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Nucleophilic addition of phosphines to rhenium allenylidenes. Unprecedented double P–H bond activation to give an η^1-*P*-phospha-1-butadienyl ligand †

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Tertiary phosphines $PMe_{3-x}Ph_x$ (x = 0–2) react with the rhenium allenylidene [(triphos)$(CO)_2$Re(C=C=CPh_2)]OTf (**1**) yielding γ-phosphonioalkynyl complexes [(triphos)$(CO)_2$Re{C≡$CCPh_2(PMe_{3-x}Ph_x)$}]OTf [x = 0, (**2**); 1, (**4**); 2 (**7**)] which convert into the α-phosphonioallenyl derivatives [(triphos)$(CO)_2$Re{C($PMe_{3-x}Ph_x$)=C=CPh_2}]OTf [x = 0, (**3**); 1, (**5**); 2 (**6**)] at higher tempereature. The reactions of **1** with secondary, $PHPh_2$, and primary, PH_2CH_2Fc (Fc = ferrocenyl), phosphines proceed with a similar mechanism, followed by single or double P–H bond cleavage. The γ-phosphonioalkynyl [(triphos)$(CO)_2$Re{C≡$CCPh_2(PHPh_2)$}]OTf (**9**) and the α-phosphonioallenyl [(triphos)-$(CO)_2$Re{C($PHPh_2$)=C=CPh_2}]OTf (**10**) have been intercepted by *in situ* NMR spectroscopy. On increasing the temperature, **10** undergoes a selective 1,3-*P*,*C*-H shift to give the α-phosphoniobutadienyl derivative [(triphos)-$(CO)_2$Re{C(=PPh_2)CH=CPh_2}]OTf (**8**). With the primary phosphine PH_2CH_2Fc, the initially formed α-phosphoniobutadienyl complex [(triphos)$(CO)_2$Re{C(=PHFc)CH=CPh_2}]OTf (**11**) transforms into the η^1-*P*-phospha-1-butadienyl complex [(triphos)$(CO)_2$Re{P(CH_2Fc)=CHCH=CPh_2}]OTf (**12**) upon heating at 50 °C.

Introduction

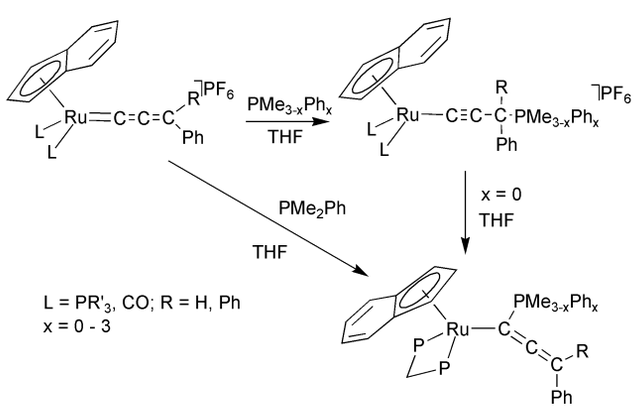
Transition metal allenylidenes, $[L_nM{=}C{=}C{=}CRR']^{n+}$, contemporaneously described by Fischer[1] and Berke,[2] have been considered for many years as the "exotic higher homologues" of vinylidene complexes.[3] Only after Selegue's discovery of the easy activation of propargylic alcohols by metal fragments to form allenylidenes,[4] these compounds have become sufficiently abundant to allow for their chemistry to be studied in detail.[5] Ruthenium is the metal that forms the large majority of known allenylidene complexes.[5a]

The metal–allenylidene moiety exhibits both σ-donor and π-acceptor properties, which can be finely tuned by varying the substituents at the C_γ carbon atom.[5] Metal allenylidenes are being widely used to synthesize original organic molecules,[6] especially *N*- and *S*-heterocycles,[7] and are receiving increasing attention in homogeneous catalysis,[8,9] especially for alkene methatesis.[9] Moreover, the unsaturated carbon chain makes allenylidenes useful precursors to carbon-rich linear oligomers and polymers with applications in material science and optoelectronics.[10]

In previous studies, we have shown that the π-donor rhenium(I) fragment $[(triphos)(CO)_2Re]^+$ [triphos = MeC-$(CH_2PPh_2)_3$][11] is able to stabilise a variety of alkylidene,[12] vinylidene[12b,c] and allenylidene[12c,13] complexes whose diverse chemistry rivals that of analogous ruthenium counterparts.[6]

Amongst the $[(triphos)(CO)_2Re(C{=}C{=}CRR')]^+$ complexes synthesized so far, the γ,γ′-diphenylsubstitued derivative $[(triphos)(CO)_2Re(C{=}C{=}CPh_2)]^+$ (**1**) has proved to be particularly suited for investigating the reactivity of the allenylidene moiety towards electrophiles and nucleophiles.[14–16]

In this paper, we report a study of the reactivity of **1** with primary, secondary and tertiary phosphines. The reactions with primary and secondary phosphines, yielding phosphoniobutadienyl and phosphabutadienyl complexes, respectively, have no precedent in the relevant literature, and their discovery may give access to a new class of organometallics.[6] In contrast, several reports have appeared in the literature describing the addition of tertiary phosphines to metal allenylidenes.[6,17] Complete regioselectivity has been observed by Gimeno and coworkers for the nucleophilic addition of $PMe_{3-x}Ph_x$ phosphines (x = 0–3) to the C_γ carbon atom of the indenyl complexes $[(Ind)Ru(L)_2\{C{=}C{=}C(Ph)R\}]PF_6$ (Ind = C_9H_7; L = PR_3, CO; R = H, Ph), yielding cationic γ-phosphonioalkynyl derivatives $[(Ind)Ru(L)_2\{C{\equiv}CC(Ph)R(PMe_{3-x}Ph_x)\}]PF_6$ (Scheme 1).[18] Steric congestion at C_γ, caused by the two phenyl substituents, was considered responsible for the lack of reactivity of the diphenylallenylidene derivative with either PPh_3 or $PMePh_2$. The



Scheme 1

† Based on the presentation given at Dalton Discussion No. 6, 9–11th September 2003, University of York, UK.

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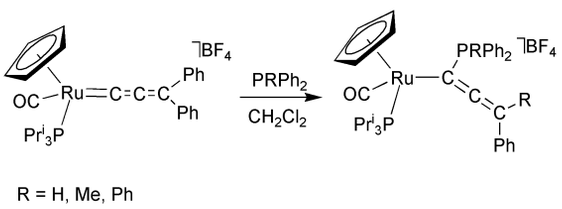
γ-phosphonioalkynyl derivatives are stable, yet for L = ½dppm and $PR_3 = PMe_3$, a slow rearrangement to the α-phosphonioallenyl isomer occurred.[18] Remarkably, the combination of ½dppm and PMe_2Ph gave selectively an α-phosphonioallenyl species. Relevant results reported by Gimeno and coworkers are illustrated in Scheme 1.

Regioselective attack at C_α has also been reported by Esteruelas and coworkers for the reactions of $[CpRu(CO)(PPr^i_3)(C{=}C{=}CPh_2)]BF_4$ with $PHPh_2$, $PMePh_2$, and PPh_3, yielding α-phosphonioallenyl complexes $[CpRu(CO)(PPr^i_3)\{\eta^1\text{-}C(PRPh_2){=}C{=}CPh_2\}]BF_4$ (R = H, Me, Ph) (Scheme 2).[19] It was concluded that the addition of bulky phosphines to the C_α atom is kinetically and thermodynamically favoured over the alternative pathway involving the direct attack by the nucleophile at the γ-carbon atom.



Scheme 2

Regioselective additions of tertiary phosphines to either terminal or proximal carbon atoms of allenylidene ligands have been also observed with manganese,[20] chromium,[21,22] iron[23] and cluster compounds.[24]

Despite the large body of experimental[25,26] and theoretical studies,[17,20a] no clear-cut explanation for the factors controlling the regiochemistry of phosphine addition to allenylidene ligands has been yet provided, and the outcome of the reactions is still largely unpredictable.

In an attempt of providing a clue to rationalize the regioselectivity of the addition of tertiary phosphines to metal allenylidenes, **1** has been reacted with tertiary phosphines $PMe_{3-x}Ph_x$ ($x = 0$, PMe_3; $x = 1$, PMe_2Ph; $x = 2$, $PMePh_2$; $x = 3$, PPh_3) differing from each other for the nucleophilicity and steric hindrance. The results of this investigation are reported in this paper, together with those obtained with the secondary phosphine $PHPh_2$ and the primary phosphine PH_2CH_2Fc (Fc = ferrocenyl).

Results and discussion

X-Ray crystal structure of $[(triphos)(CO)_2Re(C{=}C{=}CPh_2)]BPh_4$

X-Ray crystal structure determinations of allenylidene complexes have been reported for many transition metals, including chromium, molybdenum, tungsten, manganese, iron, ruthenium, osmium, rhodium and iridium.[29] No data is still available for rhenium allenylidenes, which might reflect their low number. Indeed, besides the triphos derivatives from this laboratory, the known rhenium allenylidenes are limited to the mononuclear tris-phosphite complexes $[Re(C{=}C{=}CPh_2)(CO)_2P_3\}]^+$ [P = $P(OEt)_3$, $PPh(OEt)_2$, $PPh_2(OEt)$],[30] the macrocyclic-phosphine complex $[\{12[ane]P_3iBu_3\}Re(CO)_2(C{=}C{=}CPh_2)]OTf$[31] and the binuclear species $[(CO)_9Re_2(C{=}C{=}C^tBu_2)]$.[32]

After many unsuccessful attempts,[13] well-shaped dark purple single crystals of **1** were serendipitously obtained by addition of $NaBPh_4$ to a dichloromethane/ethanol solution of **1** containing imidazole and slow crystallization under nitrogen.

