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Reaction of rhenium alkynyl carbene complexes with tertiary phosphines produces dihydrophospholium rhenium complexes by a formal CH insertion process

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Abstract

Addition of PPh_2CH_3 to the alkynyl carbene complex $Cp(CO)_2Re{=}C(Tol)(C{\equiv}CPh)$ (**1a**) led to formation of the dihydrophospholium complex $Cp(CO)_2Re[C{=}C(Ph)PPh_2CH_2CH(Tol)]$ (**4**). When the reaction was monitored by low temperature NMR spectroscopy, initial phosphine addition to the carbene carbon atom of **1a** to give σ-propargyl complex $Cp(CO)_2ReC(PPh_2CH_3)(Tol)C{\equiv}CPh$ (**5**) was observed at −78°C. Upon warming to −20°C, **5** rearranged to the σ-allenyl complex $Cp(CO)_2Re(Tol)C{=}C{=}C(Ph)(PPh_2CH_3)$ (**6**) via phosphine dissociation and readdition. Upon further warming to room temperature, **6** rearranged to **4**. A protonation-deprotonation mechanism for the conversion of **6** to **4** is supported by the observation that reaction of **6** with DOTf produces the cationic allene complex $Cp(CO)_2Re[\eta^2\text{-}2,3\text{-}(Tol)DC{=}C{=}C(Ph)(PPh_2CH_3)]OTf$ (**11-d**), which is converted to **4-d** upon treatment with KO-*t*-Bu. The reaction of **1a** with $Ph_2PCH{=}CH_2$ led to the formation of the cyclopropane $Cp(CO)_2Re[C{=}C(Ph)PPh_2CHCH_2C(Tol)]$ (**8**). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Alkynyl carbene complexes; Rhenium; Dihydrophospholium; Allene; Allenyl; Ylide

1. Introduction

Alkynyl carbene complexes have emerged as a new class of synthetically useful compounds [1]. The addition of nucleophiles to $(CO)_5M$ alkynyl carbene complexes (M = Cr, Mo, W) is often the initial step in these reactions. Recently, we reported the synthesis of the non-donor substituted alkynyl carbene complex $Cp(CO)_2Re{=}C(Tol)(C{\equiv}CPh)$ (**1a**) (Tol=C_6H_4-*p*-CH_3), its isomerization to $Cp(CO)_2Re{=}C(Ph)(C{\equiv}CTol)$ (**1b**) via a 1,3-rhenium shift and its dimerization to $[Cp(CO)_2Re]_2$-[TolC≡CC(Ph)=C(Ph)C≡CTol)] (**2**) by coupling of the remote alkynyl carbons (Scheme 1) [2].

To explore electronic effects on the rates of dimerization and 1,3-rhenium shift reactions, we sought to replace the electron withdrawing CO ligands with electron-rich phosphine ligands. Here we report that the reaction of phosphines with rhenium alkynyl carbene complexes leads to the formation of novel cyclic zwitterionic dihydrophospholium compounds.

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2. Results

2.1. $\{Cp(CO)_2Re[C{=}C(Tol)PPh_2CHCH(Tol)]\}_2$ (3)

The addition of 1,2-bis(diphenylphosphino)ethane (DIPHOS) to a black solution of $Cp(CO)_2Re{=}C(Tol)$-C≡Tol (**1c**) produced $\{Cp(CO)_2Re[C{=}C(Tol)PPh_2$-$CHCH(Tol)]\}_2$ (**3**) as an orange solid in 72% yield (Scheme 2). No formation of products resulting from replacement of CO by phosphine was seen. Mass spectrometry established the formula of **3** as a 2:1 **1c**:DIPHOS addition product ($m/z = 1449$, $M^+ - 1$). ^{1}H-NMR spectroscopy showed a single product of high symmetry: only a single Cp resonance (δ 4.22) and only two tolyl CH_3 resonances were observed (δ 2.17 and 2.49). $^{31}P\{^1H\}$-NMR spectroscopy showed a single resonance at δ 44.4. Two low frequency CO stretches at 1879 and 1802 cm^{-1} in the IR spectrum indicated an electron rich rhenium center; the CO stretches of starting material **1c** are 1961 and 1888 cm^{-1}.

