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Activation of 2-propyn-1-ols by the rhenium(I) fragment $[\{MeC(CH_2PPh_2)_3\}Re(CO)_2]^+$. Synthesis and characterization of cationic Re(I) complexes containing unsaturated η^1-carbon ligands

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Abstract

The $[\{MeC(CH_2PPh_2)_3\}Re(CO)_2]^+$ auxiliary has been found to activate 1-ethynyl-1-cyclohexanol and 1-phenyl-2-propyn-1-ol yielding a variety of η^1-carbon ligands, which includes hydroxyvinylidene, alkenylvinylidene, alkoxycarbene, η^1-C_{sp}-enynyl, secondary allenylidene, acyl, hydroxycarbene and alkoxycarbene groups. The reactivity of the allenylidene complex $[\{MeC(CH_2PPh_2)_3\}Re(CO)_2\{C{=}C{=}C(H)Ph\}]^+$ toward water and methanol has been investigated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Rhenium; Propargyl alcohols; Allenylidene; Hydroxyvinylidene; Hydroxycarbene; Triphos ligand

1. Introduction

The metal-assisted elimination of water from ω-alkynols is a reaction that offers access to a variety of metal-η^1-carbon assemblies with great potential in organic synthesis and homogeneously catalysed reactions leading to C-C bond formation [1]. Ruthenium and, to a lesser extent, osmium are by far the most studied metals for the activation of ω-alkynols, especially α-alkynols that are usually known as propargyl alcohols [1b]. Increasing interest is being received by rhenium since we reported on the capability of the $16e^-$ fragment $[(triphos)(CO)_2Re]^+$ (triphos = $MeC(CH_2PPh_2)_3$) to transform either propargyl alcohols into vinylidene, allenylidene, carbene, carbyne and alkynyl compounds [2,3] or β-, γ-, and δ-alkynols into oxacyclocarbene ligands [3].

In this paper is reported the synthesis, characterization and chemistry of other cationic rhenium (I) compounds containing unsaturated η^1-carbon ligands derived from the activation of propargyl alcohols. Novel examples of ligands bound to the $[(triphos)(CO)_2Re]^+$ auxiliary include hydroxyvinylidene, alkenylvinylidene, η^1-C_{sp}-enynyl, *secondary* allenylidene, acyl, hydroxy- and alkoxycarbene.

2. Results and discussion

Selected ^1H-, $^{31}P\{^1H\}$- and $^{13}C\{^1H\}$-NMR data for all compounds are collected in Table 1.

2.1. Reaction of [(triphos)(CO)$_2$Re(OTf)] with 1-ethynyl-1-cyclohexanol

The reaction of $[(triphos)(CO)_2Re(OTf)]$ (OTf = triflate, OSO_2CF_3) (**1**) with a slight excess of 1-ethynyl-1-cyclohexanol in dichloromethane at room temperature yielded a microcrystalline greenish–grey solid (Scheme 1). Unambiguous characterization of this product as

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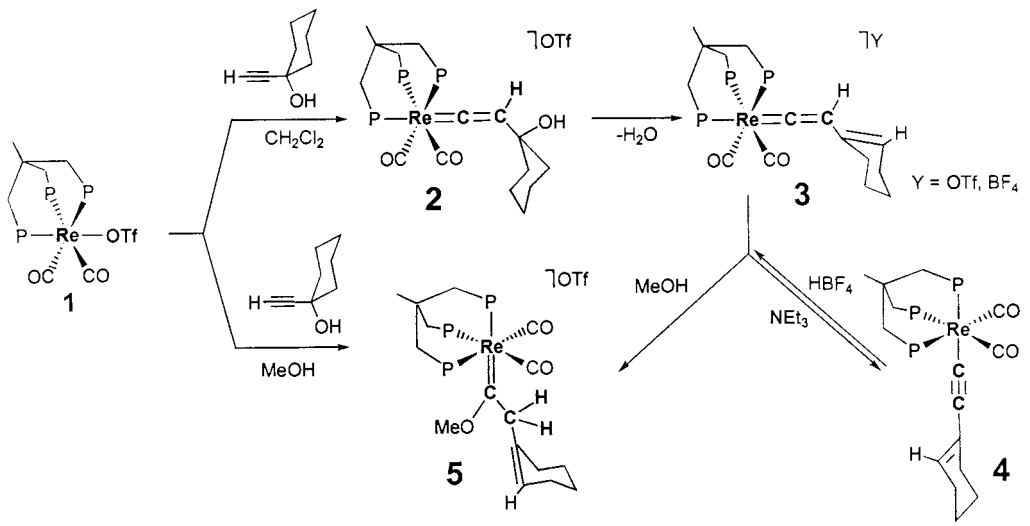
the alkenylvinylidene complex [(triphos)$(CO)_2$Re-{C=C(H)(*cyclo*-C_6H_9)}](OTf) (**3**) was straightforwardly obtained from a comparison of its IR and NMR data with those of other Re(I)-triphos vinylidene complexes [4]. The only spectroscopic ^{1}H-NMR features deserving a comment are a quartet at 3.91 ppm, due to the vinylidene hydrogen atom, and a triplet at δ 5.36 ascribed to the unique vinyl proton of the cyclohexenyl substituent. In keeping with the presence of a vinylidene ligand, the $^{13}C\{^1H\}$-NMR spectrum contains a doublet of triplets at 357 ppm and a multiplet at ca. 192 ppm assigned to the C_α carbon atom and to the two carbonyl carbon atoms, respectively. The multiplicity observed for these latter (AA′ portion of an AA′MM′X pattern) is typical for the $[(triphos)(CO)_2Re]^+$ moiety in which the carbonyl groups are magnetically inequivalent [5].