The structure of **1/BPh$_4$** consists of $[(triphos)(CO)_2Re(C{=}C{=}CPh_2)]^+$ cations and tetraphenylborate anions in a 1 : 1 ratio with no interspersed solvent molecules. An ORTEP drawing of the complex cation is presented in Fig. 1, while selected bond lengths and angles are collected in Table 1.

Table 1 Selected bond distances (Å) and angles (°) for **1/BPh$_4$**

Re1–P1	2.479(1)	C1–O1	1.155(5)
Re1–P2	2.464(1)	C2–O2	1.144(5)
Re1–P3	2.470(1)	C3–C4	1.237(6)
Re1–C1	1.938(4)	C4–C5	1.359(6)
Re1–C2	1.937(4)	C5–C6	1.476(6)
Re1–C3	1.996(4)	C5–C12	1.462(6)
P1–Re1–P2	84.02(3)	P2–Re1–C3	94.6(1)
P1–Re1–P3	85.42(3)	P3–Re1–C3	177.5(1)
P2–Re1–P3	87.62(3)	C1–Re1–C2	91.4(2)
P1–Re1–C1	174.3(1)	C1–Re1–C3	86.8(2)
P2–Re1–C1	90.8(2)	C2–Re1–C3	83.4(2)
P3–Re1–C1	91.9(1)	Re1–C3–C4	171.7(4)
P1–Re1–C2	93.8(1)	C3–C4–C5	172.1(5)
P2–Re1–C2	176.9(1)	C4–C5–C6	119.2(4)
P3–Re1–C2	94.5(1)	C4–C5–C12	119.5(4)
P1–Re1–C3	96.0(1)		

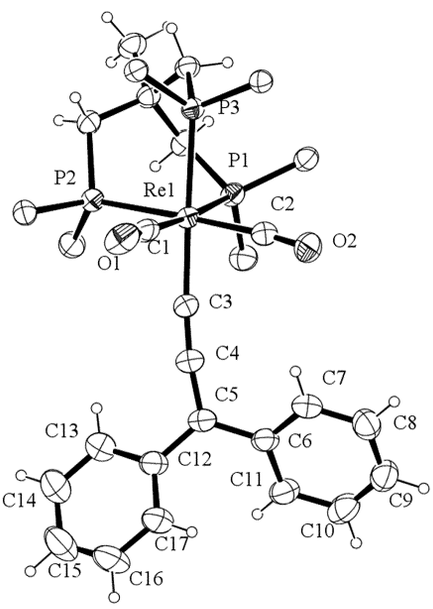


Fig. 1 ORTEP view and atom numbering of the cation $[(triphos)(CO)_2Re(C{=}C{=}CPh_2)]^+$ for **1/BPh$_4$**, showing thermal ellipsoids at 30% probability. For the sake of clarity, only the *ipso* carbons of the phenyl rings of the triphos ligand are shown.

In keeping with characterization of **1** in solution,[13] the rhenium allenylidene cation exhibits an octahedral geometry with three facial coordination positions occupied by the triphos ligand and by two mutually *cis* carbonyl ligands. The allenylidene fragment occupies the remaining sixth position *trans* to one of the three PPh_2 groups. Because of the sp hybridisation of the C3 and C4 atoms of the diphenylallenylidene ligand, the Re1–C3–C4–C5 chain is almost linear with the Re1–C3–C4 and C3–C4–C5 angles measuring 171.7(4) and 172.1(5)°, respectively. The Re1–C3 distance of 1.996(4) Å is typical for a Re=C double bond,[33] while the C3–C4 and C4–C5 bond lengths of 1.237(6) and 1.359(6) Å are shorter and longer than a typical C=C double bond (1.31 Å), respectively. This metrical feature is indicative of a significant contribution of the zwitterionic canonical form $Re^-–C{\equiv}C–C^+Ph_2$ to the structure of the compound, which is also observed in other allenylidene metal complexes.[5]

The three Re–P distances are almost equivalent, indicating a similar *trans* influence of the diphenylallenylidene and CO ligands.

Reaction of 1 with tertiary phosphines

1 Reaction of 1 with trimethylphosphine. These reactions are summarized in Schemes 3–6, while Table 2 collects selected

Table 2 Selected ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectral data and IR absorptions for the rhenium complexes **2**–**12**