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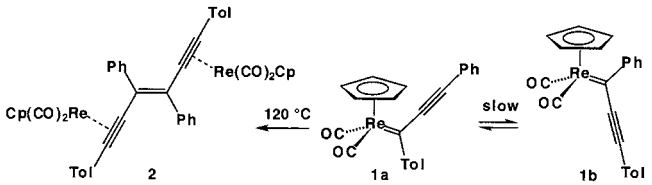
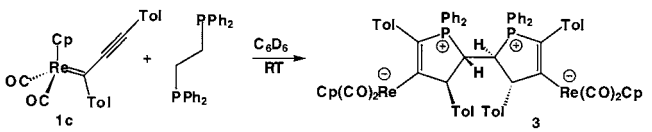


Scheme 1.

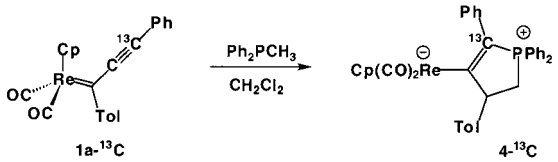


Scheme 2.

X-ray crystallography showed that **3** contained two symmetrically related 5-membered 3,4-dihydrophospholium units (Fig. 1). The remarkable formation of **3** requires the addition of phosphorus to one terminus of the alkynyl carbene ligand, insertion of the other terminus of the alkynyl carbene ligand into a methylene CH bond of DIPHOS, and a 1,2-migration of rhenium to the central carbon of the alkynyl carbene ligand.

2.2. $Cp(CO)_2Re[C{=}C(Ph)PPh_2CH_2CH(Tol)]$ (4)

To determine whether the formation of dihydrophospholium products involved bond formation between phosphorus and the carbene carbon or the remote alkynyl carbon, the reaction of PPh_2CH_3 with the unsymmetric alkynyl carbene complex $Cp(CO)_2Re{=}C(Tol)C{\equiv}CPh$ (**1a**) was studied (Scheme 3).



Scheme 3.

Addition of Ph_2PCH_3 to **1a** led to the clean formation of the dihydrophospholium compound $Cp(CO)_2Re[C{=}C(Ph)PPh_2CH_2CH(Tol)]$ (**4**) in 91% yield. In the $^{13}C\{^1H\}$-NMR spectrum of **4-^{13}C**, derived from reaction of PPh_2CH_3 with **1a-^{13}C**, the labeled carbon appeared as a doublet at δ 117 ($^1J_{CP} = 64$ Hz). In the $^{31}P\{^1H\}$-NMR spectrum, the phosphorus resonance appeared as a doublet at δ 34.0 with a 64 Hz coupling to ^{13}C. These spectra are consistent with formation of a bond between phosphorus and the remote alkynyl carbon.

The X-ray crystal structure of **4** unambiguously established the regiochemistry of the addition of phosphine to **1a** (Fig. 2). Conjugate addition of phosphine occurred at the remote alkynyl carbon of the alkynyl carbene complex.

2.3. Low temperature observation of intermediates from Ph_2PCH_3 and 1a

The reactions of **1a** and of **1a-^{13}C** with PPh_2CH_3 were studied by low temperature-NMR spectroscopy in an effort to detect intermediates in the complex transformation leading to **4**. When Ph_2PCH_3 was added to black solutions of **1a** and **1a-^{13}C** in CD_2Cl_2 at -80°C,