The chemoselective formation of **3** from the reaction between **1** and 1-ethynyl-1-cyclohexanol is typical for the reactions of propargyl alcohols with coordinatively unsaturated transition-metal fragments [1].[4] In the case at hand, the labile triflate ligand is readily displaced by the propargyl alcohol that undergoes alkyne-to-vinylidene tautomerization (formal 1,2-H shift), most likely via a π-1-alkyne intermediate [6c].[5] Hydroxyvinylidene complexes are generally unstable with respect to intramolecular dehydration involving either hydroxy and C_β–H groups or hydroxy and proximal $C_\delta H_2$ groups to give allenylidene or alkenylvinylidene derivatives, respectively (Scheme 2). The selective formation of the alkenylvinylidene **3** is most likely due to the ring strain that would affect an allenylidene-3-cyclohexane product [1]. Consistently, we have recently shown that the reaction of **1** with the tertiary propargyl alcohols HC≡CC(OH)RPh (R = CH_3, Ph) gives exclusively allenylidene products [2].

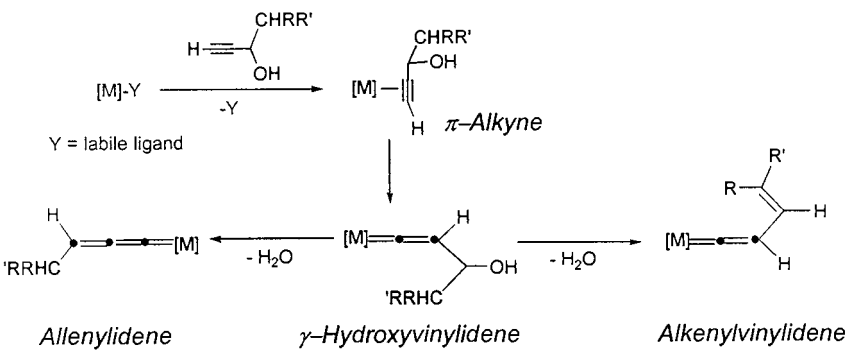
On the other hand, electronic factors may be as important as steric factors to drive the formation of either alkenylvinylidene or allenylidene products [8]. In particular, electron-rich metal, fragments would favour the formation of the alkenylvinylidene ligand which is a better π-acceptor than the allenylidene isomer [6b]. The formation of unstable allenylidenes as kinetically con-

[4] Examples of reactions of transition metal complexes with 1-ethynyl-1-cyclohexanol are given in [6].

[5] Examples of arrested π-propyn-1-ol complexes are given in [7].



Scheme 1.



Scheme 2.

Table 1
^{1}H-, $^{13}C\{^{1}H\}$- and $^{31}P\{^{1}H\}$-NMR spectral data and IR absorptions for the complexes [a]

