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Backward synthesis of rhenium(I) γ-hydroxyvinylidene and γ-methoxyvinylidene complexes and their conversion to the allenylidene $[Re\{C{=}C{=}CPh_2\}(CO)_2(MeC(CH_2PPh_2)_3)](OSO_2CF_3)$

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The reactivity of the rhenium(I) allenylidene complex $[Re\{C{=}C{=}CPh_2\}(CO)_2(triphos)](OTf)$ (**1**) [triphos = $MeC(CH_2PPh_2)_3$] towards ionic nucleophiles and electrophiles has been explored. Nucleophiles regioselectively attack the C_γ carbon atom leading to the formation of σ-alkynyl complexes, while electrophiles attack the C_β atom yielding carbyne complexes. The sequential addition of OH^- and H^+ to **1** at low temperature gave the γ-hydroxyvinylidene complex $[Re\{C{=}C(H)C(OH)Ph_2\}(CO)_2(triphos)](OTf)$ which regenerated **1** above −40 °C *via* H_2O elimination.

Introduction

The presence of as many as three reactive carbon atoms in the allenylidene group constitutes the main reason for the considerable attention that is presently paid to transition metal complexes containing this poly-unsaturated ligand.[1] Indeed, in the allenylidene ligand, which exhibits both σ-donor and π-acceptor properties, the C_α and C_γ carbon atoms are electrophilic in nature, while the C_β atom behaves as a nucleophilic center. Moreover, the regioselectivity of nucleophilic addition is strongly dependent on both the supporting metal fragment and the C_γ substituents.[1] This wealth of diverse and spatially close reactivity centers, in addition to the intrinsic reactivity of the metal center itself, makes the chemistry of allenylidene complexes a topic of much current interest in both organometallic synthesis[2] and homogeneous catalysis.[3]

As a part of our ongoing investigation of the chemistry of cumulene ligands stabilized by the Re(I) fragment $[Re(CO)_2(triphos)]^+$ (triphos = $MeC(CH_2PPh_2)_3$),[4] we have recently synthesized and characterized the allenylidene derivative $[Re\{C{=}C{=}Ph_2\}(CO)_2(triphos)](OTf)$[5] (**1**), which represents a rare example of rhenium allenylidene obtained by activation of a propargyl alcohol (OTf = $^-OSO_2CF_3$).[6]

In this paper, we report a study of the reactivity of **1** towards various nucleophiles and electrophiles. We have found, *inter alia*, that the backward allenylidene to γ-hydroxyvinylidene conversion at the $[Re(CO)_2(triphos)]^+$ fragment can be achieved in a stepwise manner involving nucleophilic addition of OH^- to the allenylidene C_γ atom, followed by electrophilic attack by H^+ at the C_β atom of the σ-alkynyl product.

Results and discussion

Synthesis and characterization of the σ-alkynyl complexes $[Re\{C{\equiv}CC(R)Ph_2\}(CO)_2(triphos)]$ [R = OH (2), OMe (3), H (4), Me (5), CH_2NO_2 (6), $CH_2C(O)CH_3$ (7)]

Unlike several isoelectronic metal allenylidenes, **1** does not react with neutral molecules containing O–H bonds such as water[7] or alcohols.[7,8] Due to the presence of two terminal carbonyl ligands, the metal center in the $[Re(CO)_2(triphos)]^+$ fragment is not particularly electron-rich and therefore one would expect nucleophilic attack at the C_α atom by the oxygen atom from water or alcohol followed by proton transfer to C_β as occurs in analogous reactions involving isoelectronic ruthenium(II) allenylidene complexes.[7,8] The addition of ROH across the C_β–C_γ bond of **1** is thermodynamically disfavored as it would result in the plain transformation of the allenylidene group into the γ-hydroxyvinylidene $Re{=}C{=}C(H)C(OH)Ph_2$ which is in fact a precursor to **1** (*vide infra*).[1,5] The fact that no reaction takes place between **1** and water or alcohols reflects electronic[7,8] and steric[9] effects. Indeed, α,β-unsaturated hydroxy- and alkoxy-carbenes are inherently unstable and very few examples of such compounds have been isolated.[10–16] Accordingly, the apparent stability of **1** in the presence of water and alcohols might be determined predominantly by electronic factors, which is consistent with our observation that both thiols and amines smoothly react with **1** to give isolable α,β-unsaturated thio- and amino-carbene derivatives.[17] On the other hand, the six phenyl substituents at the phosphorus atoms provide remarkable steric congestion at C_α and therefore one cannot rule out a steric contribution to the stability of **1**. As a matter of fact, metal allenylidene complexes bearing from three to four diphenylphosphino groups do not similarly react with water or alcohols (*e.g.* $[RuCl(dppm)_2\{C{=}C{=}CPh_2\}]^+$ (dppm = bis(diphenylphosphinomethane)),[18] $[(NP_3)RuCl\{C{=}C{=}CPh_2\}]^+$ ($NP_3 = N(CH_2CH_2PPh_2)_3$),[19] or $[MCl_2(PPh_3)_2\{C{=}C{=}CPh_2\}]$ (M = Ru, Os),[20] while complexes containing two or less diphenylphosphino groups, such as $[(PNP)RuCl_2\{C{=}C{=}CPh_2\}]$[21] (PNP = *n*-PrN($CH_2CH_2PPh_2)_2$) or $[Ru(CO)(\eta^1\text{-}OCMe_2)(PPr^i_3)(Cp)]$, readily react with water or alcohols yielding α,β-unsaturated hydroxy- or alkoxy-carbenes as either final or intermediate products.

In accord with previous experimental and theoretical evidence,[22] we have found that anionic nucleophiles regioselectively attack the C_γ atom in **1** to give σ-alkynyl compounds with the formula $[Re\{C{\equiv}CC(OR)Ph_2\}(CO)_2(triphos)]$ [R = H (**2**); Me (**3**)] (Scheme 1).[4a] A similar regioselectivity in nucleophilic addition to C_γ has been observed upon reactions of **1** with either $LiHBEt_3$ or various sources of carbon nucleophiles

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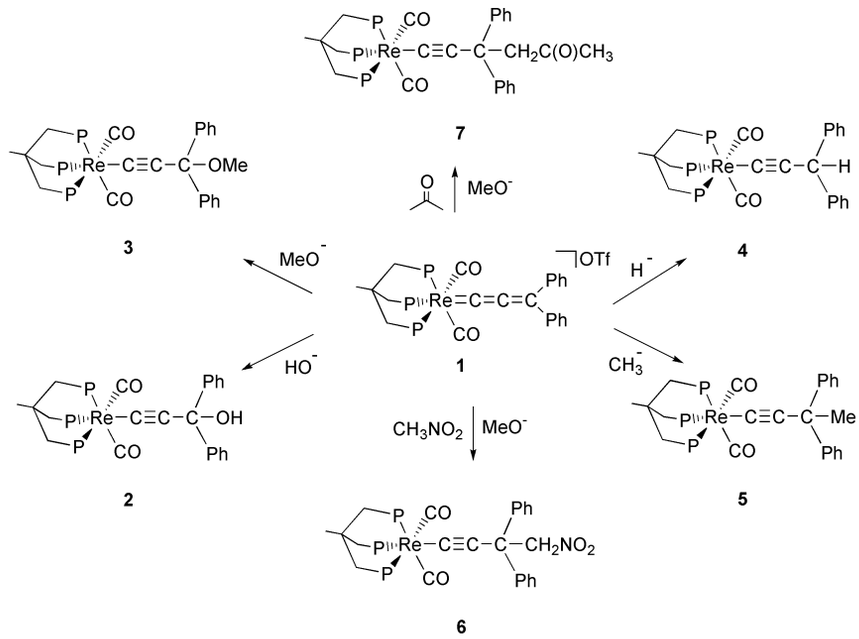


Scheme 1

such as CH_3Li, NO_2CH_2Na and $CH_3C(O)CH_2Na$. In all cases, γ-functionalized σ-alkynyl products with the general formula [Re{C≡CC(R)Ph_2}$(CO)_2$(triphos)] were obtained [R = H (**4**); CH_3 (**5**), CH_2NO_2 (**6**), $CH_2C(O)CH_3$ (**7**)] (Scheme 1).