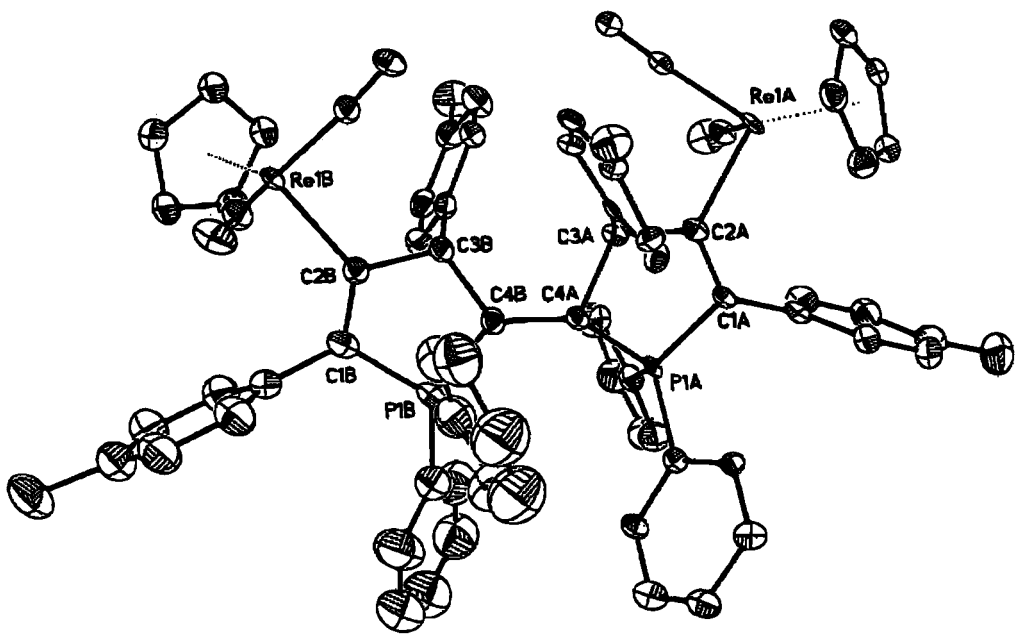


Fig. 1. X-ray crystal structure of $\{Cp(CO)_2Re[C{=}C(Tol)PPh_2CHCH(Tol)]\}_2$ (**3**). Re(1)–C(2) 2.11(2) Å, C(1)–C(2) 1.37(3) Å.

phosphine addition to the carbene carbon produced the σ-propargyl complexes $Cp(CO)_2ReC(PPh_2CH_3)$-(Tol)C≡CPh (**5**) and $Cp(CO)_2ReC(PPh_2CH_3)$(Tol)-C≡^{13}CPh (**5-^{13}C**) (Scheme 4, Table 1). In the ^{13}C-NMR spectrum of **5** at −80°C, alkyne carbon resonances appeared at δ 91.7 (d, $J_{CP} = 9.0$ Hz) and 95.0 (d, $J_{CP} = 9.0$ Hz) with long range couplings to phosphorus. The ^{13}C-NMR spectrum of **5-^{13}C** showed a label enhanced resonance at δ 91.5 (d, $^3J_{CP} = 9.5$ Hz). The ^{13}C-NMR resonance of the σ-propargyl carbon bonded to rhenium in **5** appeared at characteristic high field (δ 1.4).

When the solutions **5** and **5-^{13}C** were warmed to −40°C, dissociation of Ph_2PCH_3 and regeneration of starting materials **1a** and **1a-^{13}C** was observed. The Cp resonance of alkynyl carbene complex **1a** at δ 5.89 reappeared in the ^{1}H-NMR spectrum. The yellow solutions of **5** turned black as **1a** was reformed at −40°C.

