Addition of E−H Bonds (E = S, N) across the C_α=C_β Bond of the Allenylidene Ligand in [Re{C=C=CPh$_2$}(CO)$_2$(triphos)](OSO$_2$CF$_3$) (Triphos = MeC(CH$_2$PPh$_2$)$_3$)

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Reaction of the rhenium(I) allenylidene complex [Re{C=C=CPh$_2$}(CO)$_2$(triphos)]OTf (**1**; triphos = MeC(CH$_2$PPh$_2$)$_3$, OTf = $^-$OSO$_2$CF$_3$) with thiophenol, 2-thionaphthol, or allyl mercaptan gave selectively the α,β-unsaturated thiocarbene complexes [Re{C(SR)CH=CPh$_2$}(CO)$_2$(triphos)]OTf (R = Ph (**2**), α-naphthyl (**3**), CH$_2$CH=CH$_2$ (**4**)). A reversible reaction was observed for PhSH in DMSO at 80 °C. Compounds **2** and **3** have been found to react with sodium alkoxides, yielding the kinetic thioallenyl products [Re{C(SR)=C=CPh$_2$}(CO)$_2$(triphos)] (R = Ph (**6a**), α-naphthyl (**7a**)). These equilibrated in room-temperature solution with the thermodynamic thioalkynyl products [Re{C≡CC(SR)Ph$_2$}(CO)$_2$(triphos)] (R = Ph (**6b**), α-naphthyl (**7b**)) to give stationary states (**6a**/**6b**, 40/60; **7a**/**7b**, 20/80). Deprotonation of the thioallyl complex **4** gave the stable allenyl derivative [Re{C(SCH$_2$CH=CH$_2$)=C=CPh$_2$}(CO)$_2$(triphos)] (**8**). Ammonia, aniline, and propargylamine each reacted with **1** to give the azoniabutadienyl compounds [Re{C(=NHR)CH=CPh$_2$}(CO)$_2$(triphos)]OTf (R = H (**9**), Ph (**10**), CH$_2$C≡CH (**11**)) via N−H bond addition across the C_α=C_β double bond. NMR spectroscopy showed the γ-alkynylammonium complex [Re{C≡CCPh$_2$(NH$_3$)}(CO)$_2$(triphos)]OTf (**12**) to be a transient intermediate along the reaction of **1** with ammonia. Treatment of **10** or **11** with sodium methoxide resulted in the selective deprotonation of the nitrogen atom to give the azabutadienyl compounds [Re{C(=NR)CH=CPh$_2$}(CO)$_2$(triphos)] (R = Ph (**13**), CH$_2$C≡CH (**14**)). The molecular structure of the azoniabutadienyl complex **11** was determined by a single-crystal X-ray analysis. The geometry around the rhenium center conforms to a slightly distorted octahedron, with the polyphosphine sitting on a face of the coordination polyhedron. In keeping with the azoniabutadienyl structure, the Re−C_α bond length is 2.151(7) Å, and the C_α−N distance is 1.300(9) Å.

Introduction

Transition-metal allenylidenes are receiving increasing attention due to the wealth of their applications to organometallic chemistry,[1,2] homogeneous catalysis,[3] and the design of new materials.[1,2] Indeed, the M=C=C=C moiety, with its unsaturated carbon chain and its alternating array of electrophilic/nucleophilic carbon sites, makes allenylidene complexes unique organometallic reagents for use in both fundamental and applied chemistry, especially in processes whereby the formation of a C−C or C−heteroatom bond is sought.

The large majority of known allenylidene complexes contain ruthenium(II) and osmium(II), which are versatile metals but not so much as to represent all the possible reaction paths of the whole transition-metal series.[1] A systematic study of the chemistry of metal allenylidenes containing other elements than those of group 8 is therefore highly desirable for an in-depth understanding of the chemicophysical properties of the metal−allenylidene moiety and eventually the design of new allenylidene-based reactions.

In a series of recent papers from this laboratory, it has been shown that rhenium(I) can be a valid alternative to group 8 d^6 metal ions to study the intrinsic reactivity of the allenylidene ligand.[4,5] This goal was

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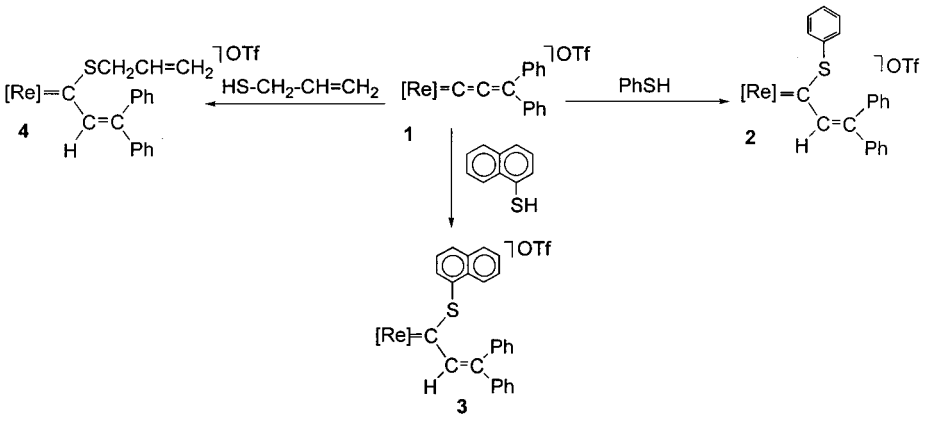
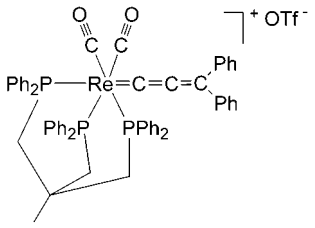
Scheme 1



achieved by using the square-pyramidal 16e⁻ $[Re(CO)_2(triphos)]^+$ auxiliary to convert various propargyl alcohol derivatives to allenylidene ligands (triphos = $MeC(CH_2PPh_2)_3$). Two terminal CO groups (nonsterically demanding, π-acceptors) and one facial triphosphine (sterically demanding, σ-donor) in the metal auxiliary apparently give rise to an optimum combination of electronic and steric effects for the stabilization of cationic rhenium(I) allenylidenes without depressing the C_3 ligand-centered reactivity, which in fact has been shown to be very rich toward nucleophiles, electrophiles, and dipolarophiles.[5] This paper reports some results obtained on studying the reactivity of the disubstituted allenylidene $[Re\{C{=}C{=}CPh_2\}(CO)_2(triphos)]OTf$ (**1**; OTf = $^-OSO_2CF_3$) toward thiols and amines. Many reactions



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were unexplored and have therefore allowed the discovery of unprecedented synthetic paths to a variety of organometallics, which includes α,β-unsaturated thiocarbene, thioallenyl, thioalkynyl, azoniabutadienyl, ammonioalkynyl and azabutadienyl derivatives.

Results and Discussion

Reactions of 1 with Thiols and Thiolates. Complex **1** reacts with either aliphatic or aromatic thiols to afford α,β-unsaturated thiocarbenes via regioselective addition of the S−H bond across the allenylidene C_α−C_β bond. The reactions with thiophenol, thionaphthol, and allyl mercaptan were conveniently carried out in oxygen-free dichloromethane to give $[Re\{{=}C(SR)CH{=}CPh_2\}(CO)_2(triphos)]OTf$ in excellent yields (R = C_6H_5 (**2**), α-naphthyl (**3**), $CH_2CH{=}CH_2$ (**4**)) (Scheme 1).

The presence of an α,β-unsaturated thiocarbene ligand in **2**−**4** was unambiguously demonstrated by routine IR and NMR ($^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H) spectra. Further support was received by elemental analysis, while DEPT-135 and 2D-NMR experiments (^1H,^1H-COSY, ^1H,^1H-NOESY, and $^1H-^{13}C$-HMQC) were useful to determine the time-averaged preferred conformations in solution. The only IR features deserving comment are two strong ν(CO) bands in the range 1977−1911 cm^{-1}, typical for α,β-unsaturated rhenium carbenes stabilized by $[Re(CO)_2(triphos)]^+$, and a medium-intensity band at ca. 1550 cm^{-1} due to the vinyl C=C stretching vibration.[4−7]

Relevant spectroscopic parameters for all new compounds are given in Table 1.

The room-temperature $^{31}P\{^1H\}$ NMR spectra of **2**−**4** consist of three multiplets, indicating the magnetic inequivalence of the two phosphorus atoms trans to the carbonyl groups. AMX spin systems are rarely observed for octahedral $[Re(CO)_2(triphos)L]^+$ fragments (L = unidentate ligand):[8] their formation reflects either the presence of a dissymmetric and bulky L ligand or a ligand linked to the metal via a multiple bond. In either case, the ligand cannot freely rotate around the Re−L axis. The present α,β-unsaturated thiocarbene ligands conform to these characteristics, as they have no symmetry element and are sufficiently bulky to sterically interact with the phenyl groups on the triphos ligand; the most important contribution to hindered rotation should be the presence of a Re−C bond with double-bond character, however.

In an attempt to determine the energy barrier to rotation, the thiophenyl carbene **2** was studied by variable-temperature NMR spectroscopy in DMSO-d_6. Increasing the temperature of the probe head to 70 °C did not appreciably affect the signal at −20.38 ppm (trans to the thiocarbene), which maintained the pseudo-

(6) (a) Bianchini, C.; Mantovani, N.; Marvelli, L.; Peruzzini, M.; Romerosa, A.; Rossi, R. *J. Organomet. Chem.* **2001**, *617*−*618*, 233. (b) Bianchini, C.; Marchi, A.; Marvelli, L.; Peruzzini, M.; Romerosa, A.; Rossi, R. *Organometallics* **1996**, *15*, 3804. (c) Bianchini, C.; Marchi, A.; Marvelli, L.; Masi, D.; Peruzzini, M.; Rossi, R. *Eur. J. Inorg. Chem.* **1998**, 211. (d) Peruzzini, M.; Akbayeva, D.; Bianchini, C.; de los Rios, I.; Ienco, A.; Mantovani, N.; Martelli, L.; Rossi, R. *Inorg. Chim. Acta*, in press.

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(8) In the ample family of $[(triphos)Re(CO)_2(L)]^{0,+}$ complexes, $^{31}P\{^1H\}$ NMR spectra featuring AMX patterns have previously been observed only for the agostic complex $[(triphos)Re(CO)_2(L)]^+$ (L = agostic C(phenyl)−H···Re interaction) at low temperature: Bianchini, C.; Marchi, A.; Marvelli, L.; Peruzzini, M.; Romerosa, A.; Rossi, R.; Vacca, A. *Organometallics* **1995**, *14*, 3203.