It is worth noticing that no trace of the isomeric η^1-allenyl derivatives [Re{C(OR)=C=CPh_2}$(CO)_2$(triphos)], which might form by either direct nucleophilic attack at the allenylidene C_α atom or tautomerization of the γ-functionalized σ-alkynyl complex,[1] was observed even for prolonged reaction times. The stability of the allenylidene C_α atom towards anionic nucleophiles reflects particular steric and electronic properties of **1** as η^1-allenyl ligands can be synthesized by nucleophilic addition to the allenylidene C_α atom.[2i]

Complexes **2**–**7** are air-stable crystalline solids with good solubility in benzene, THF, acetone and halogenated hydrocarbons. Their unambiguous characterization was achieved by means of elemental analysis and conventional spectroscopic techniques (IR and multinuclear [^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H}] NMR) (Table 1).

In keeping with the presence of a σ-alkynyl ligand, the IR spectra of **2**–**7** exhibit strong and sharp $\nu_{C\equiv C}$ absorptions between 2097 and 2083 cm^{-1}. The $\nu_{C\equiv O}$ stretching frequencies of the two ancillary carbonyl ligands are shifted to lower energy (1952–1880 cm^{-1}) as compared with the parent metallacumulene **1** (2000, 1921 cm^{-1}), which reflects the neutral character of **2**–**7**.[4a] The ^{31}P{^{1}H} NMR spectra consist of first-order AM_2 patterns with chemical shifts and coupling constants similar to those reported for σ-alkynyl rhenium(I) complexes with the triphos ligand.[4] The ^{13}C{^{1}H} NMR spectra exhibit AXX′Y patterns for the two magnetically inequivalent CO ligands,[4,5,23] while doublets of triplets and triplets are features of the alkynyl C_α and C_β atoms, respectively.[4a,24] The presence of the $CH_2C(O)CH_3$ functional group attached to the terminal C_γ atom in **7** is shown by characteristic IR ($\nu_{C=O}$ 1706 cm^{-1}), ^{13}C{^{1}H} NMR ($\delta_{C=O}$ 209.8, δ_{CH_2} 58.3, δ_{CH_3} 28.5) and ^{1}H NMR (δ_{CH_3} 2.39, δ_{CH_3} 1.05) signals. Similarly, the functionalized alkynyl in **6** can be recognized by the NMR resonances of the nitromethyl substituent [^{1}H ($\delta_{CH_2NO_2}$ 5.20) and ^{13}C{^{1}H} ($\delta_{CH_2NO_2}$ 85.1)].

Protonation and alkylation of the rhenium σ-alkynyls

Consistent with the chemistry of σ-alkynyl metal complexes,[25] **4** and **5** readily reacted with 1 equivalent of $HOSO_2CF_3$ in dichloromethane yielding the corresponding vinylidene derivatives [Re{C=C(H)CHPh_2}$(CO)_2$(triphos)](OTf) (**8**) and [Re{C=C(H)CCH_3Ph_2}$(CO)_2$(triphos)](OTf) (**9**) (Scheme 2). Unambiguous evidence for the presence of vinylidene ligands in **8** and **9** was provided by NMR spectroscopy that showed the typical ^{1}H NMR resonances at *ca.* δ 3.5 for the vinylidene proton as well as ^{13}C NMR absorptions at *ca.* δ 345 (dt) and *ca.* δ 120 (d) for the C_α and C_β vinylidene atoms, respectively.[25] The ^{31}P NMR spectra appear as first-order AM_2 spin systems with chemical shifts and coupling constants in line with those reported for other Re(I) vinylidene complexes containing phosphine ligands.[4a,6] Due to the greater π-acceptor ability of the vinylidene ligand as compared to the alkynyl one,[25] the resonance of the *trans* phosphorus donor (triplet) is significantly shifted downfield in **8** and **9** in comparison with **4** and **5** (δ *ca.* −5 *vs.* δ *ca.* −19).

The protonation of **6** gave the vinylidene [Re{C=C(H)-C$H_2NO_2Ph_2$}$(CO)_2$(triphos)](OTf) (**12**), while **7** was converted to a complex mixture of products that denied first-order analysis and therefore the reaction was not investigated further.

Under similar conditions, the alkylation of **4** and **5** with $MeOSO_2CF_3$ gave the tertiary vinylidenes [Re{C=C(Me)-CHPh_2}$(CO)_2$(triphos)](OTf) (**10**) and [Re{C=C(Me)-CCH_3Ph_2}$(CO)_2$ (triphos)](OTf) (**11**) with NMR properties in line with those of the secondary vinylidenes **8** and **9** except for the NMR signals due to the methyl substituent at C_β (Table 1).

Unlike **4** and **5**, the reactions of the γ-hydroxy- and γ-methoxy-alkynyls **2** and **3** with protic acids at room temperature did not produce the expected vinylidenes, instead they regenerated the parent allenylidene **1** *via* elimination of water and methanol, respectively (Scheme 2). To our surprise, the reactions of **2** and **3** with MeOTf at room temperature also gave **1** together with stoichiometric amounts of MeOH and OMe_2, respectively.

Low-temperature protonation and alkylation of the rhenium σ-alkynyls

Intrigued by the formation of MeOH and Me_2O upon methylation of **2** and **3**, respectively, we decided to carry out a variable-temperature NMR study of these electrophilic additions.

The reaction of five equivalents of either triflic or tetrafluoroboric acid with a CD_2Cl_2 solution of **2** at −78 °C gave a dark violet solution containing the new γ-hydroxyvinylidene complex [Re{C=C(H)C(OH)Ph_2}$(CO)_2$(triphos)](OTf) (**13**) along with variable amounts of **1** (10–20%) (selected ^{31}P and ^{1}H NMR

Table 1 ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectral data (δ in ppm, J in Hz) and IR absorptions (KBr, ν in cm^{-1}) for the complexes