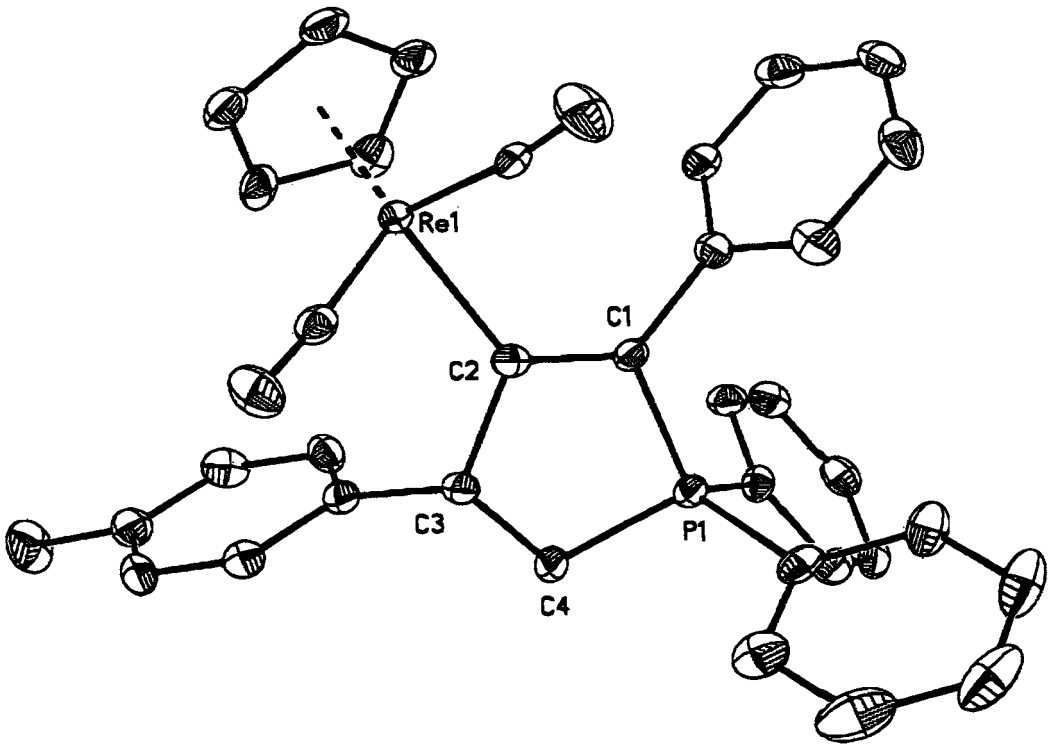
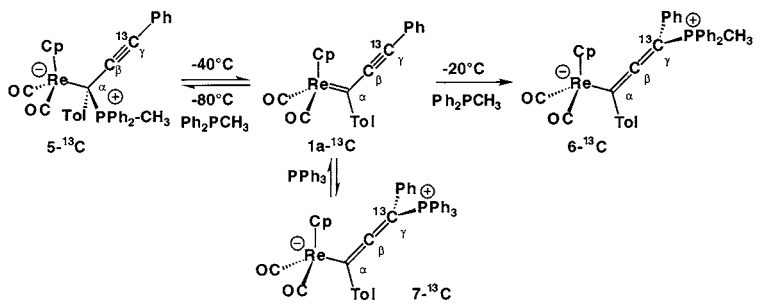


Fig. 2. X-ray crystal structure of $Cp(CO)_2Re[C{=}C(Ph)PPh_2CH_2CH(Tol)$ (**4**). Re(1)–C(2) 2.120(3) Å, C(1)–C(2) 1.383(4) Å.

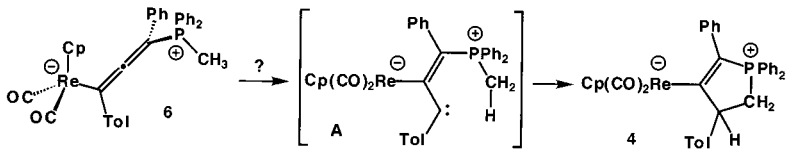


Scheme 4.

Table 1
Selected ^{1}H-, ^{13}C- and ^{31}P-NMR shifts (ppm) and C-P coupling constants (Hz) of compounds **5**, **6**, and **7**

	*C*p-^{1}H	δ C_α	$^1J_{C\alpha P}$	δ C_β	$^2J_{C\beta P}$	δ C_γ	$^3J_{C\gamma P}$	δ ^{31}P
5	4.64	1.42	[a]	95.00	9.0	91.66	9.0	27.5
6	4.98	96.82	12.9	185.15	9.0	59.58	105.0	20.0
7	4.82	98.19	13.5	185.15	9.0	58.57	107.3	20.2

[a] Broad signal, $\omega_{1/2} = 97$ Hz.



Scheme 5.