Table 1. ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR Spectral Data and IR Absorptions for the Complexes 2−14 (at Room Temperature, in CD_2Cl_2)

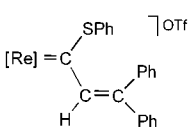
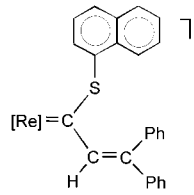
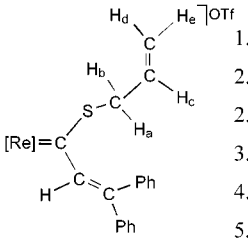
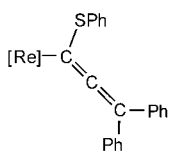
Complex	^{1}H δ (ppm), *J* (Hz)	$^{13}C\{^{1}H\}$ δ (ppm), *J* (Hz)	$^{31}P\{^{1}H\}$ δ (ppm), *J* (Hz) / IR (KBr, cm^{-1})
 **2** [b, e]	1.71 (q, J_{HP} 2.6, 3H, C***H***$_{3\ triphos}$) 2.73 (m, 6H, C***H***$_{2\ triphos}$) 6.71 (d, J_{HP} 6.0, 1H, C***H***=CPh$_2$)	292.2 (dt, $J_{CPtrans}$ 31.1, J_{CPcis} 8.2, Re=***C***) 196.9 (dt, $J_{CPtrans}$ 47.6, J_{CPcis} 7.6, ***C***O) 194.8 (dt, $J_{CPtrans}$ 47.6, J_{CPcis} 6.7, ***C***O) 142-146 (all s, CH=***C***Ph$_2$ + ***C*** $_{ipso}$) 140.0 (d, J_{CP} 4.3, ***C***H=CPh$_2$) 39.8 (q, J_{CP} 10.1, ***C***H$_{3\ triphos}$) 39.2 (q, J_{CP} 3.3, CH$_3$-***C*** $_{triphos}$) 37.1 (m, ***C***H$_2$-P$_{ax\ triphos}$) 34.5 (m, ***C***H$_2$-P$_{eq\ triphos}$)	δ_A −10.69 J_{AM} 25.4 δ_M −19.81 J_{AX} 21.0 δ_X −21.49 J_{MX} 20.3 ν(CO) 1973 (vs), 1915 (vs) ν(C=C) 1559 (w) ν(OTf) 1271 (s)
 **3** [b, e]	1.70 (q, J_{HP} 2.3, 3H, C***H***$_{3\ triphos}$) 2.30-3.10 (br m, 6H , C***H***$_{2\ triphos}$) 6.82 (d, J_{HP} 5.1, 1H, C***H***=CPh$_2$)	291.2 (dt, $J_{CPtrans}$ 31.1, J_{CPcis} 8.3, Re=***C***) 191.0 (br m, ***C***O) 147.1 (d, $J_{CPtrans}$ 4.4, ***C***H=CPh$_2$) 140 - 146 (all s, CH=***C***Ph$_2$ + ***C*** $_{ipso}$) 39.9 (q, J_{CP} 10.2, ***C***H$_{3\ triphos}$) 39.3 (q, J_{CP} 4.4, CH$_3$-***C*** $_{triphos}$) 37.1 (dm, J_{CPax} 22.2, ***C***H$_2$-P$_{ax}$) 34.7 (br m, ***C***H$_2$-P$_{eq\ triphos}$)	δ_A −10.20 J_{AM} 24.0 δ_M −19.45 J_{AX} 25.2 δ_X −21.09 J_{MX} 22.0 ν(CO) 1977 (vs), 1911 (vs) ν(C=C) 1530 (w) ν(OTf) 1271 (s)
 **4** [d, e]	1.70 (q, J_{HP} 2.7, 3H, C***H***$_{3\ triphos}$) 2.40-2.85 (brm, 6H, C***H***$_{2\ triphos}$) 2.61 [i] (dd, J_{HaHb} 13.2, J_{HaHc} 7.2, 1H, ***H***$_a$) 3.43 [i] (dd, J_{HbHa} 13.2, J_{HbHc} 7.2, 1H, ***H***$_b$) 4.94 [i] (dq, J_{HdHc} 16.5, J_{HdHabe} 1.5, 1H,***H***$_d$) 5.13 [i] (dd, J_{HeHc} 10.5, J_{HeHd} 1.5, 1H, ***H***$_e$) 5.25 [i] (ddt, J_{HcHd} 16.5, J_{HcHe} 7.2, J_{HcHab}, 1.5, 1H, ***H***$_c$) 6.8 [e] (br s, 1H, C***H***=CPh$_2$)	291.2 (dt, $J_{CPtrans}$ 30.0, J_{CPcis} 7.5, Re=***C***) 194.7 (dm, $J_{CPtrans}$ 42.0, ***C***O) 146.2 [g] (s, ***C***H=CPh$_2$) 141 - 146 (all s, CH=***C***Ph$_2$ + ***C*** $_{ipso}$) 129.7 [h] (s, ***C***H$_c$) 121.1 [h] (s, =***C***H$_d$H$_e$) 50.2 [h] (s, ***C***H$_a$H$_b$) 39.6 (q, , J_{CP} 10.3, ***C***H$_{3\ triphos}$) 38.7 (q, J_{CP} 3.9, CH$_3$ -***C*** $_{triphos}$) 36.9 (d, J_{CP} 22.6, ***C***H$_2$-P$_{ax\ triphos}$) 34.7 (d, J_{CP} 22.6, ***C***H$_2$-P$_{eq\ triphos}$) 33.2 (d, J_{CP} 22.6, ***C***H$_2$-P$_{eq\ triphos}$)	δ_A −19.53 J_{AM} 20.8 δ_M −18.68 J_{AX} 24.1 δ_X −9.77 J_{MX} 20.8 ν(CO) 1968 (vs), 1914 (vs) ν(OTf) 1269 (s) ν(C=C) not observed
 **6a** [c, f, l]	1.43 (br s, 3H, C***H***$_{3\ triphos}$) 2.20-2.75 (br m, 6H, C***H***$_{2\ triphos}$)	200.9 (s, ReC(SPh)=***C***=CPh$_2$) 198.4 (m, ***C***O) 104.3 (s, ReC(SPh)=C=***C***Ph$_2$) 90.0 (d, $J_{CPtrans}$ 25.0, Re***C***(SPh)=C=CPh$_2$) 40.0 (q, J_{CP} 9.8, ***C***H$_{3\ triphos}$) 39.6 (q, J_{CP} 3.7, CH$_3$-***C*** $_{triphos}$) 35.6 (d, J_{CPax} 22.0, ***C***H$_2$-P$_{ax\ triphos}$) 33.6 (td, J_{CPeq} 16.0,J_{CPax} 5.0, ***C***H$_2$-P$_{eq\ triphos}$)	δ_A −5.31 J_{AM} 17.8 δ_M −19.01 ν(CO) + ν(C=C=C) 1948 (vs), 1888 (vs)

Table 1 (Continued)

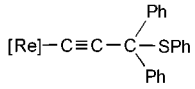
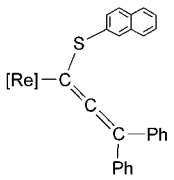
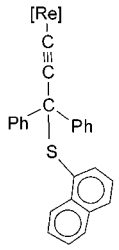
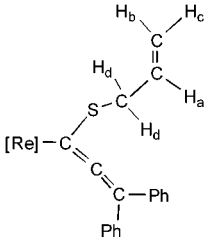
Complex	^{1}H δ (ppm), *J* (Hz)	^{13}C{^{1}H} δ (ppm), *J* (Hz)	^{31}P{^{1}H} δ (ppm), *J* (Hz) IR (KBr, cm^{-1})
 **6b** *c, f, l*	1.48 (br s, 3H, C***H***$_3$ triphos) 2.20-2.75 (br m, 6H, C***H***$_2$ triphos)	198.4 (m, ***C***O) 113.7 (d, $J_{CPtrans}$ 13.5, Re-C≡***C***) 100.2 (dt, $J_{CPtrans}$ 34.3, J_{CPcis} 12.5, Re-***C***≡C) 62.5 (s, ***C***Ph$_2$SPh) 40.0 (q, J_{CP} 9.8, ***C***H$_3$ triphos) 39.6 (q, J_{CP} 3.7, CH$_3$-***C*** triphos) 36.7 (d, J_{CPax} 20.8, ***C***H$_2$-P$_{ax}$ triphos) 34.4 (td, J_{CPeq} 15.5, J_{CPax} 7.0, ***C***H$_2$-P$_{eq}$ triphos	δ$_A$ –4.24 J_{AM} 17.1 δ$_M$ –20.38 ν(C≡C) 2083 (m) ν(CO) 1948 (vs), 1888 (vs)
 **7b** *c, f, l*	1.46 (br s, 3H, C***H***$_3$ triphos) 2.15-2.65 (br m, 6H, C***H***$_2$ triphos)	199.6 (s, ReC(SNp)=***C***=CPh$_2$) 197.5 (m, ***C***O) 106.3 (s, ReC(SNp)=C=***C***Ph$_2$) 92.1 (d, $J_{CPtrans}$ 22.4, Re***C***(SNp)=C=CPh$_2$) 39.7 (q, J_{CP} 10.1, ***C***H$_3$ triphos) 39.5 (q, J_{CP} 3.5, CH$_3$-***C*** triphos) 37.2 (d, J_{CPax} 21.1, ***C***H$_2$-P$_{ax}$ triphos) 35.0 (td, J_{CPeq} 15.7,J_{CPax} 5.8, ***C***H$_2$-P$_{eq}$ triphos)	δ$_A$ –4.75 J_{AM} 17.01 δ$_M$ –20.89
 **7b** *c, f, l*	1.41 (q, J_{HP} 2.1, 3H, C***H***$_3$ triphos) 2.38 (d, J_{HP} 7.5, 2H, C***H***$_2$-P$_{ax}$ triphos) 2.20-2.75 (br m, 4H, C***H***$_2$-P$_{eq}$ triphos)	197.8 (m, ***C***O) 111.7 (d, $J_{CPtrans}$ 14.6, Re-C≡***C***) 100.7 (dt, $J_{CPtrans}$ 33.0, J_{CPcis} 14.7, Re-***C***≡C) 82.6 (s, ***C***Ph$_2$SNp) 40.7 (q, J_{CP} 10.3, ***C***H$_3$ triphos) 39.7 (q J_{CP} 4.6, CH$_3$-***C*** triphos) 35.4 (d, J_{CPax} 22.9, ***C***H$_2$-P$_{ax}$ triphos) 33.8 (td, J_{CPeq} 14.0, J_{CPax} 5.0, ***C***H$_2$-P$_{eq}$ triphos)	δ$_A$ –5.35 J_{AM} 17.1 δ$_M$ –18.24 ν(C≡C) 2076 (m) ν(CO) 1937 (vs), 1872 (vs)
 **8** *c, f*	1.45 (q, J_{HP} 2.7, 3H, C***H***$_3$ triphos) 2.20-2.75 (br m, 6H, C***H***$_2$ triphos) 3.43^i (psdt, J_{HdHa} 7.2, J_{HdHc} 1.0, J_{HdHb} 1.0, 2H, ***H***$_d$) 4.92^i (ddt, J_{HcHa} 9.9, J_{HcHb} 2.1, J_{HcHd} 1.0, 1H, ***H***$_c$) 5.04^i (ddt, J_{HbHa} 17.1, J_{HbHc} 2.1, J_{HbHd} 1.0, 1H, ***H***$_b$) 5.92^i (ddt, J_{HaHb} 17.1, J_{HaHc} 9.9, J_{HaHd} 7.2, 1H, ***H***$_a$)	199.0 (d, $J_{CPtrans}$ 3.0, Re-C(SR)=***C***=CPh$_2$) 198.6 (br m, ***C***O) 124.9^g (s, ***C***H$_a$=CH$_b$H$_c$) 115.5^g (s, CH$_a$=***C***H$_b$H$_c$) 102.0 (s, Re-C(SR)=C=***C***Ph$_2$) 89.8 (dt, $J_{CPtrans}$ 26.0, J_{CPcis} 10.0, Re-***C***(SR)=C=CPh$_2$) 41.2^g (s, ***C***H$_d$H$_d$) 40.0 (q, J_{CP} 10.3, ***C***H$_3$ triphos) 39.0 (q, J_{CP} 4.7, CH$_3$-***C*** triphos) 36.2 (d, J_{CPax} 21.6, ***C***H$_2$-P$_{ax}$ triphos) 33.1 (td, J_{CPeq} 14.7, J_{CPax} 7.5, ***C***H$_2$.P$_{eq}$ triphos)	δ$_A$ –5.29 J_{AM} 16.8 δ$_M$ –19.59 ν(CO) + ν(C=C=C) 1942 (vs), 1893 (vs)