Complex	^{1}H	$^{13}C\{^{1}H\}$	$^{31}P\{^{1}H\}$		IR
1[b]	1.68 (br s, 3H, C$H_{3\ triphos}$) 2.62 (m, 6H, C$H_{2\ triphos}$)	290.7 (m, Re=*C*=C=C) 208.1 (m, Re=C=*C*=C) 192.3 (m, *C*O) 163.3 (s, Re=C=C=*C*) 40.0 (q, J_{CP} 10.0, *C*$H_{3\ triphos}$) 39.8 (q, J_{CP} 3.3, CH_3-*C*$_{triphos}$) 34.3 (m, *C*H_2-$P_{ax\ triphos}$) 33.5 (m, *C*H_2-$P_{eq\ triphos}$)	δ_A −17.82 $\delta_B = \delta_{B'}$ −17.63	$J_{AB} = J_{AB'}$ 24.4 $J_{BB'}$ −25.0	ν(CO)$_{sym}$ 2000 ν(CO)$_{antisym}$ + ν(C=C=C) 1921 ν(OTf) 1273
2[b]	1.40 (br s, 3H, C$H_{3\ triphos}$) 2.20–2.50 (br m, 6H, C$H_{2\ triphos}$) 2.75 (br s, 1H, O*H*)	198.0 (m, *C*O) 115.7 (d, $J_{CP\ trans}$ 13.3, Re-C≡*C*) 100.4 (dt, $J_{CP\ trans}$ 33.0, $J_{CP\ cis}$ 12.5, Re-*C*≡C) 53.5 (s, *C*Ph_2OH) 40.4 (q, J_{CP} 10.2, *C*$H_{3\ triphos}$) 39.8 (q, J_{CP} 5.4, CH_3-*C*$_{triphos}$) 35.8 (d, J_{CPax} 22.5, *C*H_2-$P_{ax\ triphos}$) 33.9 (td, J_{CPeq} 14.0, J_{Cpax} 4.0, *C*H_2-$P_{eq\ triphos}$)	δ_A −5.67 δ_M −18.12	J_{AM} 17.7	ν(C≡C) 2090 ν(CO) 1946, 1880
3[b]	1.44 (q, J_{HP} 2.4, 3H, C$H_{3\ triphos}$) 2.41 (d, J_{HP} 8.4, 2H, CH_2-$P_{ax\ triphos}$) 2.25–2.75 (br m, 4H, CH_2 $P_{eq\ triphos}$) 3.39 (s, 3H, OCH_3)	198.3 (m, *C*O) 111.8 (d, $J_{CP\ trans}$ 13.3, Re-C≡*C*) 100.7 (dt, $J_{CP\ trans}$ 28.9, $J_{CP\ cis}$ 13.3, Re-*C*≡C) 51.6 (s, O*C*H_3) 40.1 (q, J_{CP} 9.8, *C*$H_{3\ triphos}$) 39.7 (q, J_{CP} 4.1, CH_3-*C*$_{triphos}$) 35.8 (s, *C*Ph_2OCH_3) 35.4 (d, J_{CPax} 22.5, *C*H_2-$P_{ax\ triphos}$) 33.8 (td, J_{CPeq} 14.9, J_{Cpax} 5.8, *C*H_2-$P_{eq\ triphos}$)	δ_A −5.49 δ_M −18.42	J_{AM} 18.2	ν(C≡C) 2083 ν(CO) 1946, 1890
4[b]	1.41 (q, J_{HP} 1.87, 3H, C$H_{3\ triphos}$) 2.10–2.70 (br m, 7H, C$H_{2\ triphos}$ + C*H*Ph_2)	198.5 (br m, *C*O) 115.7 (d, $J_{CPtrans}$ 12.1, C≡*C*) 90.9 (dt, $J_{CPtrans}$ 32.2, J_{CPcis} 14.3, *C*≡C) 68.0 (s, *C*HPh_2) 40.1 (q, J_{CP} 10.1, *C*$H_{3\ triphos}$) 39.7 (q, J_{CP} 5.0, CH_3-*C*$_{triphos}$) 35.7 (d, J_{CPax} 22.7, *C*H_2-$P_{ax\ triphos}$) 33.8 (td, J_{CPeq} 15.1, J_{CPax} 5.5, *C*H_2-$P_{eq\ triphos}$)	δ_A −4.98 δ_M −18.89	J_{AM} 17.3	ν(C≡C) 2097 ν(CO) 1944, 1885
5[b]	1.42 (q, J_{HP} 2.5, 3H, C$H_{3\ triphos}$) 2.40 (d, J_{HP} 8.4, 2H, CH_2-$P_{ax\ triphos}$) 2.20–2.80 (br m, 7H, CH_2 $P_{eq\ triphos}$ + *C*H_3)	198.3 (m, *C*O) 117.8 (d, $J_{CP\ trans}$ 12.1, Re-C≡*C*) 90.3 (dt, $J_{CP\ trans}$ 31.8, $J_{CP\ cis}$ 14.3, Re-*C*≡C) 47.2 (s, *C*$Ph_2$$CH_3$) 40.1 (q, J_{CP} 9.8, *C*$H_{3\ triphos}$) 39.7 (q, J_{CP} 4.4, CH_3-*C*$_{triphos}$) 37.7 (d, J_{CPax} 22.9, *C*H_2-$P_{ax\ triphos}$) 33.7 (td, J_{CPeq} 14.3, J_{CPax} 5.5, *C*H_2-$P_{eq\ triphos}$) 31.5 (s, *C*H_3)	δ_A −5.07 δ_M −19.50	J_{AM} 17.0	ν(C≡C) 2086 ν(CO) 1942, 1889
6[a,e]	1.38 (br s, 3H, C$H_{3\ triphos}$) 2.00–3.30 (br m, 6H,C$H_{2\ triphos}$) 5.20 (s, 2H, CH_2NO_2)	198.0 (m, *C*O) 111.2 (d, $J_{CPtrans}$ 13.7, Re-C≡*C*) 98.8 (dt, $J_{CPtrans}$ 33.2, J_{CPcis} 13.3, Re-*C*≡C) 85.1 (s, *C*H_2NO_2) 52.4 (s, *C*$Ph_2CH_2NO_2$) 41.1 (q, J_{CP} 10.2, *C*$H_{3\ triphos}$) 40.2 (q, J_{CP} 4.6, CH_3-*C*$_{triphos}$) 36.1 (d, J_{CPax} 21.4, *C*H_2-$P_{ax\ triphos}$) 34.4 (m, *C*H_2-$P_{eq\ triphos}$)	δ_A −5.77 δ_M −18.31	J_{AM} 17.3	ν(C≡C) 2085 ν(CO)1946, 1888
7[a,e]	1.05 (s, 3H, C$H_{3\ (C6)}$) 1.38 (br s, 3H, C$H_{3\ triphos}$) 2.00–2.50 (br m, 6H, C$H_{2\ triphos}$) 2.39 (s, 2H, C$H_{2\ (C4)}$)	209.8 (s, $C_{(5)}$O) 198.0 (br m, *C*O) 115.3 (d, $J_{CPtrans}$ 13.0, Re-C≡*C*$_{(2)}$) 94.2 (dt, $J_{CPtrans}$ 33.0, J_{CPcis} 12.0, Re-*C*$_{(1)}$≡(C) 58.3 (s, *C*$_{(4)}H_2$) 51.0 (s, *C*$_{(3)}Ph_2CH_2COCH_3$) 40.5 (q, J_{CP} 10.6, *C*$H_{3\ triphos}$) 39.7 (q, J_{CP} 4.7, CH_3-*C*$_{triphos}$) 35.6 (d, J_{CPax} 21.2, *C*H_2-$P_{ax\ triphos}$) 34.1 (td, J_{CPeq} 14.0, J_{CPax} 4.0, *C*H_2-$P_{eq\ triphos}$) 28.5 (s, *C*$_{(6)}H_3$)	δ_A −4.00 δ_M −16.58	J_{AM} 17.5	ν(C≡C) 2085 ν(CO)1952, 1880 ν(C=O)1706

Table 1 (*Contd.*)