Upon further warming to −20°C, the new σ-allenyl complexes $Cp(CO)_2Re(Tol)C{=}C{=}C(Ph)(PPh_2CH_3)$ (**6**) and $Cp(CO)_2Re(Tol)C{=}C{=}{}^{13}C(Ph)(PPh_2CH_3)$ (**6-^{13}C**) were formed via conjugate addition of phosphine to the remote alkynyl carbon atom. In the ^{13}C-NMR spectrum of **6**, allenyl resonances were observed at δ 59.6 (d, $^1J_{CP} = 105$ Hz, C_γ), 96.8 (d, $^3J_{CP} = 13$ Hz, C_α) and 185.2 (d, $^2J_{CP} = 9$ Hz, C_β). These assignments are based on chemical shifts and ^{31}P-^{13}C coupling constants. The low frequency shifts of the terminal allenyl carbons C_α and C_γ as well as the high frequency shift of the central allenyl carbon have been observed for other transition metal allenyl complexes [3]. These chemical shift assignments are supported by the ^{13}C-NMR spectra of the labeled analogs, **6-^{13}C** and doubly labeled $Cp(CO)_2Re(Tol)C{=}{}^{13}C{=}{}^{13}C(Ph)(PPh_2CH_3)$ (**6-^{13}C$_2$**) [4]. Compound **6-^{13}C** has a label enhanced resonance at δ 59.4 (d, $^1J_{CP} = 104$ Hz, C_γ) and **6-^{13}C$_2$** has two label enhanced resonances at δ 59.2 (C_γ) and 185.4 (C_β) with a ^{13}C-^{13}C coupling constant of $^1J_{CC} = 94$ Hz.

When the solutions of **6** and **6-^{13}C** were warmed up to room temperature (r.t.), **4** and **4-^{13}C** formed cleanly. No additional intermediates were observed by ^{1}H-NMR spectroscopy.

2.4. $Cp(CO)_2ReC(Tol){=}C{=}C(Ph)PPh_3$ (7)

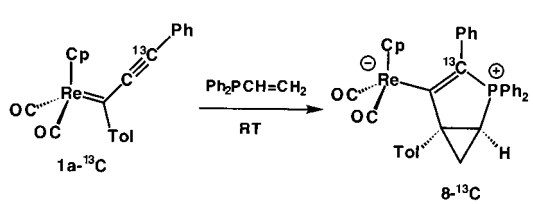
The addition of PPh_3 to the alkynyl carbene complex **1a** afforded the σ-allenyl addition product $Cp(CO)_2ReC(Tol){=}C{=}C(Ph)PPh_3$ (**7**) (Scheme 4). In the presence of an excess PPh_3, **7** is stable at r.t. and does not produce CH insertion products similar to **6**. The ^{13}C-NMR chemical shifts of the allenyl carbons of **7** (δ 98.2 for C_α 185.2 for C_β and 58.6 for C_γ) are very similar to the values of **6** (Table 1). Reaction of **1a-^{13}C** and **1a-^{13}C$_2$** with PPh_3 afforded the labeled analogs $Cp(CO)_2ReC(Tol){=}C{=}{}^{13}C(Ph)PPh_3$ (**7-^{13}C**) (label at δ 59.4, $^1J_{CP} = 107$ Hz) and $Cp(CO)_2ReC(Tol){=}{}^{13}C{=}{}^{13}C(Ph)PPh_3$ (**7-^{13}C$_2$**) (labels at δ 58.8, $^1J_{CC} = 95$ Hz, $^1J_{CP} = 107.3$ Hz; δ 187.0, $^1J_{CC} = 95$ Hz, $^2J_{CP} = 10$ Hz). This labeling pattern establishes the regiochemistry of PPh_3 addition to the remote alkynyl carbon of **1a**. The low frequency CO stretches at 1878 and 1802 cm^{-1} in the IR spectrum of **7** provide evidence for negative charge on rhenium. When **7** was isolated and redissolved, partial reappearance (20%) of starting materials **1a** and PPh_3 was observed after several hours. This demonstrates that the formation of **7** from **1a** and PPh_3 is reversible.

2.5. Reaction of **1a** with $Ph_2PCH{=}CH_2$ produces cyclopropane derivative $Cp(CO)_2Re[C{=}C(Ph)PPh_2CHCH_2C(Tol)]$ (8)

A possible mechanism for the conversion of σ-allenyl complex **6** to cyclic phospholium compound **4** involves a 1,2-migration of rhenium to give 'free carbene' intermediate **A** which could then insert into a CH bond of the PCH_3 group (Scheme 5). The possibility that such a carbene might cyclopropanate a tethered alkene prompted us to investigate the reaction of alkynyl carbene complex **1a** with $PPh_2CH{=}CH_2$ and $PPh_2CH_2CH{=}CH_2$.