Table 1 (Continued)

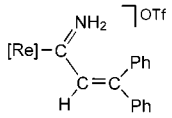
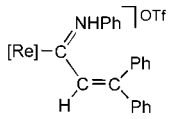
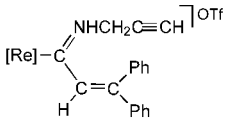
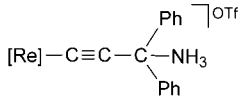
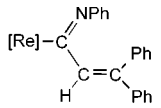
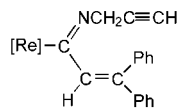
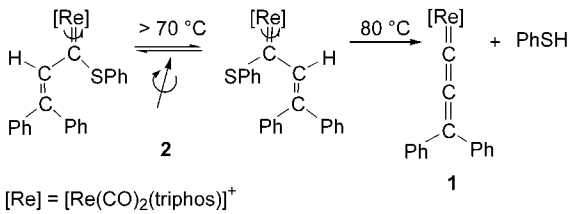
Complex	^{1}H δ (ppm), *J* (Hz)	^{13}C{^{1}H} δ (ppm), *J* (Hz)	^{31}P{^{1}H} δ (ppm), *J* (Hz) IR (KBr, cm^{-1})
 **9** [c,f]	1.58 (q, J_{HP} 2.4, 3H, C***H***$_{3\ triphos}$) 2.51 (d, J_{HP} 8.1, 2H, C***H***$_2$-P$_{ax\ triphos}$) 2.30-2.70 (br m, 4H, C***H***$_2$-P$_{eq\ triphos}$) 14.0 (br s, 2H, N***H***$_2$)	249.3 (dt, $J_{CPtrans}$ 29.6, J_{CPcis} 12.0, Re-***C***) 197.1 (dm, $J_{CPtrans}$ 42.6, ***C***O) 131.2 [g] (d, $J_{CPtrans}$ 10.0, ***C***H=CPh$_2$) 81.4 [g] (d, $J_{CPtrans}$ 3.0, CH=***C***Ph$_2$) 39.6 (q, J_{CP} 9.4, ***C***H$_{3\ triphos}$) 39.0 (q, J_{CP} 3.6, CH$_3$***C*** $_{triphos}$) 34.7 (td, J_{CPeq} 14.5, J_{CPax} 4.7, ***C***H$_2$P$_{eq\ triphos}$) 32.1 (d, J_{CPax} 22.6, ***C***H$_2$P$_{ax\ triphos}$, J_{CPeq} 3.7)	δ$_A$ –14.11 J_{AM} 21.0 δ$_M$ –12.53 ν(NH) 3324 (w), 3178 (m) ν(CO) 1959 (vs), 1899 (vs) ν(C=C) + ν(C=N) 1598 (w), 1489 (m)
 **10** [b,e]	1.69 (br s, 3H, C***H***$_{3\ triphos}$) 2.72 (m, 6H, C***H***$_{2\ triphos}$) 6.15 (d, $J_{HPtrans}$ 6.9, 1H, C***H***=CPh$_2$ 8.62 (br s, 1H, N***H***)	237.2 (dt, $J_{CPtrans}$ 31.7, J_{CPcis} 8.8, Re***C***) 199.7 (dt, $J_{CPtrans}$ 43.3, J_{CPcis} 7.3, ***C***O) OK 198.1 (dt, $J_{CPtrans}$ 46.4, J_{CPcis} 7.9, ***C***O) OK 138.0 [g] (br s, ***C***H=CPh$_2$) 138.5-141.9 [d] (all s, CH=***C***Ph$_2$ + ***C*** $_{ipso}$) 40.2 (q, J_{CP} 10.0, ***C***H$_{3\ triphos}$) 39.5 (q, J_{CP} 3.9, CH$_3$-***C*** $_{triphos}$) 37.4 (m, ***C***H$_2$-P$_{ax\ triphos}$) 35.0 (m, ***C***H$_2$-P$_{eq\ triphos}$) 31.1(m, ***C***H$_2$-P$_{eq\ triphos}$)	δ$_A$ –9.22 (ps t) J_{AM} 25.7 δ$_M$ –11.52 (ps t) J_{AX} 20.0 δ$_X$ –18.06 (ps t) J_{MX} 21.4 ν(NH) 3328 (m) ν(CO) 1958 (vs), 1896 (vs) ν(C=C) + ν(C=N) 1603 (w), 1491 (m) ν(OTf) 1265 (s)
 **11** [b,e]	1.68 (q, J_{HP} 2.6, 3H, C***H***$_{3\ triphos}$) 2.25 (t, J_{HH} 2.7, 1H, C≡C***H***) 2.65 (m, 6H, C***H***$_{2\ triphos}$) 3.21 (td, J_{HP} 5.7, J_{HH} 2.7, 1H, C***H***$_2$) 6.60 (s, 1H, C***H***=CPh$_2$) 9.71 (br s, 1H, N***H***)	236.5 (dt, $J_{CPtrans}$ 31.1, J_{CPcis} 8.1, Re-***C***) 199.1 (dt, $J_{CPtrans}$ 47.6, J_{CPcis} 8.5, ***C***O) 197.8 (dt, $J_{CPtrans}$ 45.1, J_{CPcis} 7.9, ***C***O) 138.0-142.0 (all s, CH=***C***Ph$_2$ + ***C*** $_{ipso}$) 137.2 [g] (s, ***C***H=CPh$_2$) 76.5 (s, ***C***≡CH) 76.0 (s, C≡***C***H) 40.9 [g] (d, J_{CP} 2.4, ***C***H$_2$) 40.1 (q, J_{CP} 10.4, ***C***H$_{3\ triphos}$) 39.5 (q, J_{CP} 3.1, CH$_3$-***C*** $_{triphos}$) 37.3 (m, ***C***H$_2$-P$_{ax\ triphos}$) 35.3 (m, ***C***H$_2$-P$_{eq\ triphos}$) 31.4 (m, ***C***H$_2$-P$_{eq\ triphos}$)	δ$_A$ –7.43 (ps t) J_{AM} 25.4 δ$_M$ –10.01 (ps t) J_{AX} 21.3 δ$_X$ –15.45 (ps t) J_{MX} 22.6 ν(NH) 3302 (m) ν(CO) 1954 (vs), 1892 (vs) ν(C≡C) 2072 (m) ν(C=C) + ν(C=N) 1609 (w), 1580 (m) ν(OTf) 1265(s)

Table 1 (Continued)

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})
 **12**[b, f, m]	1.28 (br s, 3H, C***H***$_{3\ triphos}$) 2.10-2.50 (br m, 6H, C***H***$_{2\ triphos}$) 2.61 (br s, 3H, N***H***$_3$)	198.0 (m, ***C***O) 115.6 (d, $J_{CPtrans}$ 14.1, Re-C≡***C***) 101.2 (dt, $J_{CPtrans}$ 31.1, J_{CPcis} 14.0, Re-***C***≡C) 69.9 (s, ***C***Ph$_2$NH$_3$) 39.6 (m, ***C***H$_{3\ triphos}$ + CH$_3$-***C***$_{triphos}$) 36.2 (d, J_{CPax} 19.9, ***C***H$_2$-P$_{ax\ triphos}$) 34.4 (td, J_{CPeq} 12.9, J_{CPax} 6.7, ***C***H$_2$-P$_{eq\ triphos}$	δ$_A$ −6.34 J_{AM} 19.4 δ$_M$ −18.63 ν(C≡C) 2080 (m) ν(CO) 1940 (vs),
 **13**[a, b, e]	1.54 (br s, 3H, C***H***$_{3\ triphos}$) 2.00-3.10 (br m, 6H, C***H***$_{2\ triphos}$) 6.23 (d, J_{HP} 7.2, 1H, C***H***=CPh$_2$)	206.2 (dt, $J_{CPtrans}$ 31.0, J_{CPcis} 7.5, Re-***C***) 201.5 (m, ***C***O) 119.9[g] (s, ***C***H=CPh$_2$) 68.7[g] (s, CH=***C***Ph$_2$) 39.7 (q, J_{CP} 9.3, ***C***H$_{3\ triphos}$) 39.3 (q, J_{CP} 3.7, CH$_3$-***C***$_{triphos}$) 36.7 (td, J_{CPeq} 18.0, J_{CPax} 7.0, ***C***H$_2$-P$_{eq\ triphos}$) 33.1 (m, ***C***H$_2$-P$_{ax\ triphos}$)	δ$_A$ −7.54 (ps t) J_{AM} 16.5 δ$_M$ −8.78 (dd) J_{AX} 16.5 δ$_X$ −29.47 (dd) J_{MX} 23.3 ν(CO) 1944 (vs), 1885 (vs) ν(C=C) + ν(C=N) 1589 (w), 1520 (m)
 **14**[a, b, e]	1.63 (q, J_{HP} 2.7, 3H, C***H***$_{3\ triphos}$) 2.29 (t, J_{HH} 2.4, 1H, CH$_2$C≡C***H***) 2.82 (d, J_{HP} 8.4, 2H, C***H***$_2$-P$_{ax\ triphos}$) 2.40-2.95 (br m, 6H, C***H***$_2$-P$_{eq\ triphos}$ + C***H***$_2$C≡CH) 6.22 (s, 1H, C***H***=CPh$_2$)	202.5 (m, ***C***O) 199.9 (dm, $J_{CPtrans}$ 34.0, J_{CPcis} 7.9, Re-***C***) 144.5[g] (s, ***C***H=CPh$_2$) 87.3[g] (s, NCH$_2$***C***≡CH) 69.1[g] (s, NCH$_2$C≡***C***H) 40.7 (q, J_{CP} 9.5, ***C***H$_{3\ triphos}$) 40.5 (q, J_{CP} 4.0, CH$_3$-***C***$_{triphos}$) 38.7[g] (m, N***C***H$_2$C≡CH) 37.6[g] (m, ***C***H$_2$-P$_{eq\ triphos}$) 33.6[g] (m, ***C***H$_2$-P$_{ax\ triphos}$)	δ$_A$ -6.47 (dd) J_{MX} 15.0 δ$_M$ -9.01 (dd) J_{AX} 20.3 δ$_X$ -30.12 (dd) J_{AM} 26.3 ν(CO) 1938 (vs), 1878 (vs) ν(C=C) + ν(C=N) 1623 (w), 1467 (m)