Complex	^{1}H	^{13}C{^{1}H}	^{31}P{^{1}H}		IR
8[b]	1.7 (q, J_{HP} 2.6, 3H, C$H_{3\ triphos}$)	343.1 (dt, $J_{CPtrans}$ 32.3, J_{CPcis} 10.4, Re=*C*=C)	δ_A −20.34	J_{AM} 25.4	ν(CO) 2008, 1946
	2.30–2.80 (br m, 7H, C$H_{2\ triphos}$ + *CH*Ph$_2$)	192.0 (td, $J_{CPtrans}$ 8.5, J_{CPcis} 20.7, *C*O)	δ_M −18.20		ν(C=C) 1660
	3.42 (dm, J_{HP} 4.1, 1H, Re=C=C*H*)	191.3 (dt, $J_{CPtrans}$ 7.9, J_{CPcis} 20.8, *C*O) 119.3 (d, $J_{CPtrans}$ 12.8, Re=C=*C*) 68.8 (s, *C*HPh$_2$) 39.9 (q, J_{CP} 9.1, *C*H$_{3\ triphos}$) 39.7 (q, J_{CP} 3.1, CH$_3$-*C*$_{triphos}$) 32.0–34.5 (br m, *C*H$_{2\ triphos}$)			ν(OTf) 1260
9[b]	1.74 (br s, 3H, C$H_{3\ triphos}$)	344.9 (dt, $J_{CPtrans}$ 32.5, J_{CPcis} 10.5, Re=*C*=C)	δ_A −18.36	J_{AM} 23.7.7	ν(CO) 2013, 1950
	2.40–3.00 (br m, 9H, C$H_{2\ triphos}$ + CH_3) 3.64 (br s, Re=C=C*H*)	191.4 (m, *C*O) 122.2 (d, $J_{CPtrans}$ 12.2, Re=C=*C*) 46.7 (s, *C*Ph$_2$CH$_3$) 40.1 (m, *C*H$_{3\ triphos}$) 39.3 (q, J_{CP} 3.7, CH$_3$-*C*$_{triphos}$) 32.6 (m, *C*H$_{2\ triphos}$) 30.4 (s, *C*H$_3$)	δ_M −15.84		ν(C=C) 1649 ν(OTf) 1269
10[b]	1.40 (br s, 3H, C$H_{3\ triphos}$)	340.6 (dt, $J_{CPtrans}$ 32.5, J_{CPcis} 13.3, Re=*C*=C)	δ_A −18.74	J_{AM} 24.4	ν(CO) 2005, 1944
	2.20–2.50 (br m, 7H, C$H_{2\ triphos}$ + *CH*Ph$_2$) 2.81 (s, 3H, Re=C=CCH_3)	190.9 (m, *C*O) 115.6 (d, $J_{CPtrans}$ 13.3, Re=C=*C*) 60.7 (s, *C*HPh$_2$) 43.2 (s, Re=C=C*C*H$_3$) 39.7 (q, J_{CP} 9.7, *C*H$_{3\ triphos}$) 39.5 (q, J_{CP} 4.0, CH$_3$-*C*$_{triphos}$) 37.8 (d, J_{CPax} 29.4, *C*H$_2$-P$_{ax\ triphos}$) 32.7 (td, J_{CPeq} 15.7, J_{CPax} 5.0, *C*H$_2$-P$_{eq\ triphos}$)	δ_M −15.28		ν(C=C) 1655 ν(OTf) 1268
11[b]	1.41 (q, J_{HP} 2.5, 3H, C$H_{3\ triphos}$)	345.5 (dt, $J_{CPtrans}$ 32.4, J_{CPcis} 11.0, Re=*C*=C)	δ_A −19.50	J_{AM} 25.1	ν(CO) 2009, 1951
	2.30 (s,, 3H, Re=C=C(Me)CCH_3Ph$_2$) 2.50–2.95 (br m, 6H, C$H_{2\ triphos}$) 3.45 (s, 3H, Re=C=CCH_3)	192.5 (m, *C*O) 122.1 (s, Re=C=*C*) 61.7 (s, Re=C=C(*C*H$_3$) CCH$_3$Ph$_2$) 47.8 (s, Re=C=C=CPh$_2$*C*H$_3$) 40.5 (m, *C*H$_{3\ triphos}$ + CH$_3$-*C*$_{triphos}$) 33.7 (m, *C*H$_{2\ triphos}$) 33.1 (s, *C*CCH$_3$Ph$_2$)	δ_M −16.97		ν(C=C) 1646 ν(OTf) 1267
12[a]	1.80 (br s, 3H, C$H_{3\ triphos}$)	338.0 (dt, $J_{CPtrans}$ 32.7 J_{CPcis} 10.2, Re=*C*=C)	δ_A −21.09	J_{AM} 25.6	ν(CO) 2018, 1952
	2.10–2.90 (br m, 6H, C$H_{2\ triphos}$) 3.25 (s, 1H, Re=C=C*H*) 5.23 (s, 2H, CH_2NO$_2$)	191.0 (br m, *C*O) 116.7 (d, $J_{CPtrans}$ 12.1, Re=C=*C*) 85.9 (s, *C*H$_2$NO$_2$) 49.6 (s, *C*Ph$_2$CH$_2$NO$_2$) 39.9 (br s, *C*H$_{3\ triphos}$ + CH$_3$-*C*$_{triphos}$) 33.1 (br m, *C*H$_{2\ triphos}$)	δ_M −17.86		ν(C=C) 1644 ν(OTf) 1260
13[a]	1.57 (br s, 3H, C$H_{3\ triphos}$) 2.20–2.80 (br m, 6H, C$H_{2\ triphos}$) 3.80 (q, J_{HP} 2.6, 1H, Re=C=C*H*)	Not recorded	δ_A −20.01 δ_M −17.36	J_{AM} 25.3	Not recorded
16[a]	[d]	Not recorded	δ_A −19.39 δ_M −14.51	J_{AM} 25.2	Not recorded
17[a]	[d]	Not recorded	δ_A −20.03 δ_M −16.60	J_{AM} 25.7	Not recorded
18[b]	1.96 (q, J_{HP} 3.3, 3H, C$H_{3\ triphos}$) 2.84 (d, J_{HP} 9.3, 2H, C$H_{2\ Pax\ triphos}$) 2.58–3.01 (br m, 4H, C$H_{2\ Peq\ triphos}$) 5.72 (dt, $J_{HPtrans}$ 3.3, J_{HPcis} 1.8, 1H, C*H*=CPh$_2$)	310.5 (d br m, $J_{CPtrans}$ 38, Re≡*C*) 185.0 (m, *C*O) 144.8 (s, *C*H=CPh$_2$) 122.1 (s, CH=*C*Ph$_2$) 39.2 (brs, *C*H$_{3\ triphos}$) 38.9 (q, J_{CP} 13.8, CH$_3$-*C*$_{triphos}$) 30.9 (m, *C*H$_{2\ triphos}$)	δ_A −27.84 δ_M −11.57	J_{AM} 29.5	Not recorded
19[a]	1.99 (br s, 3H, C$H_{3\ triphos}$) 2.86 (d, J_{HP} 10.4, 2H, C$H_{2\ Pax\ triphos}$) 2.55–3.20 (br m, 4H, C$H_{2\ Peq\ triphos}$) 3.30 (s, 3H, C(CH_3)=CPh$_2$)	311.5 (dt, $J_{CPtrans}$ 29, J_{CPcis} 8, Re≡*C*) 186.0 (m, *C*O) 124.5 (s, *C*(CH$_3$)=CPh$_2$) 118.1 (s, C(CH$_3$)=*C*Ph$_2$) 60.88 (s, C(*C*H$_3$)=CPh$_2$) 39.6 (q, J_{CP} 2.5, *C*H$_{3\ triphos}$) 39.4 (q, J_{CP} 6.1, CH$_3$-*C*$_{triphos}$) 31.4 (td, J_{CPeq} 17.1, J_{CPax} 4.0, *C*H$_2$-P$_{eq\ triphos}$) 31.0 (m, *C*H$_2$-P$_{ax\ triphos}$)	δ_A −30.26 δ_M −13.91	J_{AM} 29.3	ν(CO) 2096, 2055

The NMR spectra were recorded in CD_2Cl_2 (unless otherwise stated) at room temperature using [a] Bruker AC200 or [b] Varian VXR300 instruments. All ^{31}P{^{1}H} NMR spectra exhibit AM_2 splitting pattern. Key: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. [c] Confirmed by DEPT-135 experiment. [d] The ^{1}H NMR resonances of **16** and **17** could not be confidently assigned as both these complexes were formed in very low concentration and their resonances were likely masked by those of the most abundant species. [e] Recorded in $CDCl_3$.

data for **13** are reported in Table 1) (Scheme 3). Increasing the temperature to −40 °C completely converted the γ-hydroxyvinylidene **13** to **1**. Repeating the same experiment at −78 °C with a weaker acid such as tris(trifluoromethyl)-*tert*-butanol, $HOC(CF_3)_3$, resulted in the quantitative and selective formation of the γ-hydroxyvinylidene **13** (Fig. 1).