The reaction of **1a** with $Ph_2PCH{=}CH_2$ led to the formation of the cyclopropane derivative $Cp(CO)_2Re$-[C=C(Ph)PPh_2CHCH_2C(Tol)] (**8**) in 90% yield (Scheme 6). Reactions of labeled derivatives **1a-^{13}C** and **1a-^{13}C$_2$** with $Ph_2PCH{=}CH_2$ aided in structural and chemical shift assignments of **8**.

The ^{13}C-NMR data strongly supports the presence of a cyclopropyl unit in **8**. The ^{13}C-NMR resonances of the tertiary bridgehead carbon (δ 22.50) and the secondary cyclopropyl carbon (δ 26.11) are similar to those found in 1-phenylbicyclo[3.1.0]hex-2-ene (δ 24.3, 26.5) [5]. The high C–H coupling constants of the carbons in the cyclopropyl ring ($^1J_{CH} = 176$ Hz for the CH-unit; $^1J_{CH} = 176$ Hz, $^1J_{CH} = 162$ Hz for the CH_2-unit) are due to the high s character of the CH hybrid orbitals and are similar to those of other cyclopropanes [6a–c]. The two vinylic centers in the dihydrophospholium ring have resonances at δ 114.65 (=C–P) and 215.57 (=C–Re) similar to that in 4 (Table 1). **8-^{13}C** has a strong one bond coupling ($^1J_{CP} = 68.5$ Hz) between the ^{13}C-labeled carbon (δ 114.50) and phosphorous indicating an attack of the phosphine at the remote carbon in **1a-^{13}C**. The ^{1}H-NMR resonances of the cyclopropyl CH_2 group of **8** appear at δ 1.71 and 1.83 their small geminal coupling ($^2J = 5.8$ Hz) is characteristic of cyclopropanes [7].



Scheme 6.

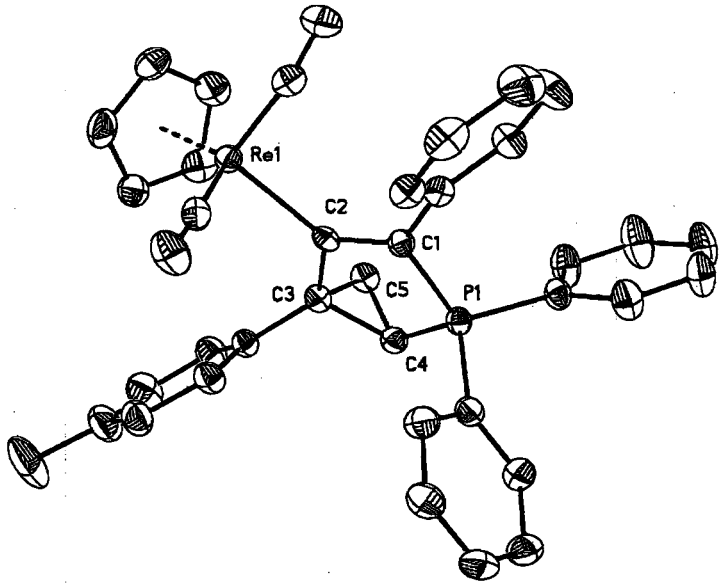


Fig. 3. X-ray crystal structure of $Cp(CO)_2Re[C{=}C(Ph)PPh_2CHCH_2C(Tol)]$ (**8**). Re(1)–C(2) 2.112(3) Å, C(1)–C(2) 1.387(5) Å.

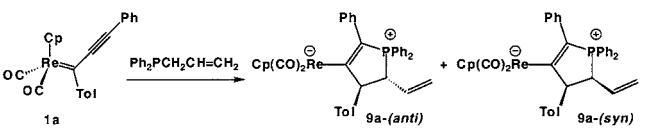
The X-ray crystal structure of **8** confirmed the structural assignment (Fig. 3). The presence of a P–CPh bond indicates that **8** is formed by initial attack of phosphorus at the remote alkynyl carbon of **1a**.