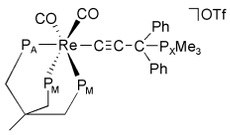
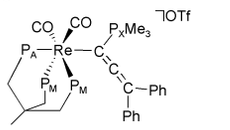
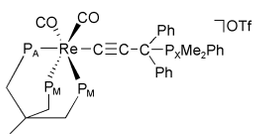
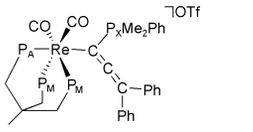
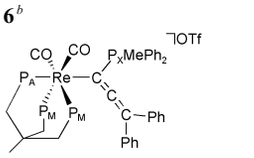
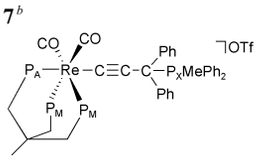
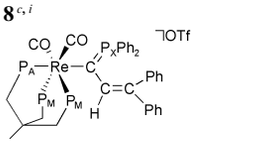
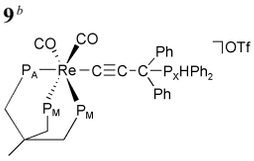
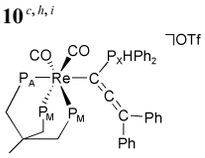
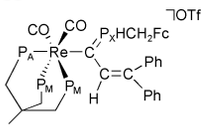
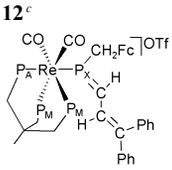
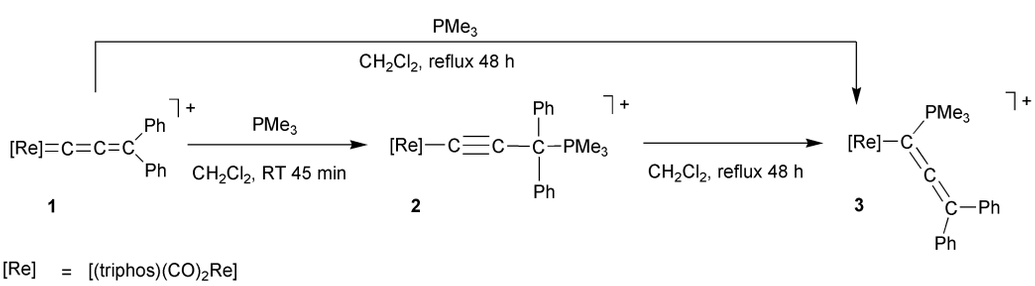
Compound	^{1}H δ/ppm, J/Hz	^{13}C{^{1}H} δ/ppm, J/Hz	^{31}P{^{1}H} δ/ppm, J/Hz IR (KBr, cm^{-1})
2[a] 	1.47 (q, J_{HP} 2.4, 3H, $CH_{3\ triphos}$) 2.13 (d, J_{HP_X} 12.6, 9H, $P(CH_3)_3$) 2.20–2.65 (br m, 4H, CH_2-$P_{eq\ triphos}$) 2.45 (d, J_{HP} 8.7, 2H, CH_2-$P_{ax\ triphos}$)	198.2 (dm, J_{CP_A} 35.6, CO) 111.5 (m, Re–C≡*C*) 103.6 (dt, J_{CP_X} 15.3, J_{CP_M} 3.0, Re–*C*≡C) 66.1 (d, J_{CP_X} 47.8, *C*(PMe_3)) 40.0 (q, J_{CP} 10.0, $CH_{3\ triphos}$) 39.5 (q, J_{CP} 4.2, CH_3–$C_{triphos}$) 34.0 (m, $CH_{2\ triphos}$) 9.9 (d, J_{CP_X} 54.3, $P(CH_3)_3$)	δ_A −7.63 (td) J_{AM} 18.2 δ_M −16.06 (dd) J_{AX} 2.0 δ_X 33.25 (td) J_{MX} 3.7 ν(C≡C) 2074 ν(CO) 1950, 1889
3[b] 	1.47 (q, J_{HP} 2.4, 3H, $CH_{3\ triphos}$) 2.14 (d, J_{HP_X} 12.3, 9H, $P(CH_3)_3$) 2.28–2.80 (br m, 6H, $CH_{2\ triphos}$)	214.2 (dt, J_{CP_X} 9.1, J_{CPB} 3.0, C=*C*=CPh_2) 197,4 (AA′XX′Y spin system, CO) 100.4 (dd, J_{CP_X} 48.3, J_{CP_A} 2.5,C=C=*C*Ph_2) 73.7 (dq, J_{CP_X} 26.0, $J_{CPA,M}$8.0,*C*=C=CPh_2) 39.8 (q, J_{CP} 9.9, $CH_{3\ triphos}$) 38.4 (q, J_{CP} 3.3, CH_3–$C_{triphos}$) 35.9 (td, J_{CPeq} 14.8, J_{CPax} 5.8, CH_2–$P_{eq\ triphos}$) 33.9 (d, J_{CPax} 20.6, CH_2–$P_{ax\ triphos}$) 15.0 (d, J_{CP_X} 54.3, $P(CH_3)_3$)	δ_A −10.88 (td) J_{AM} 18.1 δ_M −18.75 (dd) J_{AX} 8.5 δ_X 30.97 (dt) J_{MX} 7.0 ν(CO) + ν(C=C=C) 1933, 1870
4[b] 	2.45 (d, J_{HP_X} 12.0,6H, $P(CH_3)_2Ph$) 1.41(q, J_{HP} 2.2, 3H, $CH_{3\ triphos}$) 2.20–2.60 (br m, 6H, $CH_{2\ triphos}$)	197.5 (m, CO) 112.8 (m, Re–C≡*C*) 101.2 (d, J_{CP_A} 14.0, Re–*C*≡C) 68.4 (d, J_{CP_X} 49.2, *C*(PMe_2Ph)) 39.9 (q, J_{CP} 10.0, $CH_{3\ triphos}$) 39.0 (q, J_{CP} 4.2, CH_3–$C_{triphos}$) 33.5 (m, $CH_{2\ triphos}$) 14.8 (d, J_{CP_X} 54.8, $P(CH_3)_2Ph$)	δ_A −7.87 (td) J_{AM} 19.3 δ_M −16.21 (dd) J_{AX} 3.0 δ_X 27.78 (td) J_{MX} 5.5 ν(C≡C) 2070 ν(CO) 1948, 1896
5[b] 	1.52 (q, J_{HP} 2.4, 3H, $CH_{3\ triphos}$) 2.33 (d, J_{HP_X} 12.0, 6H, $P(CH_3)_2Ph$) 2.50–2.80 (br m, 6H, $CH_{2\ triphos}$)	218.3 (dt, J_{CP_X} 9.3, J_{CPB} 2.8, C=*C*=CPh_2) 199.0 (dm, $J_{CP\ trans}$ 41.6, CO) 101.5(dd, J_{CP_X} 27.1, J_{CP_A} 2.9, C=C=*C*Ph_2) 74.0 (dm, J_{CP_X} 27.1, *C*=C=CPh_2) 39.1 (q, J_{CP} 9.7, $CH_{3\ triphos}$) 38.4 (q, J_{CP} 3.8, CH_3–$C_{triphos}$) 36.2 (td, J_{CPeq} 15.2, J_{CPax} 5.8, CH_2–$P_{eq\ triphos}$) 34.7 (d, J_{CPax} 23.2, CH_2–$P_{ax\ triphos}$) 14.3 (d, J_{CP_X} 55.2, $P(CH_3)_2Ph$)	δ_M −10.33 (td) J_{AM} 18.2 δ_A −19.47 (dd) J_{AX} 7.2 δ_X 29.05 (ps q) J_{MX} 7.2 ν(CO) + ν(C=C=C) 1935, 1880
6[b] 	1.60 (q, J_{HP} 2.4, 3H, $CH_{3\ triphos}$) 2.29 (d, J_{HP_X} 12.3, 3H, PCH_3Ph_2) 2.00–2.80 (br m, 6H, $CH_{2\ triphos}$)	218.3[d] (dt, J_{CPX} 9.3, <J>$_{CPB}$ 2.8, C=*C*=CPh_2) 199.0 (dm, $J_{CP\ trans}$ 41, CO) 102.2[d] (dd, J_{CP_X} 26.6, J_{CP_A} 2.8, C=C=*C*Ph_2) 71.6[d] (dm, J_{CP_X} 27.5, *C*=C=CPh_2) 39.4 (q, J_{CP} 9.4, $CH_{3\ triphos}$) 38.0 (q, J_{CP} 3.8, CH_3–$C_{triphos}$) 36.6 (dt, J_{CPeq} 22.5, J_{CPax} 6.6, CH_2–$P_{eq\ triphos}$) 34.7 (d, J_{CPax} 22.5, CH_2–$P_{ax\ triphos}$) 11.9[d] (d, J_{CP_X} 57.1, P*C*H_3Ph_2)	δ_A −12.19 (td) J_{AM} 18.2 δ_M −19.44 (br s) J_{AX} 6.1 δ_X 25.71 (ps q) J_{MX} 6.1 ν(CO) + ν(C=C=C) 1942, 1879 ν(OTf) 1271
7[b] 	1.42 (br s, $CH_{3\ triphos}$) 2.10–2.60 (br m, 6H, $CH_{2\ triphos}$) 2.65 (d, J_{HP_X} 12.6, 3H, $P(CH_3)Ph_2$)	Not recorded	δ_A −8.77 (t) J_{AM} 16.5 δ_M −17.22 (d) δ_X 24.01 (br s) ν(C≡C) 2075 ν(CO) 1955, 1890
8[c,i] 	1.58 (q, J_{HP} 2.7, 3H, $CH_{3\ triphos}$) 2.47 (d, J_{HPax} 8.4, 2H, CH_2–$P_{ax\ triphos}$) 2.40–2.80 (m, 4H, CH_2–$P_{eq\ triphos}$) 6.64[e,f,h] (d, $^{3}J_{HP_X}$ 91.1, C*H*=CPh_2)	200.2 (m, CO) 164.1[g] (dt, $^{2}J_{CP_X}$ 32.1, J_{CP_M} 3.8, *C*H=CPh_2) 149.5[d] (dq, $^{1}J_{CP_X}$ 31.0, $J_{CPA} \approx J_{CP_M}$ 10.3, Re–*C*=PPh_2) 69.1[d] (dd, $^{3}J_{CP_X}$ 39.2, J_{CP_A} 3.0, CH=*C*Ph_2) 40.4 (q, J_{CP} 10.0, $CH_{3\ triphos}$) 38.9 (q, J_{CP} 3.6, CH_3–$C_{triphos}$) 36.0 (td, J_{CPeq} 13.0, J_{CPax} 4.0, CH_2–$P_{eq\ triphos}$) 32.4 (d, J_{CPax} 22.9, CH_2–$P_{ax\ triphos}$)	δ_A −11.39 (ps t) J_{AM} 19.2 δ_M −13.97 (dd) J_{AX} 19.2 δ_X 60.80 (ps t) J_{MX} 10.8 ν(CO) 1946, 1886 ν(OTf) 1275
9[b] 	1.39 (br s, $CH_{3\ triphos}$) 2.20–2.80 (br m, 6H, $CH_{2\ triphos}$) 8.88 (d, J_{HP} 476, PH)	Not recorded	δ_A −8.27 (t) J_{AM} 19.0 δ_M −17.35 (d) δ_X 23.46 (br s) Not recorded

Table 2 (*Contd.*)

Compound	^{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})
10 [c, h, i] 	1.63 (br s, 3H, $CH_{3\ triphos}$) 2.40–2.80 (br m, 6H, $CH_{2\ triphos}$) 7.87 [e,f] (d, J_{HP_X} 477, 1H, P*H*Ph$_2$)	218.2 (dt, J_{CP_X} 10.0, J_{CPB} 3.5, C=*C*=CPh$_2$) 197.0 (m, CO) 104.5(dd, J_{CP_X} 26.4, J_{CP_A} 2.1, C=C=*C*Ph$_2$) 67.2 (dm, J_{CP_X} 27.6, *C*=C=CPh$_2$) 39.9 (q, J_{CP} 9.2, $CH_{3\ triphos}$) 38.5 (q, J_{CP} 3.6, CH_3–*C*$_{triphos}$) 36.0 (dm, J_{CPax} 26.0, CH_2–P$_{ax\ triphos}$) 34.3 (m, CH_2–P$_{eq\ triphos}$)	δ_A −6.80 (td) J_{AM} 19.3 δ_M −18.27 (br s) J_{AX} 7.6 δ_X 18.26 (td) J_{MX} 15.4 Not recorded
11 [c, i] 	1.59 (q, J_{HP} 2.8, 3H, $CH_{3\ triphos}$) 2.30–2.80 (m, 6H, CH_2–P$_{eq\ triphos}$) 3.3 (d, J_{HP} 12.0, 2H, PC*H*$_2$–C$_5$H$_4$FeC$_5$H$_5$) 4.05 (s, 5H, PCH$_2$C$_5$H$_4$FeC$_5$*H*$_5$) 4.08 (t, J_{HH} 1.9, 2H, PCH$_2$–C$_5$*H*$_4$FeC$_5$H$_5$) 4.13 (t, J_{HH} 1.9, 2H, PCH$_2$-C$_5$*H*$_4$FeC$_5$H$_5$) 5.23 (d, $^3J_{HP}$ 88.1, P$_X$–C*H*=CPh$_2$) 6.54 (d, $^1J_{HP}$ 410.3, P$_X$HR)	200.0 (m, CO) 199.6 (m, CO) 164.5 (dt, J_{CP} 32.3, 4.5, H*C*=CPh$_2$) 150.1 (m, Re–*C*=PR) 69.8 (s, PCH$_2$–C$_5$H$_4$Fe*C*$_5$H$_5$) 68.87 (d, $^2J_{CP}$ 7.0, PCH$_2$–*C*$_5$H$_4$FeC$_5$H$_5$) 68.42 (d, $^3J_{CP}$ 2.6, PCH$_2$–*C*$_5$H$_4$FeC$_5$H$_5$) 69.53 (s, PCH$_2$–*C*$_5$H$_4$FeC$_5$H$_5$) 64.70 (dd, J_{CP} 39.8, 5 Hz, RCH=*C*Ph$_2$) 39.99 (q, J_{CP} 9.7, *C*H$_3$–C$_{triphos}$) 39.45 (q, J_{CP} 4.2, CH_3–*C*$_{triphos}$) 35.62 (dt, J_{CP} 23.2, 4.5, PCH$_{2\ triphos}$) 35.08 (dt, J_{CP} 23.2, 4.5, PCH$_{2\ triphos}$) 32.47 (dt, J_{CP} 23.2, 4.5, PCH$_{2\ triphos}$) 24.05 (d, $^1J_{CP}$ 15.8, P*C*H$_2$–C$_5$H$_4$FeC$_5$H$_5$)	δ_A −13.57 (ddd) $J_{AM} \approx J_{AM'}$ 20.0 $\delta_{M'}$ −10.23 (ddd) J_{AX} 14.2 δ_M −8.12 (ddd) $J_{M'X}$ 10.0 δ_X 53.77 (ddd) J_{MX} 2.5 $J_{MM'}$ 28.0 ν(CO) 1932, 1866 ν(OTf) 1273
12 [c] 	1.69 (q, $J_{HH} \approx J_{HP}$ 2.4, 3H, $CH_{3\ triphos}$) 2.3–2.9 (m, PCH$_{2\ triphos}$) 4.12 (d, $^2J_{HP}$ 9.0, 2H, PC*H*$_2$–C$_5$H$_4$FeC$_5$H$_5$) 4.22 (s, 5H, PCH$_2$C$_5$H$_4$FeC$_5$*H*$_5$) 4.33 (t, J_{HH} 1.8, 2H, PCH$_2$–C$_5$*H*$_4$FeC$_5$H$_5$) 4.54 (t, J_{HH} 1.8, 2H, PCH$_2$–C$_5$*H*$_4$FeC$_5$H$_5$) 7.48 (t, $^3J_{HH} \approx {}^3J_{HP}$ 12.5, 1H, P$_X$=CH–C*H*R) 7.64 (t, $^3J_{HH} \approx {}^3J_{HP}$ 12.5, 1H, P$_X$=*CH*–CHR).	193.23 (tdd, J_{CP} 21.5, 12.7, 11.8 Hz, CO) 192.88 (tdd, J_{CP} 21.9, 12.9, 7.8 Hz, CO) 161.00 (d, $^1J_{CP}$ 46.0, P$_X$=*C*HR) 141.18 (d, $^3J_{CP}$ 38.9, RHC=*C*Ph$_2$) 127.12 (d, $^2J_{CP}$ 23.9, RH*C*=CPh$_2$) 83.58 (d, $^2J_{CP}$ 11.7, PCH$_2$–*C*$_5$H$_4$FeC$_5$H$_5$) 70.16 (d, $^3J_{CP}$ 1.5, PCH$_2$–*C*$_5$H$_4$FeC$_5$H$_5$) 69.75 (s, PCH$_2$–C$_5$H$_4$Fe*C*$_5$H$_5$) 68.90 (s, PCH$_2$–*C*$_5$H$_4$FeC$_5$H$_5$) 35.25 (d, $^1J_{CP}$ 7.5, P*C*H$_2$–*C*$_5$H$_4$FeC$_5$H$_5$)	δ_A −11.22 (dt) J_{AM} 22.4 δ_M −16.86 (dd) J_{AX} 132.7 δ_X 178.33 (dt) J_{MX} 31.3 ν(CO) 1946, 1886 ν(OTf) 1275