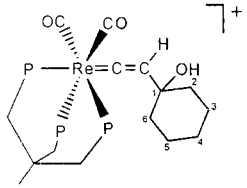
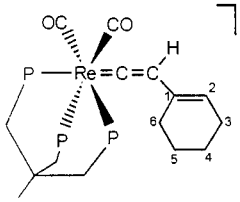
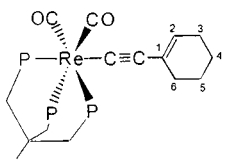
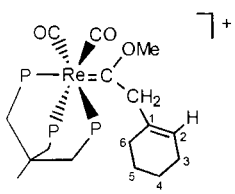
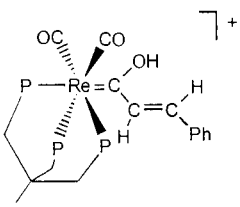
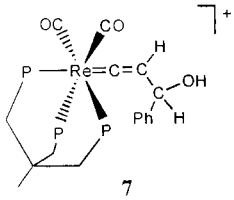
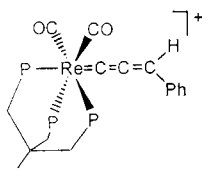
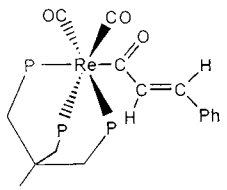
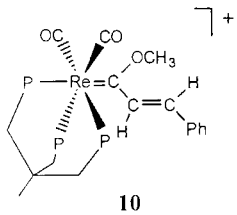
Complex	^{1}H δ (ppm), J (Hz)	$^{13}C\{^{1}H\}$ δ (ppm), J (Hz)	$^{31}P\{^{1}H\}$ δ (ppm), J (Hz) [IR (KBr, cm^{-1})]
 **2**	1.90-1.05 (m, 10H, CH_2 (C2, C3, C4, C5, C6 ring)) 1.68 (q, 3H, J_{HP} 3.1, CH_3 triphos) 2.36 (br, 1H, OH) 2.9-2.4 (m, 6H, CH_2 triphos) 3.46 (dq, $J_{HP(trans)}$ 9.1, $J_{HP(cis)}$ 2.7, J_{HH} 2.7, C=CHvinylidene)	344.0 (dt, $J_{CPtrans}$ 30.5, J_{CPcis} 10.8, Re=*C*=C) 192.0 (m, *C*O) 119.1 (dt, $J_{CPtrans}$ 15.2, J_{CPcis} 2.9, Re=C=*C*) 68.4 (s, *C*1) 40.0 (br m, *C*H_3 triphos + CH_3-*C* triphos) 36.8 (s, *C*2 + *C*6) 32.0-34.0 (br m, *C*H_2 triphos) 26.9 (s, *C*3 + *C*5) 26.4 (s, *C*4)	δ_A -19.30 J_{AM} 24.4 δ_M -16.22 not recorded
 **3**	+1.68-1.59 (m, 4H, CH_2(C4, C5, ring)) 1.78 (q, 3H, J_{HP} 3.2, CH_3 triphos) 2.28 (m, 2H, CH_2(C6, ring)) 2.05 (m, 2H, CH_2(C3, ring)) 2.81-2.53 (m, 6H, CH_2 triphos) 3.91 (q, J_{HP} 3.1, 1H, C=CHvinylidene) 5.36 (t, 1H, J_{HH} 3.8, CH(C2, ring))	357.0 (dt, $J_{CPtrans}$ 32.6, J_{CPcis} 10.9, Re=*C*=C) 192.0 (m, *C*O) 124.1 (s, *C*2) 123.0 (t, J_{CP} 1.9, *C*1) 117.2 (dt, $J_{CPtrans}$ 17.2, J_{CPcis} 2.2, Re=C=*C*) 39.4 (m, *C*H_3 triphos, CH_3-*C* triphos) 32.0-34.0 (br m, *C*H_2 triphos) 30.2, 26.5, 23.6, 22.8 (all s, *C*3, *C*4, *C*5, *C*6)	δ_A -20.27 J_{AM} 24.9 δ_M -17.22 ν(CO) 2008, 1946 ν(C=C)$_{vinylidene}$ 1636 ν(C=C)$_{ring}$ 1625 ν(OTf) 1269
 **4**	1.40 (br s, CH_3 triphos) 1.48–1.75 (m, 4H, CH_2(C4, C5, ring)) 1.83–2.15 (m, 4H, CH_2(C3, C6, ring)) 2.20-2.60 (br m, 6H, CH_2 triphos) 5.58 (s, 1H, =CH(C2, ring))	197.0 (m, CO) 118.0 (d, $J_{CPtrans}$ 15.9, Re-C≡*C*) 101.0 (dt, $J_{CPtrans}$ 23.1, J_{CPcis} 10.0, Re-*C*≡C) 39.5 (m, *C*H_3 triphos, CH_3-*C* triphos) 33.8 (m, *C*H_2 triphos) 31.4, 25.9, 23.5, 22.6 (all s, *C*3, *C*4, *C*5, *C*6)[c]	δ_A -6.43 J_{AM} 17.6 δ_M -20.71 ν(C≡C) 2075 ν(CO) 1946, 1879 ν(C=C) not observed
 **5**	1.60 (q, J_{HP} 2.7, 3H, CH_3 triphos) 1.59 (m, 2H, CH_2(C5, ring)) 1.74 (m, 2H, CH_2(C4, ring)) 1.94 (m, 2H, CH_2(C3, ring)) 2.22 (m, 2H, CH_2(C6, ring)) 2.27 (s, 3H, OCH_3) 2.40-2.90 (br m, 6H, CH_2 triphos) 3.14 (s, 2H, CH_2) 5.22 (s, CH(C2, ring))	307.8 (dt, $J_{CPtrans}$ 38.7, J_{CPcis} 8.5, Re=*C*) 198.4 (m, AXX'Y, J_{AX} 43.0, $J_{AX'}$ -11.7, J_{AY} 8.4, $J_{XX'}$ 22.4, *C*O) 125.3 (s, *C*2) 118.5 (s, *C*1) 64.7 (s, *C*H_2) 63.3, (s, O*C*H_3) 40.3 (q, J_{CP} 7.3, *C*H_3 triphos) 39.8 (q, J_{CP} 3.3, CH_3-*C* triphos) 36.0 (t, J_{CPeq} 12.8, *C*H_2-P_{eq} triphos) 32.2 (dt, J_{CPax} 20.7, J_{CPeq} 4.3, *C*H_2-P_{ax} triphos) 30.0, 25.9, 23.4, 22.6 (all s, *C*3, *C*4, *C*5, *C*6)	δ_A –17.60 J_{AM} 21.5 δ_M –9.47 ν(CO) 1951, 1896 ν(C=C) 1659 ν(OTf) 1262
 **6**	1.68 (q, J_{HH} 2.8, 3H, CH_3 triphos) 2.28 (br s, 1H, OH) 2.64 (m, 6H, CH_2 triphos) 7.16 (d, J_{HH} 15.7, 1H, *H*C=CHPh)[a] 7.93 (d, J_{HH} 15.7, 1H, CH=C*H*Ph)	282.7 (dt, $J_{CPtrans}$ 34.7, J_{CPcis} 8.9, Re=*C*) 197.3 (AXX'Y, J_{AX} 47.2, $J_{AX'}$ -12.3, J_{AY} 7.3, $J_{XX'}$ 24.3, *C*O) 144.3 (dt, $J_{CPtrans}$ 5.5, J_{CPcis} 1.5, *C*=C) 137.1 (s, C=*C*) 41.2 (q, J_{CP} 9.8, *C*H_3 triphos) 39.5 (q, J_{CP} 4.9, CH_3-*C* triphos) 34.7 (td, J_{CPax} 14.5, J_{CPeq} 5.5, *C*H_2-P_{ax} triphos) 33.8 (dt, J_{CPeq} 14.6, J_{CPax} 4.2, *C*H_2-P_{eq} triphos)	δ_A -17.50 J_{AM} 21.8 δ_M -13.97 ν(OH) 3050 br ν(CO) 1968, 1904 ν(C=C) 1597 ν(OTf) 1269
 **7**	1.71 (q, J_{HP} 2.7, 3H, CH_3 triphos) 2.00-2.80 (br m, 6H, CH_2 triphos) 2.02 (br s, 1H, OH) 3.08 (br t, 1H,C=CHvinylidene) 10.51 (t, J_{HP} 2.4, 1H, CHPh)	340.9 (dt, $J_{CPtrans}$ 32.3, J_{CPcis} 10.4, Re=*C*=C) 191.2 (br m, *C*O) 127 (s, Re=C=*C*) 41.7 (s, *C*(OH)(H)Ph) 39.8 (q, J_{CP} 9.5, *C*H_3 triphos) 39.6 (q, J_{CP} 3.0, CH_3-*C* triphos)	[b] δ_M -17.86 J_{AM} 24. δ_A -19.20 not recorded