[a] At 253 K. [b] Bruker ACP200 spectrometer. [c] Varian VXR300 spectrometer. [d] Bruker DRX 500 spectrometer. [e] ^{31}P{^{1}H} NMR spectra exhibit an AMX splitting pattern. [f] ^{31}P{^{1}H} NMR spectra exhibit an AM$_2$ splitting pattern. [g] Assigned by DEPT-135 experiment. [h] Assigned by ^{13}C−^{1}H HETCOR. [i] Assigned by ^{1}H−^{1}H COSY. [l] These spectra were recorded on the equilibrium mixture of products. [m] The ^{13}C{^{1}H} NMR spectrum wasecorded at 233 K. Key: s, singlet; d, doublet; t, triplet, q, quartet; m, multiplet; br, broad.

Scheme 2

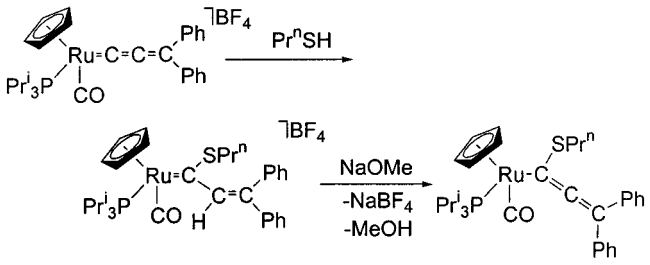


triplet multiplicity; in contrast, the other two resonances (trans to CO) significantly broadened. On further increase of the temperature to 80 °C, these two signals collapsed into the baseline, thus indicating the approach of a freely rotating thiocarbene ligand (Scheme 2).

Unfortunately, the fast exchange regime of the spectrum could not be attained, due to the concomitant decomposition of the complex to regenerate the parent allenylidene **1** and free thiophenol. This transformation was quantitative in a few minutes at 90 °C. However, when the NMR tube was cooled to 25 °C, the AMX pattern of **2** was completely restored. To the best of our knowledge, this is the first reported case of reversible S−H bond addition to a metal−allenylidene system.

The ^{13}C{^{1}H} NMR spectra of the thiocarbenes **2**−**4** showed the α-carbons of the carbene ligands to have a doublet of triplets at ca. 290 ppm with coupling constants (J(CP$_{trans}$) ≈ 31, J(CP$_{cis}$) ≈ 8 Hz) typical for rhenium(I) carbene complexes stabilized by triphos.[4−6] In agreement with the magnetic inequivalence of the two CO groups trans to phosphorus, the spectrum of the thiophenyl derivative **2** contained two distinct doublets of triplets (δ_{CO} 196.9 and 194.8) for the two carbonyl carbons. The olefinic carbons of the α,β-unsaturated carbene substituents gave rise to singlets between 147

Scheme 3

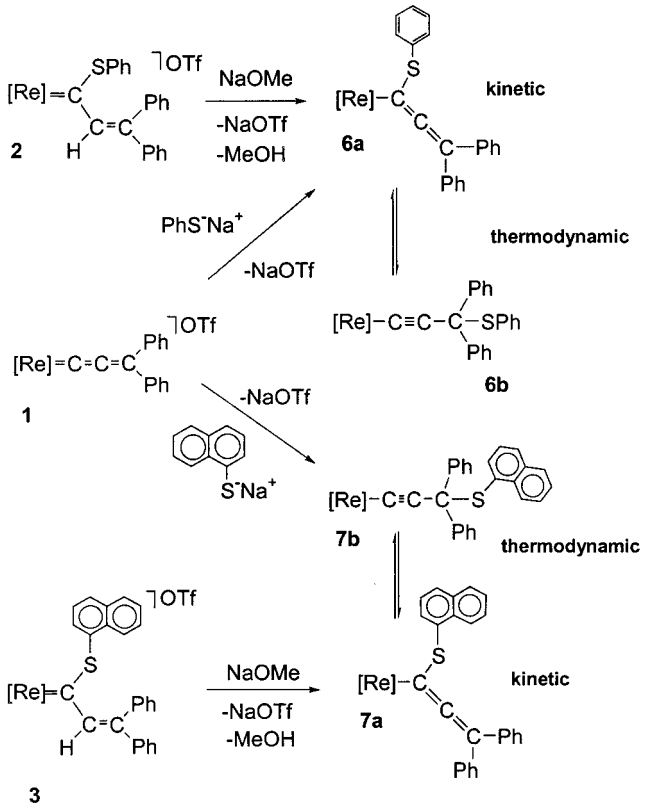


and 140 ppm, with the exception of **3**, in which the *C*H═ carbon atom appeared as a doublet (δ 147.1) with a small coupling ($J(CP_{trans})$ = 4.4 Hz) to the trans phosphorus atom. In the thioallyl carbene **4**, an upfield vinylic pair of singlets ($\delta_{CH=}$ 129.7, $\delta_{CH_2=}$ 121.1) and a DEPT-135 inverted CH_2 signal (δ 50.2) featured the allylic substituent on the sulfur atom. 2D-NMR spectra (^{1}H,^{1}H-COSY, ^{1}H,^{1}H-NOESY, and ^{1}H,^{13}C-HMQC) allowed the assignment of the five protons of the SCH_2-CH═CH_2 group, in which the CH_2 protons appeared as a diastereotopic pair at 4.94 and 5.13 ppm. The ^{1}H NMR spectra of **2**−**4** showed singlets for the CH proton of the C*H*═CPh_2 unit at 6.71 (**2**) and 6.82 ppm (**3**), whereas the corresponding signal of **4** was not observed due to overlapping with the aromatic proton resonances. However, the unambiguous identification of this proton at ca. 6.8 ppm was obtained from a ^{1}H,^{13}C-HMQC NMR spectrum. ^{1}H,^{1}H-NOESY experiments did not show any cross-peak involving the C_β vinyl proton and any hydrogen from the phenyl substituents at phosphorus. This evidence, supported by the X-ray structure of an azoniabutadienyl complex (see below, compound **11**), suggests that the preferred conformation of the thiocarbene ligand in **2**−**4** is such as to accommodate the CH═CPh_2 group between the two Re−CO vectors away from the phosphorus atoms.

The addition of thiols to cumulene metal complexes is a known reaction for vinylidene compounds and gives either thiocarbenes[9] or S-bonded thioaldehydes.[10] In contrast, the plain reaction of thiols with allenylidene complexes has been much less studied: to the best of our knowledge, this reaction is essentially limited to one example reported by Esteruelas and co-workers, who reacted the cationic ruthenium(II) complex [Ru(CO)(PPr^i_3){C═C═CPh_2}(η^5-C_5H_5)]BF_4 (**5**) with Pr^nSH, giving the α,*β*-unsaturated thiocarbene [Ru(CO)(PPr^i_3){C(SPr^n)CH═CPh_2}(η^5-C_5H_5)]BF_4 (Scheme 3).[11a] The same authors have also reported a cyclization reaction with pyridine-2-thiol.[11b]

Like Esteruelas' ruthenium(II) derivative, treatment of **2** and **3** with either sodium methoxide or potassium *tert*-butoxide in THF at room temperature resulted in the selective deprotonation of the CH═CPh_2 group of the thioalkoxycarbene to give the kinetic 1-*S*-thioallenyl products [Re{C(SR)═C═CPh_2}$(CO)_2$(triphos)] (R = C_6H_5 (**6a**), α-naphthyl (**7a**)). With time, the thioallenyl compounds partially transformed into the alkynyl derivatives [Re{C≡CC(SR)Ph_2}$(CO)_2$(triphos)] (R = C_6H_5 (**6b**), α-naphthyl (**7b**)) to give stationary states (Scheme 4).

Scheme 4



A detailed in situ NMR study has been carried out for the reaction between the thiophenyl precursor **2** and $KOBu^t$. The addition of a saturated THF solution of the alkoxide to an acetone-d_6 solution of **2** at room temperature gave selectively the expected allenyl complex **6a**. During the time necessary to record the first ^{31}P{^{1}H} NMR spectrum only a trace amount (<1%) of the alkynyl isomer **6b** was observed, in fact. On standing at room temperature, the isomerization of **6a** to **6b** slowly took place and, after 2 h at room temperature, a 61/39 ratio between the two compounds was calculated by NMR integration. This product composition did not vary over 1 week, which indicates the attainment of a stationary state. A stationary state was also observed for the thioallenyl and alkynyl products **7a** and **7b**, obtained by reaction of **3** with NaOMe. In this case, however, a 20/80 product ratio was observed, which reflects the larger size of the naphthyl substituent. In the absence of in-depth theoretical studies, it would be hazardous to propose a mechanism for the present allenyl−alkynyl isomerization. We can only rule out an intermolecular process, as both the isomerization rate and the stationary state composition were independent of the concentration of the thioallenyl species.