The conversion of **2** to **1** *via* **13** is mechanistically relevant to the metal-mediated transformation of propargylic alcohols HC≡CC(R)(R′)OH into allenylidene ligands M=C=C=C(R)-(R′) and water which proceeds *via* a cascade mechanism primarily proposed by Selegue (Scheme 4).[26] This mechanism involves the sequential conversion of the propargyl alcohol to π-alkyne, γ-hydroxyvinylidene and then allenylidene ligands. In the latter step, an equivalent amount of water is released.[4c,5,27] In a few reactions only, γ-hydroxyvinylidene compounds have been either intercepted spectroscopically or isolated in the solid state.[10–16]

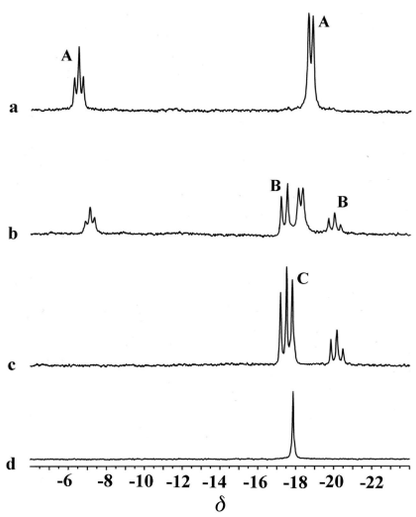
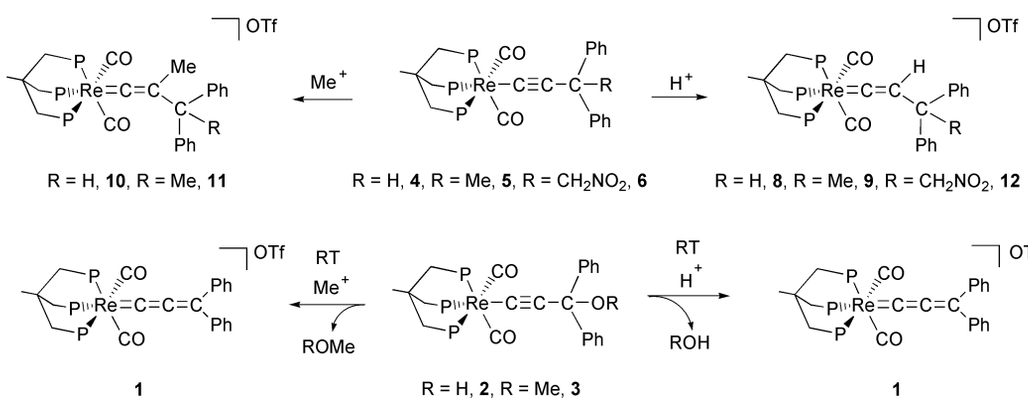


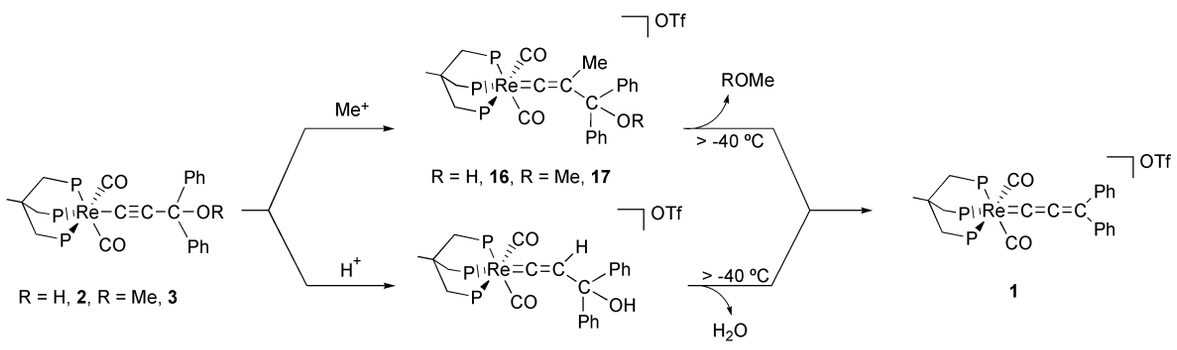
Fig. 1 Reaction of [Re{C≡CC(OH)Ph_2}$(CO)_2$(triphos)] (**2**) with $HOC(CF_3)_3$ (1 : 5) in CD_2Cl_2: (a) $^{31}P\{^1H\}$ NMR spectrum of **2** at −78 °C; (b) $^{31}P\{^1H\}$ NMR spectrum immediately after addition of $HOC(CF_3)_3$ at −78 °C; (c) at −40 °C; (d) at −20 °C. A: [Re{C≡CC(OH)-Ph_2}$(CO)_2$(triphos)] (**2**). B: [Re{C=C(H)C(OH)Ph_2}$(CO)_2$(triphos)]-(OTf) (**13**). C: [Re{C=C=CPh_2}$(CO)_2$(triphos)](OTf) (**1**).

The protonation of γ-hydroxyalkynyl complexes has been previously investigated *in situ*.[28–30] In no case, however, was the formation of a hydroxyvinylidene species detected during the protonation reaction so that the primary regiochemistry of H^+ addition to the hydroxyalkynyl moiety is still unclear, *i.e.* it has not been demonstrated whether the proton attacks primarily the terminal hydroxy substituent or the C_β atom. For example, the protonation of [$CpOs(PPr^i_3)_2$(H){C≡CC(OH)Ph_2}]PF_6 (**14**) has been suggested to involve the direct protonation of the OH group exclusively on the basis of the inertness of **14** to convert to the corresponding vinylidene.[28] The unambiguous detection of the 3-hydroxyvinylidene complex **13** during the protonation of **2** at low temperature clearly points to the alternative pathway in which the proton is selectively delivered to the C_β carbon of the hydroxyalkynyl ligand to give a vinylidene intermediate, which rearranges to allenylidene **1** and water above −40 °C. The low activation barrier of γ-hydroxyvinylidene to allenylidene conversion explains why no trace of **13** was detected by variable-temperature NMR spectroscopy in the course of the reaction between HC≡CCPh_2(OH) and the Re(I) fragment $[Re(CO)_2(triphos)]^+$, generated from [Re(OTf)$(CO)_2$(triphos)] (**15**).[4c] The activation of the propargyl alcohol by the Re(I) fragment occurred at −5 °C, well above the temperature at which **13** spontaneously degrades to **1** and water.