All the NMR spectra were recorded in CD_2Cl_2, at room temperature (20 °C) on a [a] Bruker AC200, [b] Varian VXR300 or [c] Bruker DRX500 instrument. All the ^{31}P{^{1}H} NMR spectra exhibit an AM_2X splitting pattern. Key: d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. [d] Assigned by DEPT-135 experiment. [e] Assigned by ^{31}P–^{1}H HMQC NMR experiment. [f] Assigned by ^{1}H{^{31}P} NMR. [g] Assigned by ^{13}C–^{1}H HMQC NMR experiment. [h] Registered at 0 °C. [i] In $CDCl_3$.

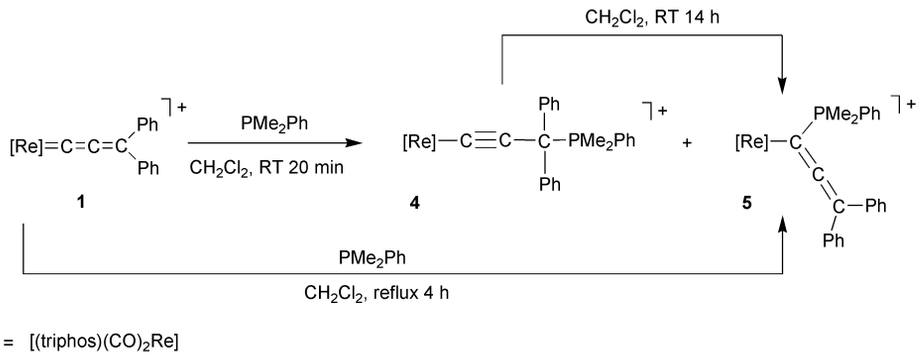


Scheme 3

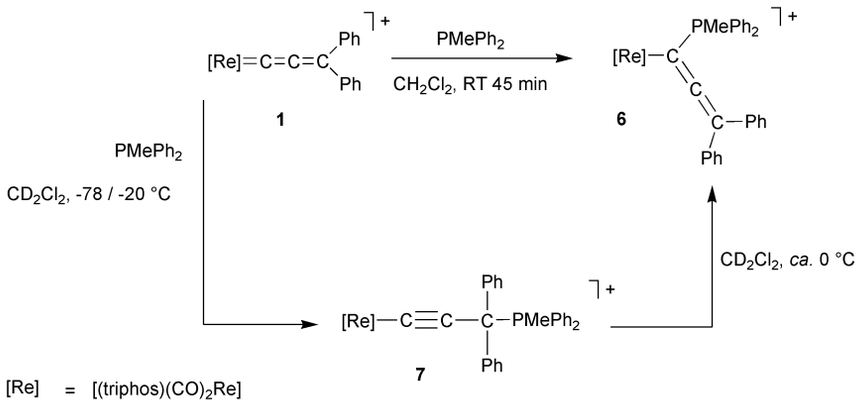
spectroscopic NMR (^{31}P, ^{1}H and ^{13}C) and IR data relative to the new rhenium(I) complexes described in this paper.

The reaction of **1** with 1.2 equivalents of PMe_3 in CH_2Cl_2 at room temperature (Scheme 3) gave the γ-phosphonioalkynyl complex [(triphos)(CO)$_2$Re{C≡CCPh$_2$(PMe$_3$)}]OTf (**2**) as a brownish red powder in fairly good yield. The IR spectrum of **2** contains a strong ν(C≡C) absorption band at 2074 cm^{-1} and two strong bands at 1950 and 1889 cm^{-1} that can be safely assigned to asymmetric and antisymmetric CO stretching frequencies, respectively. The ^{31}P{^{1}H} NMR spectrum consists of an AM_2X pattern. The low-field triplet of doublets at δ 33.25 is assigned to the quaternary phosphonium atom linked to the γ-carbon of the allenylidene ligand. The small coupling constants featuring this multiplet are similar to those reported for the related complexes [(Ind)Ru(dppm){CC≡CPh$_2$(PMe$_3$)}]PF$_6$,[18] and [Cp*Ru(PEt$_3$)$_2${CC≡CR$_2$(PEt$_3$)}]BPh$_4$ (R = Me, C$_5$H$_{10}$).[25] The other two high-field multiplets exhibit NMR parameters that are typical for triphos-P atoms in rhenium σ-alkynyl complexes [(triphos)(CO)$_2$Re(C≡CCPh$_2$R)]$^{0,+}$.[12a,14,15]

On standing in dichloromethane, **2** transformed into the α-phosphonioallenyl isomer [(triphos)(CO)$_2$Re{C(PMe$_3$)=C=CPh$_2$}]OTf (**3**) *via* selective migration of the PMe_3 ligand from C_γ to C_α. This conversion was very slow at room temperature. After 7 days, an NMR analysis in CD_2Cl_2 showed the presence of a *ca.* 4 : 1 mixture of **2** and **3**. A fast isomerisation occurred in refluxing CH_2Cl_2 where a complete transformation of **2** into **3** occurred in two days. Consistent with the NMR study, the reaction of PMe_3 with **1** in refluxing CH_2Cl_2 gave pure **3** in two



Scheme 4



Scheme 5

days. The isomerisation of **2** into **3** is irreversible. As a consequence of the **2** to **3** isomerisation, the resonance of the P_X phosphorus atom of PMe_3 shifts slightly highfield (δ_X 30.97) and shows larger coupling constants to the phosphorus atoms of triphos [$J(P_AP_X)$ 8.5, $J(P_MP_X)$ 7.0 Hz]. Particularly informative to validate the presence of an allenyl ligand in **3** was the $^{13}C\{^1H\}$ NMR spectrum showing a set of three resonances assigned to C_α (δ = 73.7), C_β (δ = 214.2), and C_γ (δ = 100.4), respectively, that are very similar to those reported for cationic α-phosphonioallenyl complexes.[18,19] The IR ν(C=C=C) absorption, usually considered as a *prima facie* evidence for proving the existence of a cumulenyl moiety, is not visible in the IR spectrum of **3** due to overlapping with the strong and broad ν(CO) bands (1880–1970 cm^{-1}).

2 Reaction of 1 with dimethylphenylphosphine. Treatment of the allenylidene **1** with PMe_2Ph as described above gave a mixture of two regioisomers resulting from γ- and α-attacks by the phosphine to the unsaturated carbon chain (Scheme 4). These rhenium(I) complexes, [(triphos)$(CO)_2$Re{C≡CCPh_2-(PMe_2Ph)}]OTf (**4**) and [(triphos)$(CO)_2$Re{C(PMe_2Ph)=C=CPh_2}]OTf (**5**) were formed in *ca.* 1 : 1 ratio (^{31}P NMR integration).