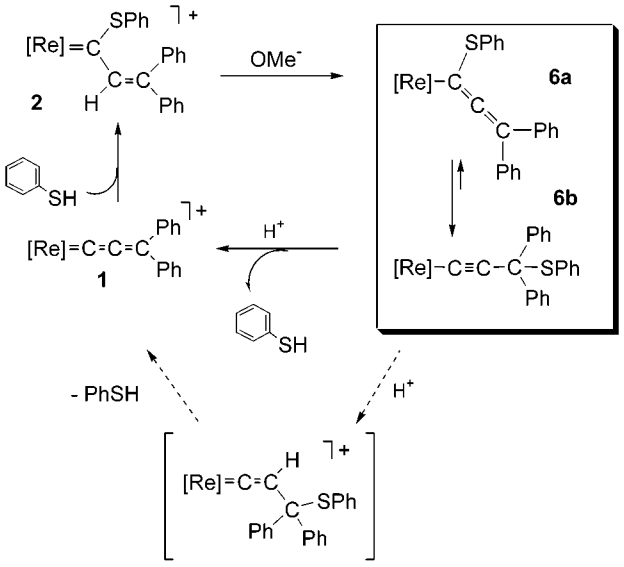
Unambiguous structural identification of the allenyl/alkynyl isomers in the thermodynamic mixture was straightforwardly obtained by means of IR and ^{13}C NMR spectroscopy. As an example, the η^1-thioallenyl ligand in **6a** showed signals at 200.9 ppm for C_β, 104.3 ppm for C_γ, and 90.0 ppm for C_α, while the σ-alkynyl isomer **6b** was featured by signals at 113.7 ppm for C_β, 100.2 ppm for C_α, and 62.5 ppm for C_γ. Furthermore, the IR

(9) Boland-Lussier, B. E.; Hughes, R. P. *Organometallics* **1982**, *1*, 635.

(10) Bianchini, C.; Glendenning, L.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *J. Chem. Soc., Chem. Commun.* **1994**, 2219.

(11) (a) Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423. (b) Esteruelas, M. A.; López, A. M. In *Recent Advances in Hydride Chemistry;* Peruzzini, M., Poli, R., Eds.; Elsevier: Amsterdam, 2001; Chapter 7, pp 213−215.

Scheme 5



spectrum of **6b** contained a band at 2083 cm^{-1} for the C=C moiety, while a band at 1888 cm^{-1} was found for the C=C=C array in **6a**.

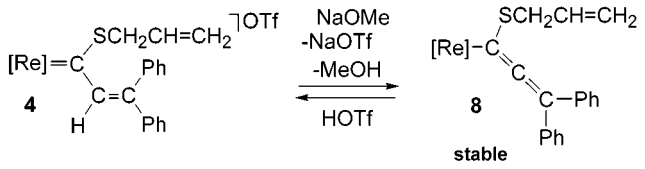
In an attempt to confirm the allenyl−alkynyl isomerization, the allenylidene complex **1** in THF was reacted with solid sodium thiophenate at room temperature in a Schlenk tube (Scheme 4). After workup of the resulting brown solution, a brownish solid was isolated that ^{31}P NMR spectroscopy showed to be a 60:40 mixture of **6a** and **6b**. An identical product ratio was observed also when the reaction was performed in a 5 mm NMR tube in acetone-d_6 at room temperature for 2 h. However, when the addition of PhSNa was made at −10 °C, only the thioallenyl complex **6a** was initially formed, which converted to the alkynyl isomer **6b** very slowly to give an 82:18 product ratio after 2 h.

Interestingly, the addition of anhydrous HBF_4·OMe_2 to the room-temperature thermodynamic mixture of **6a** and **6b**, obtained by treatment of **2** with NaOMe, gave exclusively the allenylidene precursor **1** and free PhSH (Scheme 5). This result shows that the deprotonation of the C_β carbon of **2** by the strong base somehow follows the microscopic reversibility criterion: the added proton was delivered to the position from which it was extracted (C_β) to give an unstable 3-mercapto vinylidene. Ultimately, this intermediate loses PhSH, converting to **1**. The latter reaction path is well-established for hydroxy vinylidenes and resembles the common mechanism through which allenylidene complexes are formed from propargyl alcohols.[12] Consistent with the mechanism proposed in Scheme 5 (broken arrows), both **1** and free thiophenol were detected by ^1H NMR spectroscopy (δ 3.34 for the SH proton) at the early stages of the protonation reaction of **2**. On standing at room temperature, the thiophenol resonance disappeared; formed in its place was the signal of the C_β−H hydrogen of the α,β-unsaturated thiocarbene **2**. The same reaction sequence was observed for the naphthyl derivative **3**.

The formation of thioallenyl complexes via regioselective addition of an anionic nucleophile to the C_α carbon atom is an unprecedented reaction for allenylidene metal complexes, which commonly react with such nucleophiles to give γ-alkynyl derivatives. For example, **1** is selectively converted to the stable γ-alkynyl complexes [Re{C≡C−CPh_2R}$(CO)_2$(triphos)] (R = OH, OMe, Me, H) by reaction with OH^-, OMe^-, Me^-, or H^-.[5]

(12) Selegue, J. P. *Organometallics* **1982**, *1*, 217.

Scheme 6



Unlike **2** and **3**, the allylmercapto carbene **4** was deprotonated by sodium methoxide, yielding only the allenyl complex [Re{C(SC_3H_5)=C=CPh_2}$(CO)_2$(triphos)] (**8**) (Scheme 6). Solutions of **8** were stable and showed no allenyl-to-alkynyl isomerization on standing at room temperature over 1 week or even after heating to 60 °C for 6 h. Steric effects are probably important for the stabilization of **8**, which actually contains the least bulky S substituent in the thiols investigated. Protonation of **8** with HOTf at room temperature regenerated the carbene **4** quantitatively.

Complex **8** is featured by ^{13}C and ^1H NMR spectral data, which agree with the presence of an η^1-thio(allyl)-allenyl ligand. In particular, three ^{13}C resonances at 199.0, 102.0, and 89.8 ppm could unequivocally be assigned to the C_β, C_γ, and C_α carbon atoms of the allenyl moiety, while three singlets at 124.9, 115.5, and 41.2 ppm were attributed to the allyl substituent.

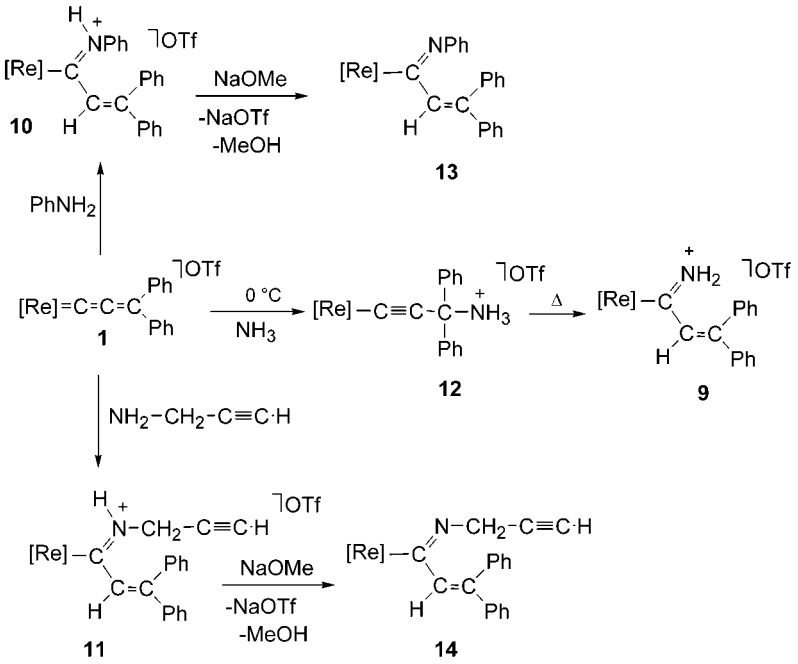
Reaction of 1 with Ammonia and Primary Amines. Ammonia and aromatic or aliphatic primary amines, exemplified here by aniline and propargylamine, reacted with **1**, showing the same regioselectivity: i.e., N−H bond addition across the C_α=C_β double bond. The products isolated were not the expected aminocarbenes, however; instead, azoniabutadienyl products were obtained (Scheme 7).

Bubbling gaseous ammonia through a dry CH_2Cl_2 solution of **1** at room temperature, followed by elimination of excess NH_3 and solvent under reduced pressure, gave the α,β-unsaturated azoniabutadienyl complex [Re{C(=NH_2)CH=CPh_2}$(CO)_2$(triphos)]OTf (**9**) as a brown solid in excellent yield. Careful dehydration of the solvent was necessary to avoid the formation of the γ-hydroxyalkynyl complex [Re{C≡CCPh_2(OH)}$(CO)_2$-(triphos)] by regioselective OH^- attack at C_γ.[5]

Monitoring by NMR spectroscopy the reaction between a $CDCl_3$ solution of **1** and ammonia at 0 °C in a 5 mm tube revealed the formation of a kinetic product preceding the azoniabutadienyl complex. This intermediate species was the γ-ammonioalkynyl complex [Re{C≡CCPh_2(NH_3)}$(CO)_2$(triphos)]OTf (**12**), whose formation apparently involved amine attack at the C_γ atom of the allenylidene precursor. Complex **12** was not stable at 0 °C and transformed slowly into the azoniabutadienyl derivative **9**. The conversion was complete in ca. 4 h. All our attempts to isolate pure **12** were unsuccessful; however, the elimination of the solvent at −40 °C gave a mixture of **9** and **12**, in which the latter compound was present in a ca. 30% amount.

The structural formulation proposed for **12** relies on a thorough spectroscopic analysis in $CDCl_3$ solution. The

Scheme 7



$^{31}P\{^{1}H\}$ NMR spectrum showed an AM_2 pattern with NMR parameters (δ_A −6.34, δ_M −18.63, $J(PP)$ = 19.4 Hz) typical of rhenium σ-alkynyl complexes of the general formula $[Re\{C{\equiv}CCPh_2R\}(CO)_2(triphos)]^{0,+}$.[5,6b] Specific structural information was obtained from a proton NMR spectrum that contained a broad singlet at 2.61 ppm due to the three ammonium protons of the NH_3 group and from a $^{13}C\{^{1}H\}$ NMR spectrum at −40 °C that allowed us to assign the resonances of the C_α (101.2 ppm, $J(CP_{trans})$ = 31.1 Hz, $J(CP_{cis})$ = 14.0 Hz) and C_β (115.6 ppm, $J(CP_{trans})$ = 14.1 Hz) carbon atoms of the alkynyl moiety.[5,6b] Consistent with the presence of a C≡C triple bond in **12** was also an IR stretching frequency at 2080 cm^{-1}. To the best of our knowledge, no γ-ammonioalkynyl metal complex has ever been described, although their syntheses have been previously attempted.[2] For example, the reaction of NH_3 with the Rh^{I} allenylidene *trans*-$[Rh\{C{=}C{=}CPh_2\}(O{=}CMe_2)(P^iPr_3)_2)]PF_6$ resulted in the simple acetone substitution by NH_3 instead of its addition to the allene ligand.[13]

Stable azoniabutadienyl complexes were also formed by reaction of **1** with aniline and propargylamine at room temperature in CH_2Cl_2 to give $[Re\{C(=NHPh)CH{=}CPh_2\}(CO)_2(triphos)]OTf$ (**10**) and $[Re\{C(=NHCH_2C{\equiv}CH)CH{=}CPh_2\}(CO)_2(triphos)]OTf$ (**11**), respectively. With the less basic and more sterically demanding aniline, much longer reaction times were required to complete the reaction (5 h instead of 1 h with propargylamine).