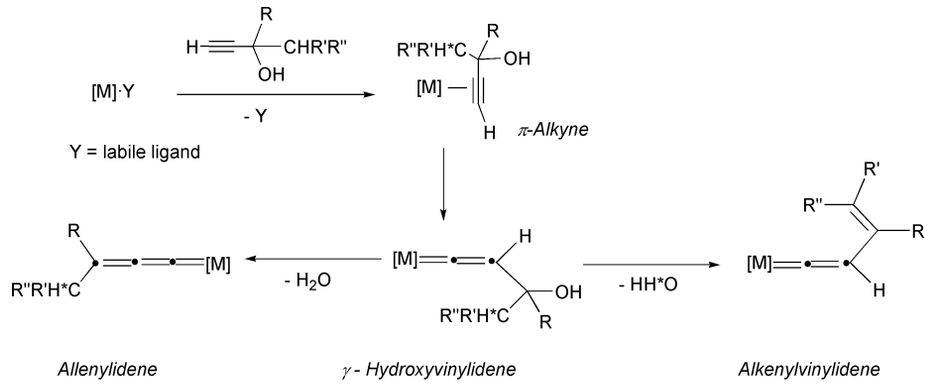
A similar scenario accounts for the reactions between **2** and Me^+ and between **3** and H^+ (Scheme 3) which gave **1** and MeOH. Indeed, the intermediate hydroxyvinylidene complex [Re{C=C(Me)C(OH)Ph_2}$(CO)_2$(triphos)](OTf) (**16**) was detected at low temperature, while the protonation of the methoxyalkynyl complex **3** did not allow us to intercept any intermediate species preceding the formation of **1** and MeOH even at −80 °C. Gimeno and co-workers have similarly reported that MeOH is liberated from the methoxyvinylidene intermediate [$(\eta^5$-$C_9H_7)$Ru$(PPh_3)_2$(C=C(H)CH(Ph)OMe}]$^+$ obtained by



Scheme 2



Scheme 3



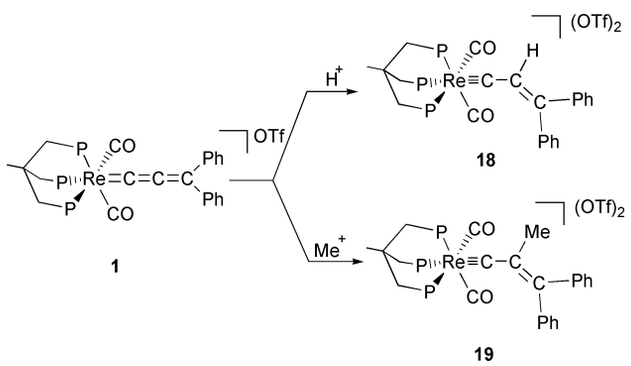
Scheme 4

reacting $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ with HC≡CCH(Ph)OH/$NaPF_6$.[10]

Upon methylation with MeOTf at room temperature, the γ-methoxyalkynyl complex **3** quantitatively converted to **1** releasing one equivalent of Me_2O. When the reaction was performed at low temperature, the 2-methyl-3-methoxyvinylidene intermediate $[Re(CO)_2\{C{=}C(Me)C(OMe)Ph_2\}(triphos)](OTf)$ (**17**) was intercepted by NMR spectroscopy ($^{31}P\{^1H\}$ NMR: AM_2 pattern with δ_A −20.03, δ_M −16.60, J_{AM} = 25.7 Hz) (Scheme 3). On increasing the temperature to *ca.* 20 °C, **17** transformed into **1** with contemporaneous formation of Me_2O. The elimination of dimethyl ether from γ-methoxyvinylidene complexes has no precedent in the literature and confirms that the formation of metalloallenylidenes represents the thermodynamic sink of any Selegue type reaction.

Reaction of 1 with electrophiles: synthesis and characterization of dicationic rhenium carbyne complexes

In line with the chemistry of metallacumulenes,[1,31,32] the C_β atom in **1** was selectively attacked by HOTf and MeOTf to give the emerald-green carbyne complexes $[Re(CO)_2\{{\equiv}CC(H){=}CPh_2\}(triphos)](OTf)_2$ (**18**) and $[Re(CO)_2\{{\equiv}CC(Me){=}CPh_2\}(triphos)](OTf)_2$ (**19**), respectively (Scheme 5). A fivefold excess



Scheme 5

of electrophile was necessary for quantitative formation of the carbynes.

The $^{31}P\{^1H\}$ NMR spectra of the two Re(I) carbyne products exhibit AM_2 patterns with peculiar chemical shifts and coupling constants for triphos–Re(I) carbenes,[4a,b] vinylidenes[4a] and allenylidenes.[4c,5] The triplet resonance due to the phosphorus atom *trans* to the carbyne carbon atom is remarkably shifted to high field [δ_A −27.84 (**18**), −30.18 (**19**)] as compared to the vinylidene precursor, while the *J*(PP) constant is unusually large for Re(I) triphos complexes [$J(P_AP_M)_{ave}$ = 29.5 Hz].[4,5] In the ^1H NMR spectrum of **18**, a doublet of triplets at 5.72 ppm features the =CH proton, while the resonances of the two sp^2 carbon atoms of the alkenyl ligand fall at 144.8 (CH=) and 122.1 (=CPh_2) ppm in the $^{13}C\{^1H\}$ NMR spectrum. The sp carbyne carbon atoms appear as highly deshielded doublets of multiplets at δ 310.5 and 311.5.

Although the two carbynes could be obtained quantitatively in the NMR tube, all our attempts to isolate pure samples in the solid state from their CH_2Cl_2 solutions were unsuccessful due to extensive formation of the parent allenylidene **1**. By adding MeOTf to a stirred suspension of **1** in benzene, **19** immediately precipitated as a greenish yellow solid, which proved to be extremely moisture-sensitive and regenerated **1** rapidly even in the solid state unless handled in a dry box. A satisfactory elemental analysis and the observation in the IR *ν*(CO) region of two strong absorptions at high wavenumbers (2096, 2055 cm^{-1}) confirmed the carbyne nature of **19**. Dissolution of the solid product in wet CD_2Cl_2 gave **1** even at low temperature, which reflects a particulary strong acidic character for the rhenium(I) dicationic carbyne complex, as well as the great thermodynamic stability of the allenylidene **1**.

An osmium carbyne complex $[CpOs(PPr^i_3)_2\{{\equiv}CC(H){=}CPh_2\}](PF_6)_2$ has been prepared by protonation of a parent allenylidene. Unlike **19**, the Os complex could be isolated in the solid state and was also authenticated by X-ray crystallography.[28]

Conclusion

The results presented in this paper show that the γ-hydroxyvinylidene $[Re\{C{=}C(H)C(OH)Ph_2\}(CO)_2(triphos)](OTf)$ is intermediate to the allenylidene $[Re\{C{=}C{=}CPh_2\}(CO)_2(triphos)](OTf)$ in the course of the reaction of the Re(I) fragment $[Re(CO)_2(triphos)]^+$ with the propargyl alcohol HC≡$CCPh_2OH$. The intermediacy of the γ-hydroxyvinylidene complex could not be observed by the straightforward reaction due to the very low activation barrier for water elimination from the latter complex.

The allenylidene complex represents a true thermodynamic sink: it also forms quantitatively by spontaneous extrusion of dimethyl ether from the γ-methoxyvinylidene complex $[Re(CO)_2\{C{=}C(Me)C(OMe)Ph_2\}(triphos)](OTf)$ that involves both C–C and C–O bond breaking.

Experimental

All reactions and manipulations were routinely performed under a dry nitrogen atmosphere by using standard Schlenk techniques. Tetrahydrofuran (THF) was freshly distilled over $LiAlH_4$; acetone and benzene were distilled over P_2O_5; 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. The complex $[Re\{C{=}C{=}CPh_2\}(CO)_2(triphos)](OTf)$[5] (**1**) was prepared as previously reported. All the other reagents and chemicals were reagent grade and, unless otherwise stated, were used as received from commercial suppliers. The solid complexes were

collected on sintered glass-frits and washed with either light diethyl ether or *n*-pentane 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[33] and DAVINS.[34] The initial choices of shifts and coupling constants were refined by iterative least-squares calculations using the experimental digitised 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, N) were performed using a Carlo Erba model 1106 elemental analyser.