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

Complex	^{1}H δ (ppm), J (Hz)	^{13}C{^{1}H} δ (ppm), J (Hz)	^{31}P{^{1}H} δ (ppm), J (Hz) [IR (KBr, cm^{-1})]
 **8**	1.70 (q, J_{HP} 3.4, 3H, CH_3 triphos) 2.40-2.90 (br m, 6H, CH_2 triphos) 6.09 (dt, J_{HP} 4.1, J_{HP} 2.0, 1H, C=C=CH)	310 (m, Re=C=C=C) 208 (m, Re=C=C=C) 192 (br m, CO) 142 (s, Re=C=C=C) 40.2 (q, J_{CP} 9.8, CH$_3$ triphos) 39.6 (q, J_{CP} 3.0, CH$_3$-C triphos) 31.8-35.7 (br m, CH$_2$ triphos)	δ_M -15.65 J_{AM} 2 δ_A -20.53 not recorded
 **9**	1.42 (br s, 3H, CH_3 triphos) 2.45 (m, 6H, CH_2 triphos) 6.27 (d, J_{HH} 15.6, 1H, HC=CHPh) 7.74 (d, J_{HH} 15.5, 1H, CH=CHPh)	257.4 (dt, $J_{CPtrans}$ 29.1, J_{CPcis} 9.7, C=O) 202.1 (m, CO) 149.7 (d, J_{CP} 8.8, C=C) 138.6 - 140.6 (all s, C_{ipso}) 123.9 (s, C=C) 40.2 (q, J_{CP} 9.24, CH$_3$ triphos) 39.8 (br s, CH$_3$-C triphos) 35.5 (m, CH$_2$ triphos)	δ_A -10.69 J_{AM} 17.1 δ_M -14.72 ν(CO) 1939, 1871 ν(C=C) 1610 ν(CO)$_{acyl}$ 1520
 **10**	1.65 (br s, 3H, CH_3 triphos) 2.65 (m, 6H, CH_2 triphos) 2.75 (s, 3H, OCH_3) 6.85 (d, J_{HH} 15.8, 1H, HC=CHPh) 7.84 (d, J_{HH} 15.8, 1H, CH=CHPh)	288.5 (dt, $J_{CPtrans}$ 37.0, J_{CPcis} 9.7, Re=C) 199.9 (m, CO) 150.5 (s, C=C) 136.5 (s, C=C) 135.6-137.7 (all s, C_{ipso}) 62.9 (s, OCH$_3$) 39.8 (q, J_{CP} 10.6, CH$_3$ triphos) 39.1 (q, J_{CP} 3.7, CH$_3$-C triphos) 34.8 (td, J_{CPax} 12.7, J_{CPeq} 2.3, CH$_2$-P$_{ax}$ triphos) 31.5 (dt, J_{CPeq} 22.9, J_{CPax} 2.9, CH$_2$-P$_{eq}$ triphos)	δ_A -17.08 J_{AM} 20.9 δ_M –9.49 ν(CO) 1956, 1892 ν(C=C) 1609 ν(OTf) 1271

[a] NMR spectra were recorded in CD_2Cl_2 (or $CDCl_3$ for complexes **5**, **9** and **10**) at room temperature. Only the ^{1}H and ^{13}C resonances due to the rhenium coordinated organyl ligand, the triphos skeleton resonances and the CO groups are reported in the table. Key: s, singlet; d, doublet; t, triplet, q, quartet; m, multiplet; br, broad. All ^{31}P{^{1}H}-NMR spectra exhibit an AM_2 splitting pattern. ^{1}H and ^{13}C spectra were assigned by a thorough analysis of ^{13}C{^{1}H}-DEPT-135, ^{1}H,^{1}H-COSY and ^{1}H,^{13}C-HMQC-NMR experiments.
[b] Masked by the aromatic protons. Detected by a ^{1}H,^{1}H-COSY-NMR experiment.
[c] AB_2 spin system.
[d] C_1 and C_2 not observed.

trolled products has been also reported [8b]. The Re(I) system $[(triphos)(CO)_2Re]^+$ has been found capable of stabilising both vinylvinylidene and allenylidene ligands [2] and, therefore, the selective formation of the alkenylvinylidene **3** seems to be mainly driven by steric effects. This does not exclude that the higher thermodynamic stability of the conjugate C=C system in vinylvinylidene complexes may contribute to disfavour the cumulated C=C structure of allenylidenes [6].

Monitoring the reaction between **1** and 1-ethynyl-1-cyclohexanol by variable-temperature NMR spectroscopy shed some light on the reaction mechanism allowing us to intercept the hydroxyvinylidene kinetic product $[(triphos)(CO)_2Re\{C=C(OH)(cyclo\text{-}C_6H_{10})\}](OTf)$ (**2**) at low temperature. At -18°C, **2** was sufficiently stable to be studied by ^{13}C-NMR spectroscopy [$\delta(C_\alpha)$ 344.0, $\delta(C_\beta)$ 119.1], while it slowly transformed into **3** at room temperature.

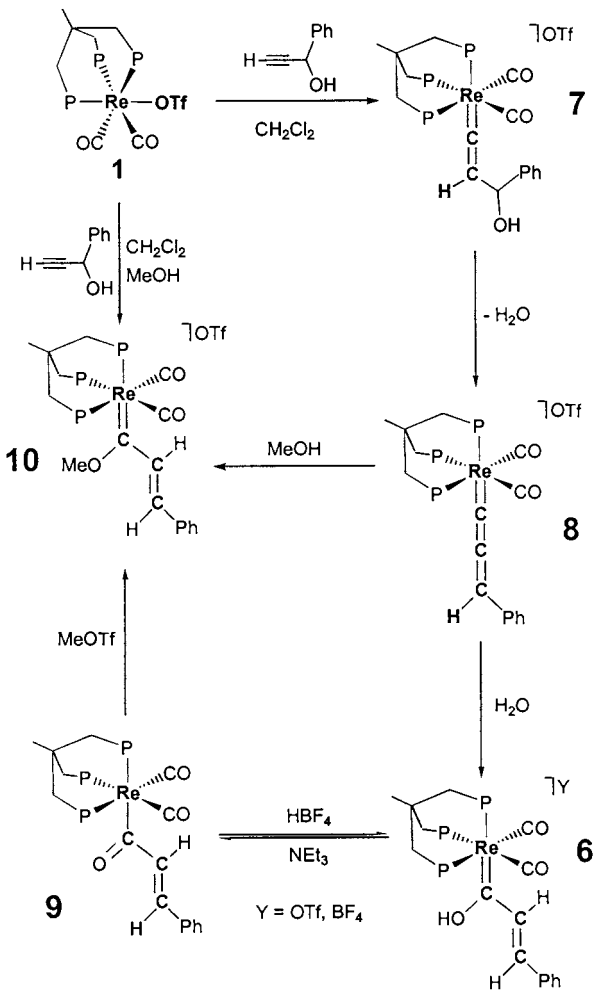
Indirect experimental support to the proposed structure for **3** has been provided by the reversible reaction with bases such as NEt_3 yielding the η^1-C_{sp}-enynyl derivative $[(triphos)(CO)_2Re\{C\equiv C(cyclo\text{-}C_6H_9)\}]$ (**4**) (Scheme 1). η^1-C_{sp}-Enynyl complexes are quite rare as this bifunctional unsaturated ligand, commonly generated by reductive coupling of vinylidene and alkynyl ligands [9], prefers to use the triple bond and the C_α vinyl carbon atom for η^3-coordination.[6]