NMR monitoring of the reactions between **1** and aniline or propargylamine did not show any intermediate species along the transformation into **10** and **11**, respectively. The lack of detected intermediates is probably due to direct addition of the N−H bond across the $C_\alpha{=}C_\beta$ bond in **1** with no preliminary attack at C_γ, as a consequence of the larger cone angle of both aniline and propargylamine as compared to ammonia.

The solid-state structure of **11** as determined by a single-crystal X-ray analysis consists of $[Re\{C(=NHCH_2C{\equiv}CH)CH{=}CPh_2\}(CO)_2(triphos)]^+$ cations and triflate anions in a 1:1 ratio with no interspersed solvent molecules. An ORTEP[14] view of the complex cation is shown in Figure 1, while selected bond distances and angles are listed in Table 2.

The coordination geometry around the rhenium atom can be described as a distorted octahedron with three contiguous coordination positions taken by triphos, two mutually cis positions taken by two CO groups, and the last position taken by a carbon atom from an azoniabutadienyl ligand. The Re−P2 and Re−P3 distances involving the two mutually cis P atoms trans to CO (2.502(2) and 2.486(2) Å, respectively) are in agreement with analogous distances in many rhenium(I) complexes containing the $[Re(CO)_2(triphos)]^+$ fragment.[4,6a−d,15] The Re−P1 distance trans to the σ-organyl ligand is significantly shorter (2.442(2) Å) than the other Re−P separations, which is consistent with a weaker trans influence of the azoniabutadienyl ligand as compared to CO. In keeping with the formulation of these complexes as azoniabutadienyl derivatives rather than aminocarbenes, the Re1−C3 distance (2.151(7) Å) is typical for a single bond, while the C3−N1 distance (1.300(9) Å) is that of a C=N double bond with a positive charge localized on the nitrogen atom. The single-bond distances C3−C7 (1.496(10) Å) and N1−C4 (1.498(10) Å) and the double-bond distance C7−C8 (1.340(10) Å) are indicative of the absence of any electronic delocalization in the butadienoid moiety.

In Table 3 are reported the Re−C and $Re-P_{trans}$ bond distances found in **11** and in other rhenium(I) organyl complexes containing the $[Re(CO)_2(triphos)]^+$ moiety. An inspection of this table shows that (i) the Re−C distances may vary from 1.925 to 2.171 Å on going from

(13) Windmüller, B.; Nürnberg, O.; Wolf, J.; Werner, H. *Eur. J. Inorg. Chem.* **1999**, 613.

(14) Johnson, C. K. ORTEP II; Report ORNL-5138; Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

(15) Bianchini, C.; Marchi, A.; Martelli, L.; Peruzzini, M.; Romerosa, A.; Rossi, R.; Vacca, A. *Organometallics* **1995**, *14*, 3203.

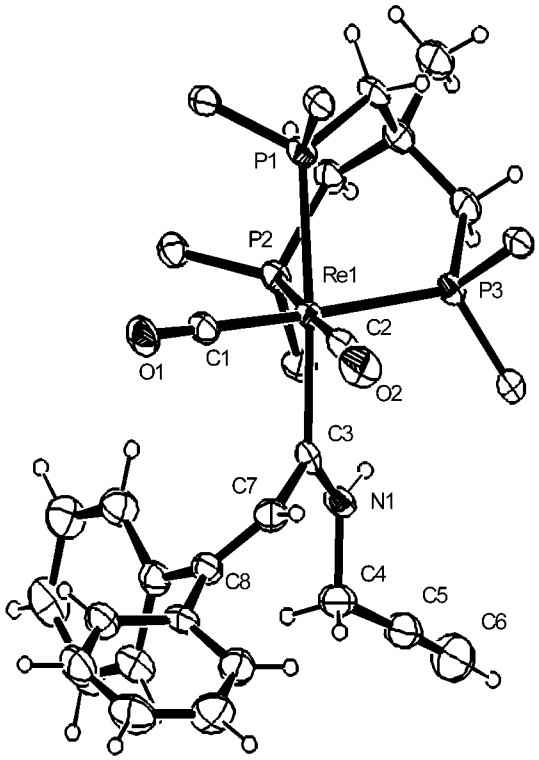


Figure 1. ORTEP view of the complex cation of **11**, [Re{C(=NHCH$_2$C≡CH)CH=CPh$_2$}(CO)$_2$(triphos)]$^+$. The ellipsoids are drawn at the 30% probability level. Only the ipso carbons of the phenyl rings of the triphos ligand are shown for the sake of clarity.

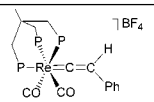
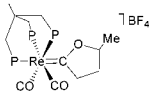
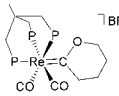
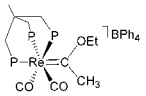
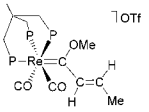
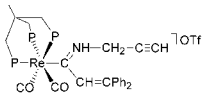
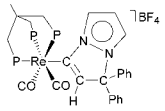
Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex Cation [Re{C(=NHCH$_2$C≡CH)CH=CPh$_2$}(CO)$_2$(triphos)]$^+$ (11)

Re(1)−P(1)	2.442(2)	C(2)−O(2)	1.159(8)
Re(1)−P(2)	2.502(2)	C(3)−N(1)	1.300(9)
Re(1)−P(3)	2.486(2)	C(3)−C(7)	1.496(10)
Re(1)−C(1)	1.925(6)	C(4)−N(1)	1.498(10)
Re(1)−C(2)	1.907(6)	C(4)−C(5)	1.462(11)
Re(1)−C(3)	2.151(7)	C(5)−C(6)	1.147(14)
C(1)−O(1)	1.147(8)	C(7)−C(8)	1.340(10)
P(1)−Re(1)−P(2)	81.70(6)	P(3)−Re(1)−C(3)	96.9(2)
P(1)−Re(1)−P(3)	85.63(6)	C(1)−Re(1)−C(2)	84.6(3)
P(2)−Re(1)−P(3)	86.75(5)	C(1)−Re(1)−C(3)	87.0(3)
P(1)−Re(1)−C(1)	90.0(2)	C(2)−Re(1)−C(3)	85.2(2)
P(1)−Re(1)−C(2)	99.1(2)	Re(1)−C(3)−N(1)	128.0(5)
P(2)−Re(1)−C(1)	99.3(2)	Re(1)−C(3)−C(7)	117.4(4)
P(2)−Re(1)−C(2)	176.0(2)	N(1)−C(3)−C(7)	114.5(6)
P(3)−Re(1)−C(1)	172.6(2)	N(1)−C(4)−C(5)	111.8(7)
P(3)−Re(1)−C(2)	89.4(2)	C(4)−C(5)−C(6)	176.5(10)
P(1)−Re(1)−C(3)	175.0(2)	C(3)−C(7)−C(8)	130.4(6)
P(2)−Re(1)−C(3)	94.2(2)		

double to single Re−C bonds and (ii) the Re−P_{trans} distances increase with the double-bond character of the Re−C bond.

On the basis of the X-ray crystal analysis of the propargyl amino derivative and the relative spectroscopic characteristics in solution, also **9** and **10** can safely be considered as azoniabutadienyl complexes. In agreement with the presence of a localized C=N double bond, the IR spectra of **9**−**11** exhibited medium-intensity ν(C=N) absorptions in the 1580−1489 cm^{-1} region. Other IR bands at ca. 3320 and 1600 cm^{-1} were assigned to ν(NH) and ν(C=C) of the azoniabutadienyl ligand, respectively. In the NH_2 derivative **9**, the band

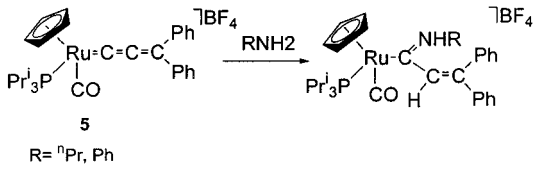
Table 3. Structural Data for X-ray-Authenticated [Re(R)(CO)$_2$(triphos)]Y Complexes

Compound	Re-C (Å)	Re-P_{trans} (Å)	Ref
	1.925(6)	2.523(2)	6b
	2.02(2)	2.466(2)	6c
	2.051(10)	2.479(2)	6d
	2.071(8)	2.482(2)	6b
	2.078(10)	2.464(3)	4
	2.151(7)	2.442(2)	this work
	2.171(4)	2.442 (2)	20

at 3324 cm^{-1} was accompanied by a twin absorption at slightly lower energies (3178 cm^{-1}). The presence of two IR absorptions in the NH region is typical for the presence of a stereochemically rigid NH_2 group; indeed, a similar IR pattern can be observed in the IR spectrum of the primary aminocarbene *fac,cis*-[Ru{C(NH$_2$)CH$_2$Ph}Cl$_2$(PNP)] (ν(NH) 3383, 3276 cm^{-1}; PNP = CH$_3$CH$_2$CH$_2$N(CH$_2$CH$_2$PPh$_2$)$_2$).[16] The ^{1}H and ^{13}C{^{1}H} NMR spectra were fully consistent with the presence of an $\eta^1(C_1)$-azoniabutadienyl ligand in all complexes. In particular, the proton spectrum of **11** showed a singlet at 6.60 ppm due to the CH azoniabutadienyl hydrogen, whereas the analogous hydrogen in **10** appeared as a doublet at 6.15 ppm (singlet in the ^{1}H{^{31}P} NMR spectrum). The NH proton was clearly visible as a broad singlet at 8.62 ppm in the spectrum of **10** but could not be identified in the spectra of **9** and **11**, likely because it was masked by the aromatic protons. The ^{13}C{^{1}H} NMR spectra of **9**−**11** exhibited well-resolved doublets of triplets at ca. 240 ppm with a J(CP$_{trans}$) value of ca. 30 Hz and a J(CP$_{cis}$) value between 12 and 8 Hz for the C_α carbon atom. These resonances are shielded by ca. 50−60 ppm with respect to the C_α resonance of several rhenium(I) carbenes[4,6] but are in line with the values reported for the azoniabutadienyl complex [Ru(CO)(PPr$^i_3$){C(=NHR)CH=CPh$_2$}(η^5-C$_5$H$_5$)]BF$_4$ (R = ^{n}Pr, Ph).[7] Interestingly, the ^{13}C chemical shifts of the C_α atoms in **9**−**11** match perfectly the signal of the unsat-

(16) Bianchini, C.; Masi, D.; Romerosa, A.; Zanobini, F.; Peruzzini, M.; *Organometallics* **1999**, *18*, 2376.