2.6. Reaction of *1a* with $Ph_2PCH_2CH{=}CH_2$ gives CH insertion product $Cp(CO)_2Re[C{=}C(Ph)PPh_2CH(CH{=}CH_2)CH(Tol)]$ (*9a*)

Reaction of $Ph_2PCH_2CH{=}CH_2$ with **1a** did not lead to cyclopropane formation but instead gave products derived from insertion into an allylic CH bond of the phosphine. The dihydrophospholium compounds $Cp(CO)_2Re[C{=}C(Ph)PPh_2CH(CH{=}CH_2)CH(Tol)]$ [**9a**-(*anti*) and **9a**-(*syn*), 5:1 ratio] were formed in 98% yield (Scheme 7). Both isomers **9a**-(*anti*) and **9a**-(*syn*) display an intact vinyl group in their ^{1}H-NMR and ^{13}C-NMR spectra. The internal vinyl hydrogen of **9a**-(*anti*) has a resonance at δ 5.36 with typical *cis* and trans couplings to the neighboring terminal hydrogens at δ 5.00 ($^3J = 16.7$ Hz) and 5.03 ($^3J = 10.0$ Hz). Similarly, the internal vinyl hydrogen resonance of **9a**-(*syn*) at δ 4.72 is coupled to the terminal vinyl hydrogens at δ 4.99 ($^3J = 10.0$ Hz) and 5.20 ($^3J = 16.8$ Hz). The internal and terminal vinyl carbons of **9a**-(*anti*) have ^{13}C-NMR shifts at δ 126.97 and 120.14. The chemical shifts of the ring carbons of both isomers are similar to those of **3** and **4**. The stereochemistry of **9a**-(*anti*) and **9a**-(*syn*) were assigned with the aid of NOE difference experiments (see Section 4).

The addition of $Ph_2PCH_2CH{=}CH_2$ to **1a**-^{13}**C** afforded a 5:1 mixture of **9a**-^{13}**C**-(*anti*) and **9a**-^{13}**C**-(*syn*). In the ^{13}C-NMR spectrum, label-enhanced resonances were seen at δ 117.15 [**9a**-^{13}**C**-(*anti*)] and δ 115.57 [**9a**-^{13}**C**-(*syn*)] with one bond couplings of $^1J_{CP} = 64.1$ Hz to phosphorous in each case. These couplings provide definitive evidence for conjugate addition of phosphine to the remote alkynyl carbon of **1a**.

Crystals of the bis-tolyl analog **9c**-(*anti*) suitable for an X-ray crystal structure analysis were obtained from reaction of **1c** with $Ph_2PCH_2CH{=}CH_2$ (Fig. 4). The dihydrophospholium unit of **9c**-(*anti*) is very similar to the core structures of **3**, **4**, and **8**.



Scheme 7.

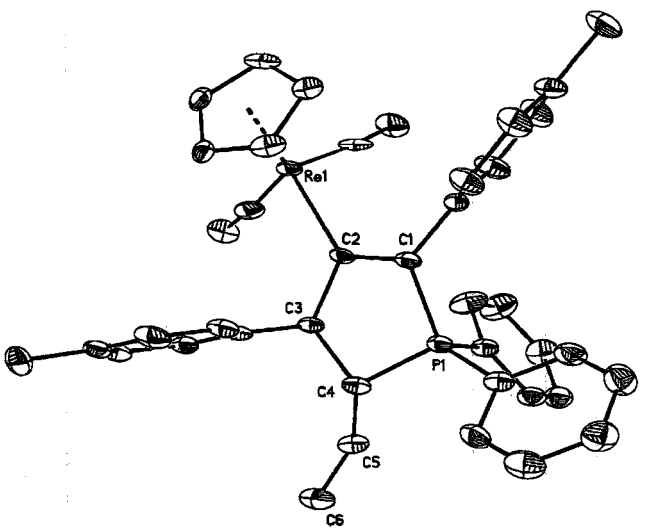
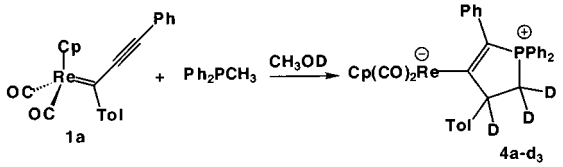


Fig. 4. X-ray crystal structure of $Cp(CO)_2Re[C{=}C(Tol)PPh_2CH(CH{=}CH_2)CH(Tol)]$ (9c). Re(1)–C(2) 2.125(5) Å, C(1)–C(2) 1.401(8) Å.