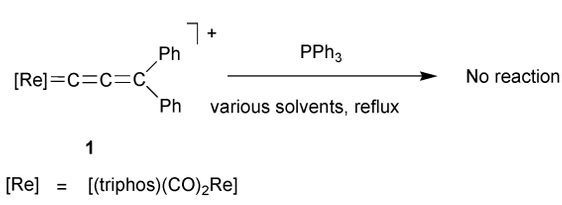
On standing overnight at room temperature in dichloromethane, **4** transformed completely into **5**. Alternatively, a pure sample of the allenyl isomer was isolated as red crystals by refluxing a CH_2Cl_2 solution of **1** and PMe_2Ph for four hours.

Carrying out the reaction between **1** and PMe_2Ph at −20 °C increased the concentration of **4** in the isolated product (3 : 1 ratio), yet the γ-phosphonioalkynyl isomer was never obtained in pure form.

3 Reaction of 1 with methyldiphenylphosphine. The allenylidene **1** reacted with $PMePh_2$ in CH_2Cl_2 at room temperature to give exclusively the α-phosphonioallenyl complex [(triphos)-$(CO)_2$Re{C($PMePh_2$)=C=CPh_2}]OTf (**6**) (Scheme 5).

This reaction does not take place *via* direct phosphine attack to the α-carbon atom of the Re=C=C=C unit. Also in this case, in fact, the phosphine attacks primarily the Cγ, atom, and then migrates to C_α. The stepwise nature of this reaction was unambiguously documented by an *in situ* ^{31}P NMR study at low temperature in CD_2Cl_2. Complex **1** reacted with $PMePh_2$ already at −78 °C, yielding selectively the γ-phosphonioalkynyl complex [(triphos)$(CO)_2$Re{C≡CCPh_2($PMePh_2$)}]OTf (**7**). The irreversible isomerisation of **7** into **6** started to occur at −20 °C and was complete in a few minutes at 0 °C.

4 Reaction of 1 with triphenylphosphine. In contrast to the more nucleophilic and less sterically demanding phosphines described above, PPh_3 did not react with **1** in either refluxing dichloromethane or other higher-boiling solvents such as $CHCl_3$, THF or dioxane (Scheme 6). In DMSO or DMF, no reaction occurred before 110 °C. Above this temperature, extensive decomposition was observed.



Scheme 6

5 Mechanistic considerations. As previously reported, tertiary phosphines may react with transition metal allenylidenes with formation of P–C bonds involving either C_α or C_γ.[6a,18–27] With only one known exception,[18] metal allenylidenes and PR_3 react with C_α regiochemistry. Whether this regioselectivity is thermodynamically or kinetically driven is still a matter of debate. Factors such as the bulkiness of the phosphine and of the C_γ-substituents have been considered important in controlling the outcome of the reaction.[18,19]

The results reported in this paper provide unambiguous evidence for a strict kinetic control. Indeed, irrespective of the bulkiness of the tertiary phosphine, it has been observed that

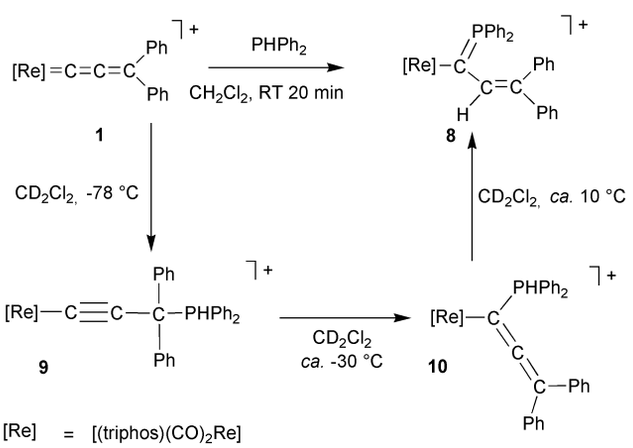
the phosphine primarily attacks the C_γ-allenylidene carbon of **1** to give γ-phosphonioalkynyl species $[(triphos)(CO)_2Re\{C{\equiv}CCPh_2(PMe_{3-x}Ph_x)\}]^+$, which thermally and irreversibly isomerise to the thermodynamically stable α-phosphonioallenyl species $[(triphos)(CO)_2Re\{C(PMe_{3-x}Ph_x){=}C{=}CPh_2\}]^+$. A similar process has been previously observed for the reaction of ammonia with **1**, resulting in the kinetic formation of the γ-ammonioalkynyl complex $[(triphos)(CO)_2Re\{C{\equiv}CCPh_2(NH_3)\}]^+$.[15]

The γ-phosphonioalkynyl ⟶ α-phosphonioallenyl isomerisation is fast even at −20 °C for $PMePh_2$. In contrast, the less bulky and more nucleophilic PMe_2Ph yields a mixture of the two isomers at room temperature, while the less sterically demanding PMe_3 affords a γ-phosphonioalkynyl complex with complete regioselectivity already at room temperature. These result provide an unambiguous correlation between the nucleophilicity of the phosphine and the propensity to attack at C_γ. They also indicate that the steric hindrance created by the supporting ligand around the metal centre, hence also around C_α, does not play a crucial role in determining the regioselectivity of the nucleophilic addition.[19] Indeed, the formation of the allenyl product is easier for $PMePh_2$ than for PMe_3, which stabilises the γ-adduct. In contrast, the steric hindrance provided by the substituents at C_γ seems to be of mandatory importance to allow for nucleophilic additions to that carbon atom. As a matter of fact, **1** does not react with PPh_3 even under reflux in dioxane. One may argue that PPh_3, being less basic than any other tertiary phosphine investigated in this paper, does not attack a relatively weak electrophile such as C_γ. This "electronic control" cannot be excluded *a priori*, yet it is not likely as a PPh_3 α-adduct has been obtained by Esteruelas with $[CpRu(CO)(PPr^i_3)(C{=}C{=}CPh_2)]^+$, which is less sterically congested at C_α than **1**,[19] while a γ-adduct has been isolated by Gimeno from the reaction of PPh_3 with the primary allenylidene $[(Ind)Ru(L)_2\{C{=}C{=}C(Ph)H\}]^+$.[18]

Reaction of 1 with primary and secondary phosphines

1 Reaction of with $PHPh_2$. The reaction between the allenylidene **1** and the secondary phosphine $PHPh_2$ was examined in an attempt to demonstrate that the typical reactivity of the metallacumulenes towards N–H bonds[6,7,15] may be extended to P–H bonds.

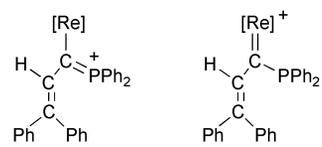
The treatment of **1** with $PHPh_2$ in CH_2Cl_2 at room temperature gave selectively the alkenylphosphinocarbene $[(triphos)(CO)_2Re\{C(PPh_2)CH{=}CPh_2\}]OTf$ (**8**) (Scheme 7).



Scheme 7

Formally, the synthesis of **8** involves a P–H addition across the $C_\alpha{=}C_\beta$ double bond, as occurs for N–H bonds from primary and secondary amines.[15] The presence of an unsaturated phosphoniobutadienyl ligand in **8** was inferred from a comparison of its NMR data with those collected for a variety of related unsaturated carbene, thiocarbene and azoniabutadienyl ligands supported by the Re(triphos) fragment.[13,15] Particularly informative was the presence in the ^1H NMR spectrum of one proton signal at 6.64 ppm, in the typical region for the vinyl protons of $[(triphos)(CO)_2Re\{C(XR)CH{=}CPh_2\}]^+$ complexes (X = O,[13] S,[15] NH).[15] This vinyl resonance is split by a strong coupling to phosphorus and collapses to a singlet in the selective decoupled $^1H\{^{31}P_X\}$ NMR spectra ($^3J_{HP_X}$ 91.1 Hz in **8**). Noticeably, proton detected 2D ^1H-^{31}P and ^1H-^{13}C heterocorrelation NMR experiments correlate the 6.64 ppm ^1H-resonance with both the phosphorus resonance at 60.80 ppm and the *CH* carbon resoanace at 164.1 ppm.

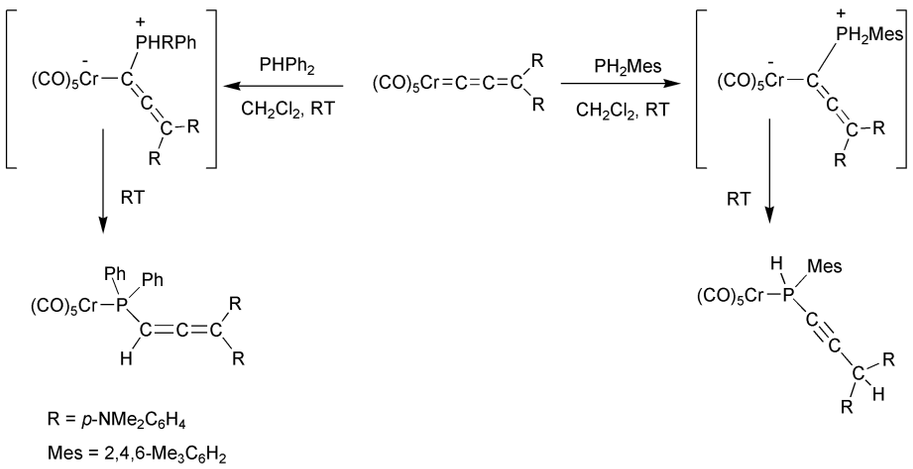
The formulation of a phophoniobutadienyl complex (**I**) rather than an alkenyl phosphinocarbene derivative (**II**) was also supported by the NMR chemical shift of the PPh_2 group bonded to C_α (P_X).