The η^1-enynyl structure of **4** is proved by the presence of a strong ν(C≡C) stretching band at 2075 cm^{-1} in the IR spectrum. The presence of this band is accompanied by two ν(CO) absorptions that are shifted to lower frequencies (1946–1879 cm^{-1}) with respect to the precursor **3**, consistent with the weaker π-acceptor character of the alkynyl ligand as compared to vinylidene [4,11]. The ^{31}P{^{1}H}-NMR spectrum displays the expected AM_2 pattern with chemical shifts and coupling constants typical for σ-alkynyl- Re(I) compounds

[6] Examples of η^1-C_{sp2}-enynyl complexes are also well documented. See [10].

[4,5]. In the $^{13}C\{^1H\}$-NMR spectrum, the alkynyl C_α and C_β atoms and the two vinyl carbon atoms give rise to multiplets in the expected region [4,12].

Gimeno and coworkers have recently reported that $[(\eta^5\text{-}C_9H_7)RuCl(PPh_3)_2]$ reacts in refluxing methanol with an excess of 1-ethynyl-1-cyclohexanol in the presence of $NaPF_6$ to give the allenylidene complex $[(\eta^5\text{-}C_9H_7)Ru\{C{=}C{=}C(C_{13}H_{20})\}(PPh_3)_2](PF_6)$ via an unprecedented coupling of two molecules of propargyl alcohol [13]. This product was also obtained by reaction of the vinylidene derivative $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2\text{-}\{C{=}C(H)R\}](PF_6)$ (R = 1-cyclohexenyl) with an excess of propargyl alcohol in refluxing methanol. Both synthetic approaches have been attempted by us using **1** and **3** as starting materials. In no case, however, was the coupling of the substrate observed, and the more ordinary methoxy carbene $[(triphos)(CO)_2Re\{C(OMe)\text{-}CH_2(cyclo\text{-}C_6H_9)\}]$ (**5**) was obtained via nucleophilic attack of MeOH at the vinylidene C_α atom. The methoxy carbene complex was characterized by IR and multinuclear NMR spectroscopy. Characteristic spectroscopic features in the ^{13}C-NMR spectrum were a low-field shifted doublet of triplets at ca. 307 ppm, diagnostic for the presence of the carbene carbon atom [2–4], and the DEPT-135 inverted singlet at 64.7 ppm that is assigned to the CH_2 β-carbon. Addition of alcohols to vinylidene complexes is a well-known reaction[7] and has also been documented for 3-hydroxyvinylidene species by Dixneuf and coworkers [15].



Scheme 3.

2.2. Reaction of [(triphos)(CO)$_2$Re(OTf)] with 1-phenyl-2-propyn-1-ol

When complex **1** was reacted with 1-phenyl-2-propyn-1-ol in dichloromethane at room temperature, the alkenylhydroxycarbene complex $[(triphos)(CO)_2Re\text{-}\{C(OH)C(H){=}CHPh\}]^+$ (**6**) was isolated in 90% yield (Scheme 3). The α,β-unsaturated-hydroxycarbene group in **6** showed ν(OH) and ν(C=C) IR absorptions at 3050 and 1597 cm^{-1}, respectively, while the two ν(CO) bands fall at 1968 and 1904 cm^{-1}. The presence of a rhenium-carbene moiety in **6** was also confirmed by the ^{31}P-NMR AM_2 spin system with typical chemical shifts at −17.50(t) and −13.97(d) ppm [$J(P_AP_M)$ 21.8 Hz] as well as ^1H-NMR resonances at 2.28 ppm (broad, OH) and 7.16 and 7.93 ppm (doublets) assigned to the $C_\beta H$ and $C_\gamma H$ protons, respectively [2–4]. The coupling constant, $J(HH) = 15.7$ Hz, is consistent with a *trans* arrangement of the two hydrogen atoms [16]. The signal of the β-proton was not directly observed in the ^1H-NMR spectrum due to overlapping with the aromatic protons resonances and its identification was made through a $^1H,^1H$-COSY-NMR experiment. In the $^{13}C\{^1H\}$-NMR spectrum, the Re=C_α(OH) carbene carbon and the olefinic C_β=C carbon appeared as doublets of triplets at 282.7 and 144.3 ppm, respectively, while a singlet resonance at ca. 137 ppm was assigned to the olefinic C_γ carbon resonance.

Hydroxycarbene metal complexes are still rare species, generally featured by a fleeting existence [4]. Rhenium seems to be the metal of choice for the stabilization of the hydroxycarbene grouping. Indeed, a stable hydroxycarbene ligand has recently been obtained by direct addition of water to a vinylidene ligand [4],[8] while α,β-unsaturated-hydroxycarbene compounds have been obtained by Esteruelas and coworkers by reaction of 1-alkynols with $[(\eta^5\text{-}C_5H_5)Ru(CO)\{\eta^1\text{-}OC(CH_3)_2\}(PPr^i_3)]BF_4$ [6b]. The reaction between **1** and 1-phenyl-2-propyn-1-ol was followed by NMR spectroscopy in CD_2Cl_2 from −25 to 25°C. This study showed that the formation of **6** is a stepwise process involving two intermediate species at least. Both intermediates appeared already at −20°C in the first $^{31}P\{^1H\}$- and ^1H-NMR spectra with a ratio of ca. 10:1.