Scheme 8



urated acyl carbon atom in [Re{C(O)CH=CPh$_2$}(CO)$_2$(triphos)]OTf (δ 257.4),[6a] which indirectly supports the double-bond character of the C=N bond in the azoniabutadienyl complexes.[17] Other relevant ^{13}C NMR resonances are listed in Table 1. Besides uninformative triphos resonances and those due to the magnetically inequivalent CO ligands, the only significant ^{13}C{^{1}H} signals were those relative to the presence of a CH=CPh$_2$ unit in all compounds and of an intact propargylic chain in **11**. NMR discrimination of the two carbonyl sites in **10** and **11** (well-resolved doublet of triplets at ca. 199 ppm) was facilitated by the presence of bulky N substituents in the azoniabutadienyl ligand that apparently hinder the free rotation around the Re−C axis (vide supra). Consistently, AMX spin systems were observed in the ^{31}P{^{1}H} spectra at room temperature, while **9**, containing a nonsterically demanding NH$_2$ group, gave an AM$_2$ ^{31}P pattern and therefore a single CO resonance in the ^{13}C{^{1}H} NMR spectrum.

The addition of ammonia and primary amines to M=C=C moieties to give aminocarbenes is a well-known reaction path for vinylidene metal complexes.[16,18,19] In principle, the addition of primary amines to metallacumulenes might give aminocarbene derivatives as well. However, this has never been observed, and in fact, the formation of azoniabutadienyl compounds occurs. Prior to the present studies, the formation of azoniabutadienyl products by reaction of primary amines with metal allenylidenes has been reported only by Esteruelas and co-workers, who obtained [Ru(CO)(PPr$^i_3$){C(=NHR)CH=CPh$_2$}(η^5-C$_5$H$_5$)]BF$_4$ (R = ^{n}Pr, Ph) by treatment of **5** with either aniline or *n*-propylamine (Scheme 8).[17]

Deprotonation of the Azoniabutadienyl Complexes. The deprotonation of **10** and **11** with sodium methoxide in THF occurs regioselectively at the nitrogen atom to give the stable azabutadienyl products [Re{C(=NR)CH=CPh$_2$}(CO)$_2$(triphos)] (R = Ph (**13**), CH$_2$-C≡CH (**14**)) (Scheme 7). Since the related thiocarbenes **2** and **3** (vide supra) are selectively deprotonated at the CH=CPh$_2$ olefinic group, one may conclude that the N−H hydrogen in azabutadienyl compounds is more acidic than the C−H hydrogen.

Azabutadienyl complexes are very rare organometallics. The unique example prior to ours has been recently prepared by Esteruelas and co-workers applying the same procedure described in this paper: i.e., deprotonation of ruthenium azoniabutadienyl complexes.[17]

The unequivocal formulation of **13** and **14** as rhenium(I) azabutadienyl compounds was achieved on the basis of a sound spectroscopic characterization as well as elemental analysis data.

The IR spectra of both compounds showed medium-intensity absorptions at ca. 1500 cm^{-1} for the ν(C=N) mode and a slightly blue-field-shifted (ca. 1600 cm^{-1}) ν(C=C) band. In agreement with the neutral character of **13** and **14**, the ν(CO) stretching frequencies shifted to lower energy (between 1944 and 1878 cm^{-1}) as compared to the cationic precursors. In the ^{13}C{^{1}H} NMR spectra, the azabutadienyl C$_\alpha$ atoms appeared as a doublet of triplets at ca. 200 ppm and are therefore slightly high-field-shifted with respect to the C$_\alpha$ resonances in the cationic precursors **10** and **11**. The other ^{13}C signals and the ^{1}H NMR signals do not deserve any particular comment; all of them were in line with the azabutadienyl structure (Table 1).

Both **13** and **14** exhibited fluxional behavior in room-temperature solutions, where ^{31}P{^{1}H} NMR AM$_2$ patterns were observed. The slow-motion regime represented by AMX spin systems was attained already at −20 °C.

Concluding Remarks

Like all cationic transition-metal allenylidenes, the reactivity of **1** is largely controlled by the electrophilic character of the C$_\alpha$ and C$_\gamma$ carbon atoms, which are subjected to nucleophilic attacks by various *soft* and *hard* nucleophiles.[1] In previous works from this laboratory,[5] it has been reported that anionic oxygen and carbon nucleophiles (OH$^-$, OMe$^-$, H$^-$, CH$_3^-$, NO$_2$CH$_2^-$, etc.), selectively attack **1** at C$_\gamma$ to give σ-alkynyl complexes, which is in accord with theoretical studies. Indeed, orbital-controlled nucleophilic attack at allenylidene complexes containing group 8 d^6 metal ions is expected to be favored at C$_\gamma$, which contains a higher percentage of complex LUMO than C$_\alpha$ as well as a lower net charge.[1,2] Electrophilic attack at C$_\beta$ in **1** has also been observed to give (vinyl)carbyne derivatives.[5]

It has been shown in this paper that *soft* nucleophiles such as thiolates attack **1** regioselectively at C$_\alpha$ to give kinetic or thermodynamic thioallenyl products, depending on the sulfur substituent, while neutral nucleophiles bearing an electrophilic hydrogen (Nu−H) add across the C$_\alpha$=C$_\beta$ bond irrespective of the nature of the nucleophilic atom (N or S). Two new reaction paths for allenylidene metal complexes have been discovered: the reversible addition of PhSH across the C$_\alpha$=C$_\beta$ bond and the regioselective attack of ammonia at C$_\gamma$ to give a transient ammonioalkynyl complex preceding a thermodynamic azoniabutadienyl product.

No specific theoretical study on rhenium(I) allenylidene compounds has been reported, and therefore it is not possible to validate the present experimental results through an analysis of the nature and gap of the HOMO and LUMO. On the other hand, the reactivity of **1** toward *hard* and *soft* anionic nucleophiles as well as amines and thiols is rather similar to that exhibited by the ruthenium(II) complex [Ru(CO)(PPr$^i_3$){C=C=CPh$_2$}(η^5-C$_5$H$_5$)]BF$_4$, for which EHT-MO calculations assign 23% and 31% of the LUMO on the C$_\alpha$ and C$_\gamma$ atoms, respectively, and 20% of the HOMO on the C$_\beta$ atom.[20]

(17) Bernad, D. J.; Esteruelas, M. A.; López, A. M.; Modrego, J.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4995.

(18) Recent reviews on vinylidene complexes include: (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193/195*, 977. (c) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311.

(19) Gamasa, M. P.; Gimeno, J.; Lastra, E.; Lanfranchi, M.; Tiripicchio, A. *J. Organomet. Chem.* **1992**, *430*, C39.

(20) Bianchini, C.; Peruzzini, M.; Rossi, R., manuscript in preparation.

In view of the comparable reactivity, one may suggest that the ruthenium and rhenium compounds have similar electronic structures. Similar but not identical, however, as the two compounds exhibit also distinct reaction paths: for example, the ruthenium complex readily reacts with water and primary alcohols, yielding isolable hydroxy- and alkoxycarbenes,[11a] whereas **1** is fully stable in the presence of either substrate.[5] An unfavorable, subtle balance of steric and electronic effects seems to be responsible for the stability of **1** toward H_2O and ROH, since the rhenium(I) allenylidenes $[Re\{C=C=CH(Ph)\}(CO)_2(triphos)]^+$ [6a] and $[Re\{C=C=CH(Me)\}(CO)_2(triphos)]^+$,[4] differing from **1** only in the substituents at the C_γ atom, are readily transformed into hydroxy- and alkoxyvinylcarbenes $[Re\{C(OR)CH=CH(R')\}(CO)_2(triphos)]^+$ by reaction with H_2O (R = H, R′ = Ph)[6a] or MeOH (R = R′ = Me).[4]

Experimental Section

General Procedure. All reactions and manipulations were routinely performed under a dry nitrogen atmosphere by using standard Schlenk-tube techniques. Tetrahydrofuran (THF) was freshly distilled over $LiAlH_4$; *n*-hexane was stored over molecular sieves and purged with nitrogen prior to use; dichloromethane and methanol were purified by distillation over CaH_2 before use. All the other reagents and chemicals were commercial products and, unless otherwise stated, were used as received without further purification. The ligand 1,1,1-tris((diphenylphosphino)methyl)ethane (triphos)[21] and the complex **1**[4] were prepared as previously reported. Sodium thiophenate and 2-thionaphthate were prepared just prior to use by treatment of the corresponding thiols with elemental sodium in THF under vigorous stirring. All reactions and manipulations were routinely performed under a dry nitrogen atmosphere by using standard Schlenk-tube techniques. The solid complexes were collected on sintered-glass frits and washed with either light diethyl ether or *n*-hexane before being dried under a stream of nitrogen unless otherwise stated. IR spectra were obtained as KBr pellets 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). ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AC200, Varian VXR300, and Bruker AVANCE DRX500 spectrometers operating at 200.13, 299.94, and 500.13 MHz (^1H) and 50.32, 75.42, and 125.75 MHz (^{13}C), respectively. Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (^1H) or the deuterated solvent multiplet (^{13}C). $^{13}C\{^1H\}$ DEPT-135 NMR experiments were run on the Varian VXR300 spectrometer. ^1H,^{13}C-2D HETCOR NMR experiments were recorded on the Bruker AVANCE DRX 500 spectrometer equipped with a 5 mm triple-resonance probe head for ^1H detection and inverse detection of the heteronucleus (inverse correlation mode, HMQC experiment) with no sample spinning. ^1H,^1H-2D COSY NMR experiments and ^1H,^1H-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. $^{31}P\{^1H\}$ 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. Elemental analyses (C, H, N, S) were performed at the University of Ferrara using a Carlo Erba Model 1106 elemental analyzer.

Synthesis and Characterization of the New Complexes. $[Re\{C(SPh)CH=CPh_2\}(CO)_2(triphos)]OTf$ (2). A solution of **1** (200 mg, 0.17 mmol) in 10 mL of dichloromethane was treated with thiophenol (86 μL, 0.83 mmol) at room temperature. The solution was heated to 35 °C with stirring for 30 min. Then, it was cooled to room temperature and additionally stirred for 1 h. During this time the color turned from dark violet to deep red. The solution was concentrated to ca. 1 mL, and a yellow solid was formed by dropwise addition of *n*-hexane (3 mL). The solid was washed with *n*-hexane (2 × 1 mL) and diethyl ether (1 × 1 mL) and dried in vacuo. Yield: 76%. Anal. Calcd for $C_{65}H_{55}F_3O_5P_3ReS_2$: C, 59.31; H, 4.21; S, 4.87. Found C, 59.47; H, 4.23; S, 4.95.