I **II**

The phosphorus multiplet at 60.80 ppm is considerably deshielded as compared to the phosphonioalkynyl and phosphonioallenyl derivatives discussed above, which may be consistent with some double-bond character of the $PPh_2{=}C$ linkage. In keeping with this hypothesis, the *C*PPh_2 carbon atom appears in the $^{13}C\{^1H\}$ NMR spectrum as a doublet of quartets (δ = 149.5), significantly high-field shifted with respect to the value of genuine Re=C carbenes.[12–15] Unexpectedly, the J_{CP} coupling constants involving the PPh_2 group and the three carbons of the butadienyl moiety are such that $^1J_{CP_X}$ (31.0 Hz) is of the same magnitude of $^2J_{CP_X}$ (32.1 Hz) and even smaller than $^3J_{CP_X}$ (39.2 Hz). A similar $^1J_{CP}$ value (35.8 Hz) has been reported for the chromium diphenylallenylphosphino complex $[(CO)_5Cr\{\eta^1\text{-}P\text{-}PPh_2C{=}C{=}C(p\text{-}NMe_2C_6H_4)_2\}]$,[22] while a comparable *J*-trend, with $^3J_{CP} > {}^1J_{CP}$, has been also observed for the η^1-phosphallenyl complex $[CpRu(CO)(PPr^i_3)\{C(PHPh_2){=}C{=}CPh_2\}]BF_4$.[19] These Cr and Ru compounds were obtained by reacting $PHPh_2$ with $[(CO)_5Cr\{C{=}C{=}C(p\text{-}NMe_2C_6H_4)_2\}]$[22] and $[CpRu(CO)(PPr^i_3)(C{=}C{=}CPh_2)]BF_4$[19] (Scheme 2), respectively, and represent the only known reactions of metal allenylidenes with secondary phosphines. A direct regioselective attack at C_α has been invoked to account for the formation of the Ru complex $[CpRu(CO)(PPr^i_3)\{\eta^1\text{-}C\text{-}C(PHPh_2){=}C{=}CPh_2\}]$, while the Cr phosphinoallenyl complex was generated through an intramolecular isomerisation of a labile η^1-*C*-phosphonioallenyl derivative. The latter reaction is shown in the left-hand side of Scheme 8.

2 The mechanism of the reaction between 1 and $PHPh_2$. Scheme 7 shows that the allenylidene **1** reacts at room temperature with $PHPh_2$ to give the phosphoniobutadienyl complex **8**, which is the thermodynamic and not the kinetic product. Therefore the mechanism by which $PHPh_2$ reacts with **1** is initially similar to those reported above for tertiary phosphines: the first product to form is the phosphonioalkynyl complex $[(triphos)(CO)_2Re\{C{\equiv}CCPh_2(PHPh_2)\}]OTf$ (**9**), which then undergoes an intramolecular isomerisation to the α-phosphonioallenyl derivative $[(triphos)(CO)_2Re\{C(PHPh_2){=}C{=}CPh_2\}]OTf$ (**10**). Complex **10** is not the thermodynamic product, however. Indeed, monitoring the reaction between **1** and $PHPh_2$ by $^{31}P\{^1H\}$ NMR spectroscopy showed the formation of **9** already after mixing the reagents at −78 °C. The γ ⟶ α isomerisation transforming **9** into **10** was appreciable at −70 °C and was complete already at −30 °C, however increasing the temper-



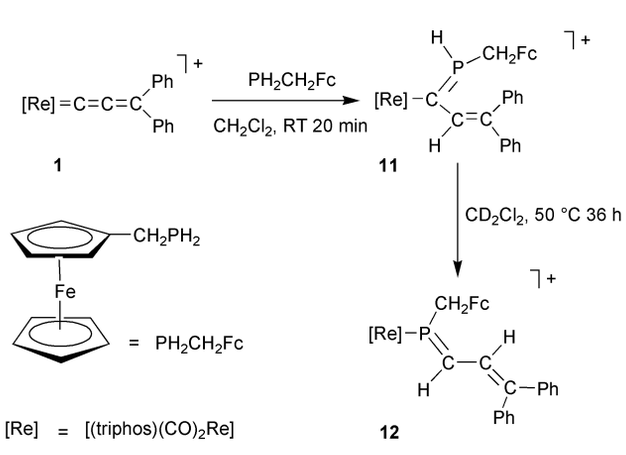
Scheme 8

ature to 10 °C, showed **10** to convert into the thermodynamic product **8**.

If one considers that the P-atom of free $PHPh_2$ resonates at −39.4 ppm, the nucleophilic addition of the phosphine to **1** causes a remarkable downfield shift of the P-resonance which moves to about 20 ppm in **9** (23.46 ppm) and **10** (18.26 ppm), then to 60.80 ppm in **8**. This trend can be accounted for by the progressive decrease of electron density on the phosphorus atom, which forms a single P–C bond in **9** and **10** and a double P=C bond in the phosphoniobutadienyl complex **8**.

3 Reaction of 1 with PH_2CH_2Fc (Fc = ferrocenyl). Unlike most primary and secondary phosphines, the (ferrocenylmethyl)phosphine, PH_2CH_2Fc, is completely air-stable in the solid state[34] and therefore is particularly suited to investigate the reactivity of a primary phosphine towards transition metal complexes.

The allenylidene **1** smoothly reacts at room temperature with PH_2CH_2Fc in dichloromethane yielding the phosphoniobutadienyl complex [(triphos)$(CO)_2$Re{C(=P(H)CH_2Fc)CH=CPh_2}]OTf (**11**) (Scheme 9). The presence of an η^1-*C*-phosphoniobutadienyl in **11** was inferred by an in-depth NMR analysis. Indeed, complexes **11** and **8** share most of the chemical-physical properties and, in particular, exhibits a quite comparable NMR fingerprint, apart for the signals ascribable to the pending ferrocenylmethyl moiety in **11** (Table 2). It is worth mentioning that the bilateral symmetry of the triphos ligand is absent in **11** as a consequence of the unsymmetrical nature of the phosphonio substituents and/or the bulkiness of the ferrocenylmethyl group. Due to the reduced symmetry, the $^{31}P\{^1H\}$ NMR spectrum of **11** consists of a four spin AMM'X system with two PPh_2 groups *trans* to carbonyls showing different chemical shifts and coupling constants.



Scheme 9

Monitoring of the reaction leading to **11** by variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy did not provide any mechanistic information. Indeed, no intermediate was observed along the transformation of **1** into **11**, occurring immediately after PH_2CH_2Fc and **1** were mixed in CH_2Cl_2 at −78 °C. However, we cannot exclude initial attack of the phosphines on C_γ, followed by migration from C_γ to C_α.

Scheme 8 (right-hand side) illustrates the reaction of the Fischer's chromium allenylidene [$(CO)_5$Cr{C=C=C(*p*-NMe_2-$C_6H_4)_2$}][22] with the primary phosphine PH_2Mes (Mes = 2,4,6-$Me_3C_6H_2$) to form an η^1-*P*-alkynylphosphine ligand. In view of the results presented in this paper, it is likely that the alkynylphosphine ligand is formed *via* P–H bond activation and 1,4-*P*,*C*-H shift from an α-phosphonioallenyl intermediate.

In contrast to Fischer's derivative, **11** is stable at room temperature in both the solid state and solution under nitrogen. On heating a solution of **11** in CD_2Cl_2 in a sealed NMR tube at 50 °C, the complex [(triphos)$(CO)_2$Re{P(CH_2Fc)=CHCH=CPh_2}]OTf (**12**) was slowly formed. This rearrangement was complete in *ca.* 36 h (^{31}P NMR monitoring), yet the reaction was not selective yielding several secondary products, that have not been identified. Heating of a CD_2Cl_2 solution of **11** at 50 °C in a sealed NMR tube gave the η^1-*P*-phospha-1-butadienyl complex [(triphos)$(CO)_2$Re{P(CH_2Fc)=CHCH=CPh_2}]OTf (**12**) in *ca.* 80% yield. Prolonged heating in CD_2Cl_2 or the use of other halogenated solvents ($CDCl_3$, $C_2D_4Cl_2$) gave poor results. Workup in CD_2Cl_2 gave an analytically pure sample of **12**, albeit in low yield (< 25%). Elimination of the solvent *in vacuo* left a reddish-brown residue which was dissolved in the minimum volume of chloroform, filtered through Celite and then stored at −10 °C for 48 h to yield **12** as thin dark brown needles.

The solution structure of **12** was determined by means of multinuclear, multidimensional NMR spectroscopy (Table 2). All the resonances were unambiguously assigned by a combination of 1D and 2D NMR spectra.