Preparations

[Re{C≡CC(OH)Ph$_2$}(CO)$_2$(triphos)] (2). A solution of **1** (200 mg, 0.17 mmol) in 5 mL of CH_2Cl_2 was slowly added to a solution of KOH (100 mg, 1.78 mmol) in 5 mL of distilled water under vigorous stirring to favour the mixing of the organic and aqueous phases. Stirring was continued for *ca.* 1.5 h until the starting deep purple colour of the organic phase became reddish orange. The dichloromethane layer was separated from the aqueous layer and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the brown-orange residue was washed with H_2O, isopropylic alcohol and *n*-hexane. Yield 72%. Anal. Calcd for $C_{58}H_{50}O_3P_3Re$: C, 64.85; H, 4.69. Found: C, 64.57; H, 4.82%.

***In situ* NMR reaction of 2 and HOSO$_2$CF$_3$.** A solution of **2** (25 mg, 0.022 mmol) in CD_2Cl_2 (0.8 mL) was prepared in a 5 mm screw-cap NMR tube and cooled to −78 °C with a dry ice/acetone bath before adding five equivalents of $HOSO_2CF_3$ through the serum cap. The tube was inserted into the NMR probe precooled at −74 °C and the progress of the reaction was monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy. At this temperature, a 1 : 5 mixture of the allenylidene **1** and of the hydroxyvinylidene [Re{C=C(H)C(OH)Ph$_2$}(CO)$_2$(triphos)](OTf) (**13**) was observed. At higher temperature, **13** converted into **1** and at −40 °C, **1** was the only detectable product. On increasing the temperature to *ca.* 0 °C the carbyne [Re(CO)$_2${≡CC(H)=CPh$_2$}(triphos)](OTf)$_2$ (**18**) (see below) was also formed.

***In situ* NMR reaction of 2 and HOC(CF$_3$)$_3$.** Ten equivalents of $HOC(CF_3)_3$ were syringed into a solution of **2** cooled to −78 °C as described above. At this temperature, the quantitative formation of **13** was confirmed by $^{31}P\{^{1}H\}$ NMR spectroscopy. Heating the NMR sample to −20 °C quantitatively transformed **2** into the parent allenylidene **1** while no trace of **18** was observed at any temperature.

***In situ* NMR reaction of 2 and CH$_3$OSO$_2$CF$_3$.** Addition of five equivalents of $CH_3OSO_2CF_3$ to a cold solution of **2** prepared as described above, caused an immediate colour change from brownish orange to dark violet indicating the formation of the parent allenylidene compound. A $^{31}P\{^{1}H\}$ NMR spectrum at −74 °C showed the presence of the secondary hydroxyvinylidene [Re{C=C(Me)C(OH)Ph$_2$}(CO)$_2$(triphos)](OTf) (**16**) as minor product (*ca.* 10%). As the temperature was increased **16** quickly transformed into **1** (the transformation was complete at −40 °C) while at higher temperature in the presence of a larger excess of methyl triflate the alkenylcarbyne [Re{≡CC(Me)=CPh$_2$}(CO)$_2$(triphos)](OTf)$_2$ (**19**) (see below) began to form. Elimination of one equivalent of MeOH was shown by GC-MS analysis and confirmed by ^{1}H NMR spectroscopy (δ_{MeOH} 3.40).

[Re{C≡CC(OMe)Ph$_2$}(CO)$_2$(triphos)] (3). A solution of **1** (200 mg, 0.17 mmol) in 10 mL of methanol was treated with a tenfold excess of sodium methoxide (92 mg, 1.70 mmol) added in small portions with vigorous stirring. The mixture was additionally stirred for 30 min during which time a pale yellow-brown solid separated. The solvent was removed under reduced pressure and the solid was washed with water, isopropylic alcohol and *n*-hexane to leave a yellowish brown powder. Yield: 78%. Anal. Calcd for $C_{59}H_{52}O_3P_3Re$: C, 65.12; H, 4.82. Found: C, 65.45; H, 4.97%.

***In situ* NMR reaction of 3 with HBF$_4$·OEt$_2$ or HOCH$_x$(CF$_3$)$_{3-x}$ (*x* = 0, 1).** Addition of five equivalents of $HBF_4{\cdot}OEt_2$ (33 μL, 0.18 mmol) to a $CDCl_3$ solution (0.8 mL) of **3** (40 mg, 0.04 mmol) at −55 °C in a 5 mm screw-cap NMR tube, caused an immediate colour change from yellow-brown to dark violet. $^{31}P\{^{1}H\}$ NMR spectroscopy showed the quantitative formation of the parent allenylidene **1** as the only rhenium–triphos species.

Replacing $HBF_4{\cdot}OEt_2$ with either $HOC(CF_3)_3$ or $HOCH(CF_3)_2$ did not affect the course of the reaction and produced **1** with no detectable intermediate. The transformation was complete at −30 °C in 15 min.

The formation of one equivalent of MeOH was confirmed in each case by both GC-MS analysis and ^{1}H NMR spectroscopy.

***In situ* NMR reaction of 3 with CH$_3$OSO$_2$CF$_3$.** A solution of **3** (40 mg, 0.04 mmol) in CD_2Cl_2 (0.8 mL) was prepared in a 5 mm screw-cap NMR tube and cooled to −78 °C with a dry ice/acetone bath before adding five equivalents of $CH_3OSO_2CF_3$ through the serum cap. The tube was inserted into the NMR probe precooled at −74 °C and the progress of the reaction was monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy. At −50 °C the formation of **3**, **1** and the 2-methyl-3-methoxyvinylidene [Re(CO)$_2${C=C(Me)C(OMe)Ph$_2$}(triphos)](OTf) (**17**) in a 10 : 10 : 1 ratio was observed. On standing at room temperature a complete transformation into **1** occurred in 1 h.

The formation of one equivalent of Me_2O was confirmed by GC-MS analysis and ^{1}H NMR spectroscopy (δ_{Me_2O} = 3.27).

[Re{C≡CC(H)Ph$_2$}(CO)$_2$(triphos)] (4). A tenfold excess of $LiHBEt_3$ (1 M THF solution, 1.7 mL, 1.7 mmol) was syringed into a solution of **1** (200 mg, 0.17 mmol) in 10 mL of THF cooled at −15 °C. The dark violet colour turned to yellow immediately. After stirring for 30 min at 0 °C, the solution was concentrated to *ca.* 1 mL and complex **4** was obtained as a pale yellow powder upon slow addition of 2 mL of *n*-hexane. The solid product was washed with water, cold isopropylic alcohol and *n*-hexane. Yield 76%. Anal. Calcd for $C_{58}H_{50}O_2P_3Re$: C, 65.83; H, 4.76. Found: C, 65.94; H, 4.92%.

***In situ* NMR reaction of 4 and HOSO$_2$CF$_3$. Synthesis of [Re{C=C(H)CHPh$_2$}(CO)$_2$(triphos)](OTf) (8).** A stoichiometric amount of $HOSO_2CF_3$ (6.7 μL, 0.07 mmol) was added to a CD_2Cl_2 solution (0.8 mL) of **4** (80.0 mg, 0.07 mmol) in a 5 mm screw-cap NMR tube. Immediately the colour changed from yellow to brownish orange and the NMR spectra showed the complete transformation of **4** into **8**.