$[Re\{C(SC_{10}H_7)CH=CPh_2\}(CO)_2(triphos)]OTf$ (3). The thionaphthyl carbene **3** was synthesized by following the above procedure using 2-thionaphthol (40 mg, 0.25 mmol) in the place of thiophenol. Workup as above and dropwise addition of diethyl ether gave a dark brown solid, which was washed with diethyl ether (2 × 1 mL) and dried in vacuo. Yield: 82%. Anal. Calcd for $C_{69}H_{57}F_3O_5P_3ReS_2$: C, 60.65; H, 4.20; S, 4.68. Found: C, 60.46; H, 4.19; S, 4.57.

$[Re\{C(SCH_2CH=CH_2)CH=CPh_2\}(CO)_2(triphos)]OTf$ (4). To a solution of **1** (200 mg, 0.17 mmol) in dichloromethane (10 mL) was added a large excess of allyl mercaptan (100 μL, 1.21 mmol), and the mixture was stirred for 24 h. The color turned from dark violet to dark red. The solvent was removed under vacuum, and the crude residue was washed with *n*-hexane (2 × 1 mL) and diethyl ether (1 × 1 mL) to afford a dark orange solid. Yield: 83%. Anal. Calcd for $C_{62}H_{55}F_3O_5P_3S_2Re$: C, 58.16; H, 4.33; S, 5.00. Found: C, 57.99; H, 4.35; S, 5.12.

$[Re\{C(SPh)C=CPh_2\}(CO)_2(triphos)]$ (6a) and $[Re\{C\equiv CC(SPh)Ph_2\}(CO)_2(triphos)]$ (6b). Method A. Solid sodium methoxide (41 mg, 0.75 mmol) was added to a solution of **2** (200 mg, 0.15 mmol) in 5 mL of THF, and the mixture was stirred at room temperature for 2 h to afford a pale brown solution. Evaporation of the solvent gave a gray solid, which was washed with cold water (1 × 1 mL), cold isopropyl alcohol (1 × 2 mL), and *n*-hexane (2 × 1 mL). Yield: 76%. $^{31}P\{^1H\}$ NMR analysis gave the following composition of the crude product: **6a** (60%), **6b** (40%).

Method B. A slight excess of solid PhSNa (26.5 mg, 0.20 mmol) was added to a stirred solution of **1** (200 mg, 0.17 mmol) in 10 mL of THF. The mixture was stirred for 30 min while the color turned from dark violet to brown. Removal of the solvent under vacuum left a brown solid that was washed with cold water (2 × 1 mL), cold isopropyl alcohol (1 × 2 mL), and *n*-hexane (2 × 1 mL). Yield: 78%. $^{31}P\{^1H\}$ NMR analysis gave the following product composition of the crude product: **6a** (60%), **6b** (40%). Anal. Calcd for $C_{64}H_{54}O_2P_3ReS$: C, 65.91; H, 4.67; S, 2.74. Found: C, 66.13; H, 4.74; S, 2.81.

$[Re\{C(SC_{10}H_7)C=CPh_2\}(CO)_2(triphos)]$ (7a) and $[Re\{C\equiv CC(SC_{10}H_7)Ph_2\}(CO)_2(triphos)]$ (7b). Method A. Addition of sodium methoxide (41 mg, 0.75 mmol) to a solution of **3** (210 mg, 0.15 mmol) in 5 mL of THF and workup as above gave a mixture of **7a** and **7b** as a brownish solid. Yield: 72%. $^{31}P\{^1H\}$ NMR analysis gave the following composition of the crude product: **7a** (20%), **7b** (80%).

Method B. A double proportion of NpSNa (62 mg, 0.34 mmol) was added as a solid to a methanol solution (10 mL) of **1** (200 mg, 0.17 mmol). The brown solid which immediately separated out was was filtered off, washed with *n*-hexane (2 × 2 mL), and dried under vacuum. Yield: 70%. $^{31}P\{^1H\}$ NMR analysis gave the following composition of the crude product: **7a** (22%), **7b** (78%). Anal. Calcd for $C_{68}H_{56}O_2P_3ReS$: C, 67.15; H, 4.64; S, 2.63. Found: C, 67.32; H, 4.75; S, 2.78.

$[Re\{C(SCH_2CH=CH_2)C=CPh_2\}(CO)_2(triphos)]$ (8). Solid sodium methoxide (43 mg, 0.80 mmol) was added in small portions over 3 min periods at room temperature into a stirred solution of **4** (200 mg, 0.16 mmol) in 10 mL of THF. The resulting solution, which turned pale brown within 10 min, was stirred for 2 h before THF was removed under reduced pressure to leave a brown solid that was washed with cold

(21) Hewertson, W.; Watson, H. R. *J. Chem. Soc.* **1962**, 1490.

water (1 × 1 mL), cold isopropyl alcohol (1 × 2 mL), and *n*-hexane (2 × 1 mL). Yield: 79%. Anal. Calcd for $C_{61}H_{54}O_2P_3SRe$: C, 69.37; H, 5.15; S, 3.03. Found: C,69.43; H, 5.19; S, 3.08.

Treatment of **8** in dichloromethane-d_2 with triflic acid (1 equiv) at room temperature gave the parent carbene **4** quantitatively (NMR analysis).

[Re{C(=NH$_2$)CH=CPh$_2$}(CO)$_2$(triphos)]OTf (9). A 5 mm NMR tube was charged with **1** (80.0 mg, 0.07 mmol) in 0.7 mL of dichloromethane-d_2, and then this solution was saturated with gaseous ammonia at 0 °C. Immediately the deep violet color changed to reddish brown. NMR analysis of the solution showed the complete transformation of **1** into **9**. The solution was poured into a Schlenk tube, and the solvent was removed under vacuum to leave a brown powdered material, which was thoroughly washed with cold ethanol (2 × 2 mL) and diethyl ether (2 × 1 mL). Yield: 88%. Scaling up the reaction (160 mg of **1**, 10 mL of CH_2Cl_2) gave solid **9** as described above. Anal. Calcd for $C_{59}H_{52}F_3NO_5P_3ReS$: C, 57.93; H, 4.28; N, 1.15; S, 2.62. Found: C, 57.61; H, 4.34; S, 2.94.

[Re{C(=NHPh)CH=CPh$_2$}(CO)$_2$(triphos)]OTf (10). A solution of **1** (200 mg, 0.17 mmol) in 10 mL of dichloromethane was treated with aniline (76 μL, 0.83 mmol) at room temperature and stirred for 5 h. During this time, the dark violet solution turned reddish orange. The solution was concentrated to ca. 1 mL, and diethyl ether (3 mL) was slowly added to precipitate a yellow solid, which was washed with diethyl ether (2 × 1 mL) and dried in vacuo. Yield: 78%. Anal. Calcd for $C_{65}H_{56}F_3NO_5P_3ReS$: C, 60.08; H, 4.34; S, 2.47; N, 1.08. Found: C, 60.14; H, 4.29; S, 2.53; N, 1.16.

[Re{C(=NHCH$_2$C≡CH)CH=CPh$_2$}(CO)$_2$(triphos)]OTf (11). Complex **11** was obtained as a pink solid from the above procedure by replacing aniline with propargylamine (55 μL, 0.80 mmol) but applying a reaction time of 2 h. The crude product was recrystallized from a mixture (1/1 v/v) of dichloromethane and diethyl ether. Yield: 72%. Anal. Calcd for $C_{62}H_{54}F_3NO_5P_3ReS$: C, 59.04; H, 4.31; S, 2.54; N, 1.11. Found C, 59.12; H, 4.40; S, 2.61; N, 1.15.

[Re{C(=NPh)CH=CPh$_2$}(CO)$_2$(triphos)] (13). A stirred THF suspension (5 mL) of **10** (200 mg, 0.15 mmol) was treated with solid sodium methoxide (42 mg, 0.77 mmol). The solution was stirred for 2 h at room temperature to give a light yellow solution. The solvent was then removed under reduced pressure to leave a yellow residue, which was washed with water (1 × 1 mL), cold isopropyl alcohol (1 × 1 mL), and *n*-hexane (2 × 1 mL) and dried in vacuo. Yield: 69%. Anal. Calcd for $C_{64}H_{55}NO_2P_3Re$: C, 66.89; H, 4.82; N, 1.22. Found: C, 66.75; H, 4.71; N, 1.24.

[Re{C(=NCH$_2$C≡CH)CH=CPh$_2$}(CO)$_2$(triphos)] (14). Treatment of **11** (200 mg, 0.16 mmol) with sodium methoxide and workup as described above gave **14** as a brown microcrystalline material. Yield: 68%. Anal. Calcd for $C_{61}H_{53}NO_2P_3Re$: C, 65.93; H, 4.81; N, 1.26. Found: C, 66.02; H, 4.85; N, 1.32.

Crystal Structure Determination of [Re{C(=NHCH$_2$C≡CH)CH=CPh$_2$}(CO)$_2$(triphos)] OTf (11). X-ray diffraction data for **11** were collected at room temperature using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation and corrected for Lorentz−polarization and absorption effects. The structure was solved by direct and Fourier methods and refined using full-matrix least squares with all non-hydrogen atoms anisotropic and hydrogens in calculated positions. The triflate anion was disordered and refined over two positions with occupancies of 0.5. The crystal data and refinement parameters are summarized in Table 4. The programs used and sources of scattering factor data are given in ref 22.

Table 4. Crystal Data for [Re{C(=NHCH$_2$C≡CH)CH=CPh$_2$}(CO)$_2$(triphos)]OTf (11)

formula	$C_{62}H_{54}F_3NO_5P_3SRe$
mol wt	1261.29
cryst syst	monoclinic
space group	$P2_1/a$
a, Å	13.9846(4)
b, Å	26.9678(4)
c, Å	16.1664(4)
β, deg	93.131(1)
V, Å^3	6087.8(2)
Z	4
D_{calcd}, g cm^{-3}	1.376
μ, mm^{-1}	2.165
θ range, deg	2.9−27.0
index ranges	$0 \le h \le 17$, $0 \le k \le 34$, $-20 \le l \le 20$
total no. of rflns	28 090
R_{int}	0.065
no. of unique rflns	11 228
no. of obsd rflns ($I \ge 2\sigma(I)$)	8837
R1 (obsd rflns)	0.052
wR2 (all rflns)	0.133
S	1.08
largest diff peaks, e Å^{-3}	−1.03, 0.98

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Supporting Information Available: Complete details on the X-ray analysis of **11**, including tables of crystal data and collection and refinement parameters, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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