The $^{31}P\{^1H\}$ NMR spectrum of **12** consists of an AM_2X spin system whose resonances were easily attributed based on NMR integration and J_{PP} coupling constants. The $^{31}P\{^1H\}$ signal observed at 178.33 ppm is assigned to the η^1-*P*-phospha-1-butadiene phosphorus (P_X) on the basis of the large downfield shift as compared to the triphos phosphorus atoms (−11.22 P_A and −16.86 ppm P_M). Similar and even larger lowfield resonances are typical for the few transition metal η^1-*P*-1-phospha-1-butadienyl complexes reported in the literature.[35] The $^2J_{P_AP_X}$ coupling value (132.7 Hz) indicates the existence of a direct Re–P_X bond, and also suggests the mutual *trans* disposition of P_X and P_A,[36–38] while the equivalence of the two P_M atoms *trans* to the carbonyl ligands points to the existence of a small rotational barrier about the Re–P bond. The dienyl nature of

the C_3-chain bounded to P_X and originally pertaining to the allenylidene ligand in **1**, was confirmed by a careful investigation of the ^1H and $^{13}C\{^1H\}$ NMR spectra. Indeed, the ^1H NMR spectrum shows two triplets (7.48 and 7.64 ppm) attributable to two η^1-*P*-1-phospha-1-butadienyl group protons. Selective $^1H\{^{31}P\}$ NMR decoupling experiments from the P_X phosphorus confirmed this assignment ($^3J_{HP}$ and $^2J_{HP}$ *ca.* 12.5 Hz, respectively). Three doublets in the $^{13}C\{^1H\}$ NMR spectrum feature the phosphabutadienyl carbons; the first two signals show positive DEPT-135 signals and exhibit ^1J proton connectivities and are therefore assigned to the CH butadienyl carbons (161.00 ppm, $^1J_{CH}$ 150.7 Hz, C_α; 127.12 ppm, $^1J_{CH}$ 149.5 Hz, C_β, respectively), while the third signal, nulling in the DEPT experiment, is ascribed to the quaternary C_γ carbon (141.18 ppm). Again, this attribution was confirmed by selective $^{13}C\{^1H\}\{^{31}P_X\}$ NMR decoupling experiments ($^1J_{CP}$ 46.0, C_α; $^2J_{CP}$ 23.9, C_β; $^3J_{CP}$ 38.9 Hz, C_γ) that showed the collapse of the J_{CP} doublets into singlets (Fig. 2).

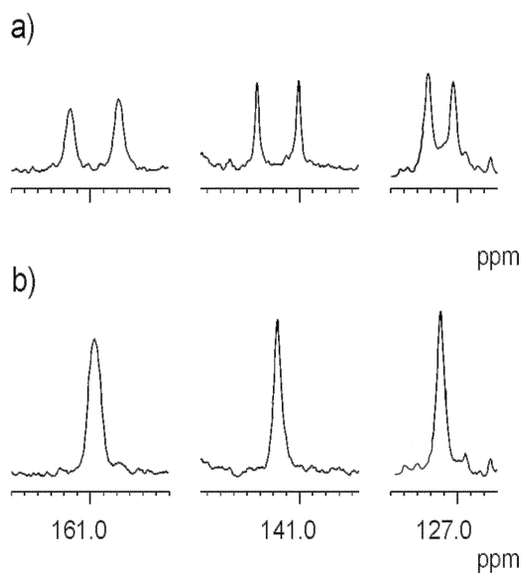


Fig. 2 Sections of the ^{13}C NMR spectrum of **12** (CD_2Cl_2, 125.80 MHz, 20 °C). (a) $^{13}C\{^1H\}$ NMR spectrum. (b) $^{13}C\{^1H\}\{^{31}P\}$ NMR spectrum acquired with selective decoupling of the P_X resonance at 178.33 ppm.

The formation of **12** from **11** involves the replacement of carbon by phosphorus in coordinating the metal centre (Scheme 9), which means that the isomerisation process, transforming the *C*-bonded phosphoniobutadienyl ligand of **11** into the *P*-bonded phosphabutadienyl of **12**, requires a preliminary 1,2-*P*,*C*-H shift. However, no intermediate species was seen to traverse the conversion of **11** to **12** on the NMR timescale. Therefore, any mechanistic consideration at this stage would be only speculation.

Conclusion

The results reported in this paper represent another chapter of the rich chemistry of allenylidene metal complexes. It has been shown that metal centres can mediate the addition of tertiary, secondary and primary phosphines to the allenylidene moiety, leading to a variety of phosphorus-containing unsaturated hydrocarbyls. As a general mechanistic trend, it has been found that phosphines attack the allenylidene-C_γ carbon atom to give kinetic γ-phosphonioalkynyl products that thermally transform into thermodynamic α-phosphonioallenyl derivatives. Only at this stage, primary and secondary phosphines undergo 1,3-*P*,*C*-H shift to give α-phosphoniobutadienyl complexes. These are the final products for PHR_2, while for PH_2R evolve to η^1-*P*-phospha-1-butadienyl derivatives *via* 1,2-*P*,*C*-H shift, followed by *C*,*P*-bonding isomerisation.

Experimental

General information

The preparation, purification and further reactions of the rhenium complexes described in this paper were carried out under an atmosphere of dry nitrogen using distilled and deoxygenated solvents. Dichloromethane was purified by distillation over P_2O_5. The compound $[(triphos)(CO)_2Re\{C{=}C{=}CPh_2\}]OTf$ (**1**) was prepared as reported in the literature.[13] Diphenylphosphine and trimethylphosphine (Argus Chemicals) were checked by NMR spectroscopy and distilled under nitrogen before use when necessary before being stored at low temperature under inert atmosphere. The primary phosphine PH_2CH_2Fc (Fc = Ferrocenyl) was synthesized following the published method of Henderson and coworkers[34] and stored under nitrogen in the refrigerator. Unless stated otherwise, all the other reagents and chemicals were reagent grade and were used as received by commercial suppliers. The solid complexes were collected on sintered glass-frits and washed with ethanol and light light petroleum (b.p. 40–60 °C) before being dried in a stream of nitrogen.

Deuterated chloroform and dichloromethane for NMR measurements (Aldrich) were dried over molecular sieves (4 Å). ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC200, Varian VXR300 or Bruker AVANCE DRX 500 spectrometers operating at 200.13, 299.94 or 500.13 MHz (^1H), 50.32, 75.42 or 125.80 MHz (^{13}C) and 81.01, 121.42 or 202.45 MHz (^{31}P), respectively. Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (^1H) or the deuterated solvent multiplet (^{13}C). Chemical shifts were measured relative to external 85% H_3PO_4 with downfield values taken as positive. ^{13}C-DEPT-135 experiments were run on the Bruker AC200 spectrometer. The NMR characterization of complexes **8**, **11** and **12** was carried out on the Bruker Avance DRX-500 spectrometer equipped with a triple resonance probe head. The assignment of the signals resulted from 1D spectra, $^{13}C\{^1H\}$-DEPT, 2D ^1H-DQF-COSY and proton detected 2D ^1H–^{13}C and ^1H–^{31}P correlations. 2D NMR spectra were recorded on degassed nonspinning samples using pulse sequences suitable for phase-sensitive representations using TPPI. J_{HH} and J_{HP} coupling constants were obtained from 1D $^1H\{^1H\}$ homonuclear and selective $^1H\{^{31}P\}$ heteronuclear decoupling experiments, J_{CP} coupling constants were obtained from 1D $^{13}C\{^1H\}$ and $^{13}C\{^1H\}\{^{31}P\}_{sel}$ spectra. The standard pulse sequence was used for the ^1H-DQF-COSY[39] experiment. The ^1H–^{31}P[40] and ^1H–^{13}C[37] correlations were recorded using the standard HMQC sequence with ^1H decoupling and with no ^1H decoupling during acquisition, respectively.

Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 1600 series FT-IR spectrometer between KBr plates. Elemental analyses (C, H) were performed using a Carlo Erba model 1106 elemental analyzer by the staff of the Microanalytical Service of ICCOM CNR.

Syntheses

$[(triphos)(CO)_2Re\{C{\equiv}CCPh_2(PMe_3)\}]OTf$ (2)

25 μL of PMe_3 (0.25 mmol) was added *via* syringe to a purple solution of **1** (250 mg, 0.21 mmol) in 15 mL of CH_2Cl_2 under vigorous stirring. The resulting solution was stirred for 30 min at room temperature during which time the colour turned brownish red. The resulting solution was concentrated to *ca.* 5 mL *in vacuo.* Addition of 20 mL of a 1 : 2 (v/v) mixture of ethanol–light petroleum gave a brownish red precipitate. The solid product was filtered off, washed with light petroleum and dried *in vacuo*. Yield 215 mg (80%). Elemental analysis: $C_{62}H_{58}F_3O_5P_4SRe$: Calc. C, 58.07; H, 4.56. Found: C, 58.25; H, 4.48.

[(triphos)(CO)$_2$Re{C(PMe$_3$)=C=CPh$_2$}]OTf (3)

A solution of **1** (200 mg, 0.17 mmol) and PMe_3 (25 μL, 0.25 mmol) in CH_2Cl_2 (30 mL) was heated under reflux for 48 h. The resulting reddish-brown solution was evaporated to *ca*. 5 mL *in vacuo* and then layered with (5 mL) of 1 : 2 (v/v) ethanol–light petroleum mixture and stored overnight to yield a reddish-brown microcrystalline solid. Yield 160 mg (75%). Elemental analysis: $C_{62}H_{58}F_3O_5P_4SRe$: Calc.: C, 58.07; H, 4.56. Found: C, 58.03; H, 4.62%.

Attempted synthesis of [(triphos)(CO)$_2$Re{C≡CCPh$_2$(PMe$_2$Ph)}]-OTf (4)

(A) Room-temperature reaction. 36 μL of PMe_2Ph (0.25 mmol) was syringed into a purple CH_2Cl_2 solution (25mL) of **1** (250 mg, 0.21 mmol). The resulting solution was stirred for 20 min at room temperature, evaporated to half volume. The addition of 20 mL of a 1 : 3 (v/v) diethyl ether–light petroleum mixture caused the separation of a red microcrystalline solid. The solid compound was collected by filtration, washed with diethyl ether and light petroleum before being dried under nitrogen.

The solid product was a *ca.* 1 : 1 mixture of the isomers [(triphos)(CO)$_2$Re{C≡CCPh$_2$(PMe$_2$Ph)}]OTf (**4**) and [(triphos)(CO)$_2$Re{C(PMe$_2$Ph)=C=CPh$_2$}]OTf (**5**). Yield 226 mg (80%). Elemental analysis: $C_{67}H_{60}F_3O_5P_4SRe$: Calc.: C, 59.86; H, 4.50. Found C, 59.68; H, 4.59%.