***In situ* NMR reaction of 8 and NEt$_3$.** A tenfold excess of NEt_3 (93 μL, 0.70 mmol) was added to a CD_2Cl_2 solution (0.8 mL) of

8 (80.0 mg, 0.07 mmol) in a 5 mm screw-cap NMR tube. ^{31}P NMR spectrum confirmed the quantitative transformation of **8** into **4**.

***In situ* NMR reaction of 4 and $CH_3OSO_2CF_3$. Synthesis of [Re{C=C(Me)CHPh$_2$}(CO)$_2$(triphos)](OTf) (10).** Addition of one equivalent of $CH_3OSO_2CF_3$ (6.2 μL, 0.07 mmol) to a CD_2Cl_2 solution (0.8 mL) of **4** (80.0 mg, 0.07 mmol) in a 5 mm screw-cap NMR tube, completely transformed **4** into **10** (^{31}P NMR analysis).

[Re{C≡CC(Me)Ph$_2$}(CO)$_2$(triphos)] (5). To a solution of **1** (200 mg, 0.17 mmol) in 5 mL of THF was added a tenfold excess of CH_3Li (1.7 M THF, 1.0 mL, 1.70 mmol) which caused a colour change from dark violet to dark orange. After stirring for 3 h at room temperature, wet THF (1.0 mL) was added dropwise to hydrolyse the excess of CH_3Li. The solvent was removed under vacuum and the pale brown residue was washed with H_2O, ethanol and *n*-hexane. Yield 78%. Anal. Calcd for $C_{59}H_{52}O_2P_3Re$: C, 66.10; H, 4.89. Found: C, 66.37; H, 4.95%.

***In situ* NMR reaction of 5 and $HOSO_2CF_3$. Synthesis of [Re{C=C(H)C(Me)Ph$_2$}(CO)$_2$(triphos)](OTf) (9).** Addition of of $HOSO_2CF_3$ (6.7 μL, 0.07 mmol) to a CD_2Cl_2 solution (0.8 mL) of **5** (80.0 mg, 0.07 mmol) in a 5 mm screw-cap NMR tube completely transformed **5** into **9**.

***In situ* NMR reaction of 9 and NEt_3.** A complete transformation of **9** into **5** took place after addition of a tenfold excess of NEt_3 (25.0 μL, 0.20 mmol) to a CD_2Cl_2 solution (0.8 mL) of **9** (30.0 mg, 0.02 mmol) in a 5 mm screw-cap NMR tube (confirmed by ^{31}P NMR spectroscopy).

***In situ* NMR reaction of 5 and $CH_3OSO_2CF_3$. Synthesis of [Re{C=C(Me)C(Me)Ph$_2$}(CO)$_2$(triphos)](OTf) (11).** A stoichiometric amount of $CH_3OSO_2CF_3$ (8.4 μL, 0.07 mmol) was added to a CD_2Cl_2 solution (0.8 mL) of **5** (80.0 mg, 0.07 mmol) in a 5 mm screw-cap NMR tube. The immediate transformation of **5** into **11** was shown by the colour change from yellow to brownish orange and confirmed by $^{31}P\{^1H\}$ NMR spectroscopy.

[Re{C≡CC(CH$_2$NO$_2$)Ph$_2$}(CO)$_2$(triphos)] (6). 200 mg of MeONa (3.70 mmol) was introduced under stirring in a Schlenk tube containing 5 mL of nitromethane. After 5 min solid **1** (200 mg, 0.17 mmol) was added in small portions and the resulting solution was stirred for 1 h at room temperature during which time the colour of the solution slowly turned from deep violet to brown. Removal of the solvent *in vacuo* yielded **6** as a brown solid which was washed with ethanol and *n*-pentane. Yield: 75%. Anal. Calcd for $C_{59}H_{51}NO_4P_3Re$: C, 63.43; H, 4.60; N, 1.25. Found: C, 64.10; H, 4.69; N, 1.37%.

***In situ* NMR reaction of 6 and $HOSO_2CF_3$. Synthesis of [Re{C=C(H)C(CH$_2$NO$_2$)Ph$_2$}(CO)$_2$(triphos)](OTf) (12).** One equivalent of $HOSO_2CF_3$ (6.7 μL, 0.07 mmol) was added to a CD_2Cl_2 solution (0.8 mL) of **6** (80.0 mg, 0.08 mmol). Immediately the colour turned from brown to reddish orange and the ^{31}P NMR spectrum showed the complete transformation of **6** into **12**.

***In situ* NMR reaction of 12 and NEt_3.** An excess of NEt_3 was added to a CD_2Cl_2 solution (0.8 mL) of **12** prepared as above in a 5 mm screw-cap NMR tube. Immediately the colour turned from reddish orange to brown and the ^{31}P NMR spectrum showed the complete transformation of **12** into **6**.

[Re{C≡CC(CH$_2$C(O)CH$_3$)Ph$_2$}(CO)$_2$(triphos)] (7). Solid MeONa (200.0 mg, 3.70 mmol) was introduced into a Schlenk tube containing 10 mL of acetone and a magnetic bar. After stirring for 30 min, addition of 200.0 mg (0.17 mmol) of **1** under stirring caused a fast colour change from dark violet to red-brown. The solution was additionally stirred for 2 h at room temperature and then filtered through Celite. Removal of the solvent under reduced pressure gave a reddish solid that was dissolved in CH_2Cl_2 (3 mL). The resulting red solution was filtered through a cotton plug and concentrated almost to dryness (0.5 mL). Addition of *n*-pentane (2.0 mL) precipitated **7** as a beige solid. Yield: 72%. Anal. Calcd for $C_{61}H_{54}O_3P_3Re$: C, 65.76; H, 4.88. Found: C, 66.10; H, 4.85%.

***In situ* NMR reaction of 7 and $HOSO_2CF_3$.** A stoichiometric amount of $HOSO_2CF_3$ (2.4 μL, 0.03 mmol) was added to a 5 mm screw-cap NMR tube charged with **7** (30 mg, 0.03 mmol) and CD_2Cl_2 (0.7 mL). A ^{31}P NMR spectrum of the resulting red solution showed the presence of a complicated mixture of products which were not studied further.

***In situ* synthesis of [Re{≡CC(H)=CPh$_2$}(CO)$_2$(triphos)](OTf)$_2$ (18).** Addition of a fivefold excess of $HOSO_2CF_3$ to a CD_2Cl_2 solution (0.8 mL) of **1** (40.0 mg, 0.03 mmol) in a 5 mm screw cap NMR tube at room temperature, caused an immediate colour change from dark purple to emerald green. NMR monitoring of the reaction revealed the quantitative formation of **18**.

Addition of water or of other nucleophiles to a solution of **18** immediately restored the purple colour of **1**.

***In situ* synthesis of [Re{≡CC(Me)=CPh$_2$}(CO)$_2$(triphos)](OTf)$_2$ (19).** Replacing $HOSO_2CF_3$ with $MeOSO_2CF_3$ in the above preparation, gave the carbyne [Re(CO)$_2${≡CC(Me)=CPh$_2$}(triphos)](OTf)$_2$ (**19**) in quantitative NMR yield.

Synthesis of 19. In a Schlenk tube **1** (40 mg, 0.03 mmol) was suspended in benzene (3 mL) and a fivefold excess of $MeOSO_2CF_3$ (16 μL) was syringed under vigorous stirring. After 15 min, the solvent was removed under reduced pressure and the greenish residue was washed with cold benzene (2 × 1 mL) and pentane (2 × 1 mL) before being dried. Anal. Calcd. for $C_{61}H_{52}F_6O_8P_3S_2Re$: C, 53.47; H, 3.82. Found: C, 54.02; H, 3.94%.

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