[7] The addition of methanol across the C=C bond of a vinylidene was firstly reported by Bruce and coworkers. See [14].

[8] For a discussion of the addition of water to vinylidenes see [17].

The species with the higher concentration (**7**) was featured by a slightly second-order AM_2 ^{31}P pattern and by three ^1H resonances at 10.51 (t, $J(HP) = 2.4$ Hz), 3.08 (broad t, $J(HP) = 4.2$ Hz) and 2.0 ppm (broad). With time the major compound converted to a species (**8**) characterized by a first-order AM_2 ^{31}P pattern and by a ^1H-NMR resonance at 6.09 ppm (dt, $J(HP_A) = 4.1$ Hz, $J(HP_M) = 2.0$ Hz). Increasing the temperature to 5°C accelerated the conversion of **7** to **8** and also led to the formation of **6**. The exclusive presence of **6** was observed after 8 h at room temperature. The life-time of each species was sufficiently long to allow for their characterization by both ^{31}P- and ^1H-NMR spectroscopy but was too short for the acquisition of reliable ^{13}C-NMR spectra. The reaction of **1** with 1-phenyl-2-propyn-1-ol was then carried out at -10°C in the presence of anhydrous Na_2SO_4. As a result, the half-life of **8** increased remarkably and allowed for its characterization by ^{13}C-NMR spectroscopy (after 8 h, the ratio between **8** and **7** was ca. 6:1 (based on ^{31}P-NMR integration), but some **6** was already formed (ca. 20%). Three weak signals at ca. 310, 208 and 142 ppm were unequivocally assigned to **8**, while a comparison with the spectrum of the reaction mixture obtained in the absence of Na_2SO_4 allowed us to attribute a signal at 340.9 ppm to **7**. When an excess of water was syringed into a solution of **8** prepared in the presence of Na_2SO_4 at -10°C, the colour changed from pale yellow to red and the hydroxycarbene **6** was immediately formed. With time, the solution became dark red and after 1 h at room temperature **6** was the only detectable species.

Incorporation of all these chemical and spectroscopic data leads us to propose a mechanism for the reaction of **1** with 1-phenyl-2-propyn-1-ol in which the γ-hydroxyvinylidene [(triphos)Re(CO)$_2${C=C(H)C(H)Ph(OH)}]$^+$ (**7**) is the first species to form [1b]. This compound spontaneously loses water and converts to the secondary allenylidene [(triphos)Re(CO)$_2${C=C=C(H)Ph}]$^+$ (**8**), which is the direct precursor to **6** by regioselective addition of water to the allenylidene C_α carbon atom. Consistently with this mechanism, we have found that: (i) Added Na_2SO_4 captured most of the water released by **7** thus increasing the stability of the allenilydene **8** in the reaction mixture; (ii) when methanol was added to a solution of **8** prepared as describe above, the alkoxycarbene [(triphos)Re(CO)$_2${C(OMe)CH=C(H)Ph}](OTf) (**10**) was selectively formed (vide infra). A detailed assignment of relevant NMR signals for both **7** and **8** is given in Table 1.

In the light of the present study, the paucity of data on metal complexes containing secondary allenylidene ligands [1b] may be rationalized in terms of their great reactivity toward water so that even traces of moisture may lead to their degradation to hydroxycarbene species and from these latter to other products [15a]. To the best of our knowledge, the only stable secondary allenylidene complexes are the ruthenium derivatives [(PP)$_2$ClRu{C=C=C(H)Ar}](PF$_6$) (PP = diphosphine) [18a–c] and [(η^5-C$_9$H$_7$)Ru(PPh$_3$)$_2${C=C=C(H)Ph}](PF$_6$) [19a].[9]

The chemistry of the hydroxycarbene complex **6** is typical for this class of compounds [6b]. The regioselective and reversible deprotonation of the hydroxy group occurred easily in dichloromethane with Et_3N to give the α,β-unsaturated acyl derivative [(triphos)Re(CO)$_2$-{C(O)CH=C(H)Ph}] (**9**) as a brown microcrystalline material. The acyl complex was converted to **6** by regioselective reaction with a protic acid such as $HBF_4{\cdot}OMe_2$ in CH_2Cl_2.

The main NMR spectroscopic properties of **9** are in line with those of the acetyl complex [(triphos)(CO)$_2$Re-{C(O)CH$_3$}] recently prepared in our laboratory [4]. The acyl ligand in **9** exhibited a ^{13}C-NMR resonance at 257.4 ppm for the Re–C=O carbon atom (dt, $J(CP_{trans}) = 29.1$ Hz, $J(CP_{cis}) = 9.7$ Hz), while the olefinic carbons appeared as a doublet at 149.7 ppm ($J(CP) = 8.8$ Hz, C_β) and a singlet at 123.9 ppm (C_γ). In the IR spectrum, the ν(CO) stretching frequencies of the carbonyl ligands were shifted to lower energy as compared to the precursor, which is consistent with the greater σ-donor and lower π-acceptor properties of the acyl ligand with respect to carbene. A band at 1520 cm^{-1} was assigned to the ν(CO) stretch of the alkenylacyl ligand, which is slightly shifted to lower energy as compared to the value reported by Esteruelas for similar ruthenium(II) compounds [6b].