(B) Low-temperature reaction. Repeating the reaction of **1** and PMe_2Ph at −20 °C gave, after similar work-up, dark red microcrystals which NMR spectroscopy showed to be a 3 : 1 mixture of **4** and **5**. Yield 180 mg (64%).

Isomerisation of 4 into 5. 150 mg of a 1 : 1 mixture of **4** and **5** was dissolved in 10 mL of CH_2Cl_2 under nitrogen and stirred overnight at room temperature. Evaporation of the solution to dryness left a red solid which was washed with light petroleum and dried *in vacuo*. A ^{31}P NMR analysis confirmed the quantitative transformation of **4** into **5**.

[(triphos)(CO)$_2$Re{C(PMe$_2$Ph)=C=CPh$_2$}]OTf (5). A solution of **1** and PMe_2Ph, prepared in CH_2Cl_2 as described above, was heated under reflux for 4 h before being cooled to room temperature and worked-up as described above to yield an analytically pure sample of **5**. Yield 210 mg (75%). Elemental analysis: $C_{67}H_{60}F_3O_5P_4SRe$: Calc.: C, 59.86; H, 4.50. Found: C, 59.09; H, 4.62.

[(triphos)(CO)$_2$Re{C(PMePh$_2$)=C=CPh$_2$}]OTf (6). To a purple solution of **1** (250 mg, 0.21 mmol) in 20 mL of CH_2Cl_2 was added 47 μL of $PMePh_2$ (0.25 mmol) *via* syringe under vigorous stirring. The mixture was stirred for 45 min at room temperature during which time the solution turned red. The solution was then concentrated to *ca.* 8 mL and then diluted with 20 mL of a 1 : 3 (v/v) diethyl ether/light petroleum mixture. The red solid which slowly separated out was filtered off, washed with light petroleum and dried *in vacuo*. Yield 207 mg (70%). Elemental analysis: $C_{72}H_{62}F_3O_5P_4SRe$: Calc.: C, 61.49; H, 4.44. Found: C, 61.70; H, 4.51.

***In situ* NMR Reaction of 1 with PMePh$_2$.** A solution of **1** (40 mg, 0.033 mmol) in CD_2Cl_2 (0.8 mL) was prepared in a 5 mm screw-cap NMR tube and cooled to −78 °C with a dry ice/acetone bath before 6.2 μL of $PMePh_2$ (*ca.* 0.033 mmol) was added through the serum cap *via* a microsyringe. The tube was inserted into the NMR probe precooled at −80 °C and the progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. At this temperature, **1** reacted with the phosphine yielding a brick-red coloured solution containing [(triphos)-(CO)$_2$Re{C≡CCPh$_2$(PMePh$_2$)}]OTf (**7**). At −20 °C a new set of NMR resonances due to the allenyl isomer **7** began to appear. The transformation of **7** into **6** was complete at *ca.* 0 °C.

[(triphos)(CO)$_2$Re{C(=PPh$_2$)CH=CPh$_2$}]OTf (8). 44 μL of neat $PHPh_2$ (0.25 mmol) was added under vigorous stirring to a purple solution of (**1**) (250 mg 0.21 mmol) in 25 mL of CH_2Cl_2 at room temperature. The solution was further stirred for 20 min during which time the colour changed to ochre. Evaporation of the solution *in vacuo* to *ca.* 10 mL and addition of 15 mL of a 1 : 3 (v/v) ethanol–light petroleum mixture gave an ochre solid which was filtered off, washed in turn with diethyl ether and light petroleum before being dried *in vacuo*. Yield 228 mg (78%). Elemental analysis: $C_{71}H_{60}F_3O_5P_4SRe$: Calc.: C, 61.24; H, 4.34. Found: C, 61.45; H, 4.34.

***In situ* NMR Reaction of 1 with PHPh$_2$.** A solution of **1** (40 mg, 0.033 mmol) in CD_2Cl_2 (0.8 mL) was prepared in a 5 mm screw-cap NMR tube and cooled to −78 °C with a dry-ice/acetone bath and 5.8 μL of $PHPh_2$ (*ca.* 0.033 mmol) was added through the serum cap. The tube was inserted into the NMR probehead precooled at −80 °C and the progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. A first spectrum run at −80 °C showed that **1** had already initiatiated to react with the phosphine yielding [(triphos)(CO)$_2$Re{C≡CCPh$_2$-(PHPh$_2$)}]OTf (**9**). At −70 °C, the resonances due to [(triphos)(CO)$_2$Re{C(PHPh$_2$)=C=CPh$_2$}] OTf (**10**) appeared in the spectrum and at −50 °C a 1 : 1 mixture of **9** and **10** was formed. At −30 °C, only the NMR signals of **10** were observed. At temperatures higher than 10 °C, the isomerisation of **10** into **8** was observed. The isomerisation was complete within 1 h at room temperature.

[(triphos)(CO)$_2$Re{C(=PHCH$_2$Fc)CH=CPh$_2$}]OTf (11). 65 mg of solid PH_2CH_2Fc (0.28 mmol) were added to a CH_2Cl_2 solution (25mL) of **1** (250 mg, 0.21 mmol). The mixture was stirred for 20 min at room temperature to give a tawny solution. Addition of an 1 : 2 (v/v) ethanol/light petroleum solution (20 mL) and slow concentration of the solution gave a burgundy red solid, which was filtered off, washed in turn with diethyl ether and light petroleum and dried *in vacuo*. Yield 242 mg (80%). Elemental analysis: $C_{70}H_{62}F_3O_5P_4SFeRe$: Calc.: C, 58.46; H, 4.34. Found: C, 58.75; H 4.45%.

***In situ* NMR Monitoring of the reaction between 1 and PH$_2$CH$_2$Fc.** A 5 mm screw-cap NMR tube cooled to −78 °C with a dry ice/acetone bath was charged with two cold (−78 °C) 0.5 mL CD_2Cl_2 solutions containing **1** (40 mg, 0.033 mmol) and PH_2CH_2Fc (7.7 mg. 0.033 mmol), respectively. The tube was gently shaken and inserted into the NMR probe precooled at −80 °C and the progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, showing the immediate reaction of **1** with the phosphine to yield **11** with no intermediate species. The reaction completed at −60 °C.

[(triphos)(CO)$_2$Re{P(CH$_2$Fc)=CHCH=CPh$_2$}]OTf (12). A 5-mm NMR tube was charged under nitrogen with a solution of **11** (120 mg, 0.083 mmol) in CD_2Cl_2 (0.8 mL) and flame sealed. The tube was positioned into an oil bath thermostatted at 50 °C for 36 h, which causes a progressive darkening of the solution. An NMR analysis of the solution confirmed the formation of **12** (*ca.* 80%) together with several secondary products which denied first order analysis. The tube was cooled to room temperature and opened under nitrogen before being evaporated to dryness *in vacuo* to give a reddish-brown residue which was washed in turn with diethyl ether and light petroleum before being dried *in vacuo*. The solid was dissolved in the minimum volume of chloroform, filtered through Celite and then stored at −10 °C for 48 h to yield *ca.* 26 mg of thin dark brown needles of **12**. Yield *ca.* 22%. Elemental analysis: $C_{70}H_{62}F_3O_5P_4SFeRe$: Calc.: C, 58.46; H, 4.34. Found: C, 58.21; H 4.53%.

Table 3 Crystallographic data for [(triphos)$(CO)_2$Re(C=C=CPh_2)]-BPh_4 (**1/BPh_4**)

Compound	**1/BPh_4**
Formula	$C_{58}H_{49}O_2P_3Re{\cdot}C_{24}H_{20}B$
M	1376.29
Space group	$P\bar{1}$
Crystal system	Triclinic
a/Å	12.2030(2)
b/Å	16.7569(3)
c/Å	19.3716(5)
α/°	113.430(1)
β/°	105.697(1)
γ/°	93.961(1)
U/Å^3	3428.3(1)
Z	2
D_c/g cm^{-3}	1.333
F(000)	1404
μ(Mo-Kα)/cm^{-1}	18.89
Measured reflns.	52404
Unique refns.	19771
R_{int}	0.062
Obs. reflns. [$I \geq 2\sigma(I)$]	15139
θ_{min}–θ_{max}/°	3–30
hkl ranges	−17, 17; −23, 23; −27, 25
$R(F^2)$ (obs. reflns.)	0.0460
$wR(F^2)$ (all reflns.)	0.1237
No. variables	803
Goodness of fit	1.044
ρ_{min}, ρ_{max}/e Å^{-3}	−1.920, 0.965

X-Ray diffraction study of [(triphos)$(CO)_2$Re(C=C=CPh_2)]BPh_4 (1/BPh_4)

Crystal data of compound **1** were collected on a Nonius Kappa CCD diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å) at room temperature (295 K). Data sets were integrated with the Denzo-SMN package[41] and corrected for Lorentz-polarization and absorption[42] effects. The crystal parameters and other experimental details of the data collections are summarized in Table 3. The structure was solved by direct methods (SIR97)[43] and refined by full-matrix least squares methods with all non-hydrogen atoms anisotropic and hydrogens included on calculated positions, riding on their carrier atoms. All calculations were performed using SHELXL-97[44] and PARST[45] implemented in WINGX system of programs.[46] An ORTEP[47] view is shown in Fig. 1. Selected bond distances and angles are given in Table 1.

CCDC reference number 207882.

See http://www.rsc.org/suppdata/dt/b3/b303216g/ for crystallographic data in CIF or other electronic format.

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