal size [mm]	0.20×0.15×0.25
Crystal System	monoclinic	Space group	*P* 21/*n* (No. 14)
a [Å]	10.689(2)	*α* [deg]	90
b [Å]	17.921(4)	*β* [deg]	94.54(2)
c [Å]	23.175(5)	*γ* [deg]	90
V [$Å^3$]	4425(2)	*Z*	4
ρ(calcd) [gcm^{-3}]	1.558	Abs. coeff. [mm^{-1}]	2.912
F(000)	2080		
θ range [deg]	2.74−22.47		
Index ranges	$-11 \leq h \leq 11, 0 \leq k \leq 19, 0 \leq l \leq 24$		
Reflections collected	5763		
Independent reflections	5763 [*R*(int) = 0.0000]		
Refinement method	Full-matrix least squares on F^2		
Data/constraints/parameters	5763/0/234		
Goodness-of-fit on F^2	1.016		
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0611$; $wR2 = 0.1226$		
R indices (all data)	$R1 = 0.1577$; $wR2 = 0.1564$		
Largest difference peak [$eÅ^3$]	0.861 and −0.796		

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (deposition number 100775). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax (internat): +44(0)123/336-033, e-mail: deposit@chemcrys.cam.ac.uk].

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