Methylation of the alkenyl(acyl) complex **9** by MeOTf gave the α,β-unsaturated methoxycarbene complex **10** that was also obtained by treatment of **8** with MeOH (see above) as well as from the one-pot reaction of **1** with 1-phenyl-2-propyn-1-ol in methanol (Scheme 3). Similar methoxyalkenylcarbenes were prepared by Gimeno and coworkers via one-pot reaction of [(η^5-C$_9$H$_7$)(PP)RuCl] (PP = diphosphine) with MeOH and 1-phenyl-2-propyn-1-ol in the presence of $NaPF_6$ [19]. However, addition of MeOH to the secondary allenylidene [(η^5-C$_9$H$_7$)(PPh$_3$)$_2$Ru{C=C=C(H)Ph}](PF$_6$) occurs reversibly to yield selectively the γ-methoxyvinylidene [(η^5-C$_9$H$_7$)(PPh$_3$)$_2$Ru{C=C(H)C(H)(OMe)Ph}](PF$_6$) [19]. A study of the NMR properties of **10** confirmed the presence of an α,β-unsaturated methoxycarbene ligand. Particularly informative were the ^1H- and $^{13}C\{^1H\}$-NMR spectra containing a ^1H-NMR singlet at 2.75 ppm (OC*H*$_3$ protons) and ^{13}C-NMR signals at 288.5 ppm ($J(CP_{trans}) = 37.0$ Hz, $J(CP_{cis}) = 9.7$ Hz, carbene C_α) and 62.9 ppm (singlet, OCH_3). The two ν(CO) bands in the IR spectrum were observed at higher frequencies (1956, 1892 cm^{-1}) as compared to the acyl

[9] The addition of MeOH to allenylidene intermediates was firstly described by Le Bozec and coworkers, see [19b]. See also [15a].

9 due to the greater π-acceptor character of the carbene Re=C_α bond [4].

3. Conclusions

We have shown here that rhenium may be an alternative to ruthenium and osmium to activate propargyl alcohols and yielding a great variety of unsaturated η^1-carbon ligands. It has also been shown that secondary allenylidene complexes may have a fleeting existence due to their remarkable tendency to react with water or alcohols to give hydroxy- or alkoxycarbene derivatives, respectively.

4. Experimental

All reactions and manipulations were routinely performed under a dry nitrogen atmosphere by using standard Schlenk techniques. Tetrahydrofuran (THF) was freshly distilled over $LiAlH_4$; dichloromethane and methanol were purified by distillation over CaH_2 prior to use; *n*-hexane was stored over molecular sieves and purged with nitrogen prior to use. The complex [(triphos)Re$(CO)_2$(OTf)] (**1**) was prepared as previously described [20]. The propargyl alcohols 1-ethynyl-1-cyclohexanol and 1-phenyl-2-propyn-1-ol were purchased from Aldrich and used as received. All the other reagents and chemicals were reagent grade and, unless otherwise stated, were used as received by commercial suppliers. The solid complexes were collected on sintered glass-frits and washed with either diethyl ether or *n*-hexane before being dried in a stream of nitrogen. 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 or 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 [21] and DAVINS [22,23]. 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 analyser. MS-FAB spectra for some products 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.

4.1. [(triphos)Re$(CO)_2${C=CH(cyclo-C_6H_9)}]OTf (3)

A slight excess of 1-ethynyl-1-cyclohexanol (30.6 μl, 0.24 mmol) was added via syringe to a suspension of **1** (200 mg, 0.20 mmol) in dichloromethane (5 ml). The solution was stirred at room temperature (r.t.) for 2.5 h and evaporated to dryness under vacuum. By slow addition of *n*-hexane a greenish–grey microcrystalline solid precipitated. Yield: 77%. Anal. Calc. for $C_{52}H_{49}F_3O_5P_3SRe$: C, 55.66; H, 4.40; S, 2.85. Found: C, 55.72; H, 4.57; S, 2.94%.

4.2. [(triphos)Re$(CO)_2${C≡C(cyclo-C_6H_9)}] (4)

A solution of **3** (200 mg, 0.18 mmol) in dichloromethane (1 ml) was treated with a tenfold excess of NEt_3 (250 μl, 1.80 mmol). The reaction mixture was stirred at r.t. for 1 h during which time the colour changed from brownish–green to orange. The solvent was then removed under vacuum and the crude product was washed with ethanol (2 × 1 ml) and dissolved with dichloromethane (1 ml). Addition of *n*-hexane (1 ml) separated **4** as an orange powder. Yield: 68%. Anal. Calc. for $C_{51}H_{48}O_2P_3Re$: C, 63.02; H, 4.98. Found: C, 63.14; H, 4.87%.

4.3. Reaction of 4 with $HBF_4{\cdot}OMe_2$

A stoichiometric amount of $HBF_4{\cdot}OMe_2$ was added to a dichloromethane-d_2 solution (0.8 ml) of **4** (30 mg, 0.03 mmol) in a 5-mm screw-cap NMR tube. ^{31}P{^{1}H} analysis of the resulting solution immediately showed the complete transformation of **4** into **3**.

4.4. [(triphos)Re$(CO)_2${C(OMe)CH_2(cyclo-C_6H_9)}] (5)

4.4.1. Method A

A solution of **1** (200 mg, 0.20 mmol) in 20 ml of methanol was treated with a fivefold excess of 1-ethynyl-1-cyclohexanol (130 μl, 1.0 mmol) and refluxed for 5 h. The resulting solution was concentrated almost to dryness and diethyl ether (5 ml) was added to give a yellowish brown precipitate. Yield: 65%. Anal. Calc. for $C_{53}H_{53}F_3O_6P_3SRe$: C, 55.20; H, 4.63; S, 2.77. Found: C, 55.87; H, 4.76; S, 3.01%.

4.4.2. Method B

A suspension of **3** (200 mg, 0.18 mmol) in 20 ml of methanol was refluxed for 4 h under stirring. After cooling to r.t., the solution was filtered and the solvent was removed under vacuum to give **5** in ca. 85 yield.

4.5. In situ NMR Reaction of 1 and HC≡C{cyclo-C_6H_{10}(OH)}

A solution of **1** (80 mg, 0.08 mmol) and 1-ethynyl-1-cyclohexanol (10.4 μl, 0.08 mmol) in dichloromethane-d_2 (0.8 ml) was prepared in a 5-mm NMR screw-cap tube cooled to −78°C under nitrogen. The tube was inserted into the spectrometer precooled to −40°C. The progress of the reaction was followed by $^{31}P\{^1H\}$- and ^1H-NMR spectroscopy. No reaction product was observed until the temperature was raised to −5°C. At this temperature, **1** started to convert to the hydroxyvinylidene complex [(triphos)$Re(CO)_2$-{C=C(H)C(Ph)H(OH)}](OTf) (**2**) and to the alkenylvinylidene **3**. After 2 h at r.t., a ^{31}P-NMR spectrum showed the solution to contain a mixture of **2** and **3** in an approximate 2:3 ratio. With time (12 h), **3** was the only species visible on the NMR timescale.

4.6. [(triphos)$Re(CO)_2$\{C(OH)CH=C(H)Ph\}](OTf) (**6**)

A slight excess of 1-phenyl-2-propyn-1-ol (27.4 μl, 0.22 mmol) was added to a suspension of **1** (200 mg, 0.20 mmol) in dichloromethane (5 ml). The dark brown mixture was stirred at r.t. for 16 h and then the solvent was evaporated in vacuo to leave a brown solid. Yield: 89%. Anal. Calc. for $C_{53}H_{47}F_3O_6P_3SRe$: C, 55.44; H, 4.12; S, 2.79. Found: C, 56.01; H, 4.05; S, 2.63%. FAB–MS: m/z 1000 (M^+), 895 $[(triphos)Re(CO)_3]^+$, 867 $[(triphos)Re(CO)_2]^+$, 839 $[(triphos)Re(CO)]^+$.

4.7. In situ NMR Reaction of **1** and HC≡CC(H)Ph(OH)

The reaction of **1** (80 mg, 0.08 mmol) and 1-phenyl-2-propyn-1-ol (9.8, μL, 0.08 mmol) was followed by $^{31}P\{^1H\}$-NMR spectroscopy in dichloromethane-d_2 (0.8 ml) in the temperature range from −25 to 25°C. A reaction took place at ca. −20°C when two sets of resonances appeared in the spectrum, which were attributed to the hydroxyvinylidene complex [(triphos)-$Re(CO)_2$\{C=C(H)C(H)Ph(OH)\}]$^+$ (**7**) (90%) and to the allenylidene derivative [(triphos)$Re(CO)_2$\{C=C=C-(H)Ph\}]$^+$ (**8**) (10%). Warming the NMR-tube to r.t. caused the fast disappearance of the signals of **7** to give **8** that more slowly transformed into **6**. A complete conversion was achieved in about 8 h at 25°C.

4.8. In situ NMR Reaction of 1 and HC≡CC(H)Ph(OH) in the presence of Na_2SO_4

A Schlenk tube cooled at −10°C, was charged with solid Na_2SO_4 (100 mg, 0.70 mmol), a stirring bar and a solution of **1** (80.0 mg, 0.08 mmol) in dichloromethane-d_2 (1.2 ml). After 5 min stirring, one equivalent of 1-phenyl-2-propyn-1-ol (9.8, μl, 0.08 mmol) was introduced via syringe. The suspension was stirred for 45 min, filtered through a cotton plug and transferred into an ice-cooled NMR tube. The $^{31}P\{^1H\}$-NMR spectrum immediately recorded at −20°C showed the presence of (**7**) (ca. 25%) and (**8**) (ca. 59%) with some unreacted **1** (ca. 16%). Warming the NMR tube to 25°C for 8 h gave a 6:1:2 mixture of **8**, **7** and **6**. With time, all **7** converted to **8**, while **6** formed more slowly.

4.9. In situ NMR Reaction of [(triphos)$Re(CO)_2$\{C=C=C(H)Ph\}]$^+$ with H_2O

Addition of water (9 μl, 0.5 mmol) to a solution enriched in **8** prepared as described above caused an immediate colour change from orange–yellow to dark red. $^{31}P\{^1H\}$-NMR analysis confirmed the disappearance of **8** and the quantitative formation of **6** within 1 h.

4.10. [(triphos)$Re(CO)_2$\{C(O)CH=C(H)Ph\}] (**9**)

An excess of NEt_3 (245 μl, 1.74 mmol) was added to a stirred solution of **6** (200.0 mg, 0.17 mmol) in dichloromethane (5 ml). The resulting dark brown solution was stirred at r.t. for 40 min and concentrated to about 1 ml. Slow addition of *n*-hexane (2.0 ml) yielded **9** as a brown microcrystalline solid. Yield: 61%. Anal. Calc. for $C_{52}H_{46}O_3P_3Re$: C, 62.58; H, 4.64. Found: C, 62.75; H, 4.75%. FAB$^+$–MS: m/z 867 [(triphos)-$Re(CO)_2]^+$.

4.11. Reaction of **9** with $HBF_4{\cdot}OMe_2$

A slight excess of $HBF_4{\cdot}OMe_2$ (4.9 μl, 0.04 mmol) was added to a solution of **9** (30 mg, 0.03 mmol) in dichloromethane-d_2 (0.8 ml). The quantitative transformation of **9** into **6** was confirmed by both ^1H- and ^{31}P-NMR spectroscopy.

4.12. [(triphos)$Re(CO)_2$\{C(OMe)CH=C(H)Ph\}](OTf) (**10**)

4.12.1. Method A

Neat MeOTf (34 μl, 0.30 mmol) was added to a stirred solution of **9** (200 mg, 0.20 mmol) in dichloromethane (5 ml). Work-up as above gave **10** as dark brown solid in ca. 72% yield.

4.12.2. Method B

The reaction between **1** (200 mg, 0.20 mmol) and 1-phenyl-2-propyn-1-ol (27.4 μl, 0.22 mmol) in

dichloromethane in the presence of methanol (6 ml, 1:5 v/v) gave **10** as brownish–orange microcrystals. Yield: 67%. Anal. Calc. for $C_{54}H_{49}F_3O_6P_3SRe$: C, 55.80; H, 4.25; S, 2.75. Found: C, 55.69; H, 4.32; S, 2.93%.

4.12.3. Method C

Addition of MeOH (100 μl) to a solution enriched in **8** prepared as described above in dichloromethane-d_2 caused an immediate colour change from orange–yellow to dark brown. $^{31}P\{^1H\}$-NMR analysis confirmed the disappearance of **8** and the quantitative formation of **10** within 1 h.

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