Scheme 8.

2.7. Deuterium incorporation in the reaction of **1a** with Ph_2PCH_3 in CH_3OD

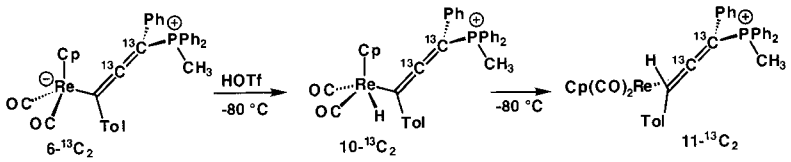
Alternative mechanisms for the conversion of the σ-allenyl intermediate **6** to the phospholium product **4** involve acid-base chemistry rather than CH insertion. Both deprotonation of the acidic phosphonium methyl group of **6** and protonation of **6** to give allene complexes were investigated. To test deprotonation of the PCH_3 group, we looked for deuterium incorporation into the product of the reaction of **1a** with Ph_2PCH_3 in the presence of a 100 fold excess of CH_3OD at r.t. Within our detection limits, complete ($>95\%$) deuterium incorporation into all three ring positions **4-d$_3$** occurred and no ($<5\%$) ring protons were seen in the ^{1}H-NMR spectrum (Scheme 8). The ^{2}H-NMR spectrum showed broad resonances at δ 2.95 (CD*D*), 3.18 (C*D*D), 5.39 (CTolD).

2.8. Low temperature protonation of **6-$^{13}C_2$**

When HOTf was added to **6-$^{13}C_2$** at -80°C and the solution was immediately monitored by ^{1}H-NMR spectroscopy at -80°C, the transient metal hydride intermediate [$Cp(CO)_2$(H)Re(Tol)C=^{13}C=^{13}C(Ph)(PPh_2-CH_3)]OTf (**10-$^{13}C_2$**) (ReH δ -8.57) was observed (Scheme 9, Table 2). In the ^{13}C-NMR spectrum, the resonance for the labeled terminal carbon C_γ appeared at δ 72.6 (t, $^1J_{CC}=97$ Hz, $^1J_{CP}=97$ Hz) and the resonance for the labeled central carbon C_β appeared at δ 201.4 ($^1J_{CC}=97$ Hz, $^2J_{CP}=7.6$ Hz). Both ^{13}C-NMR chemical shifts of **10-$^{13}C_2$** and all the coupling constants are very similar to those of its precursor **6-$^{13}C_2$**.

The σ-allenyl rhenium hydride **10-$^{13}C_2$** underwent reductive elimination to form the η^2-allenyl complex $Cp(CO)_2$Re[η^2-2,3-(Tol)HC=^{13}C=^{13}C(Ph)(PPh_2CH_3)]-OTf (**11-$^{13}C_2$**) with a half life of 30 min at -80°C. New ^{13}C-NMR resonances were observed at δ 111.35 (dd, $^1J_{CC}=86.1$ Hz, $^1J_{CP}=74.1$ Hz) for the labeled terminal carbon C_γ and δ 182.66 (dd, $^1J_{CC}=86.1$ Hz, $^2J_{CP}=8.7$ Hz) for the labeled central carbon C_β. No additional splitting due to CH coupling was observed in the ^{1}H-coupled ^{13}C-NMR spectrum, indicating that hydrogen was not bonded to either of the labeled carbons. The allenyl hydrogen resonance appeared at δ 4.4 in the ^{1}H-NMR spectrum; this hydrogen is shifted to lower frequency than seen for typical 1-phenylallenyl hydrogens (δ 6.5–7.0) [8]) due to π-complexation to the $Cp(CO)_2$Re fragment. Compound **11-$^{13}C_2$** was stable in solution at r.t.

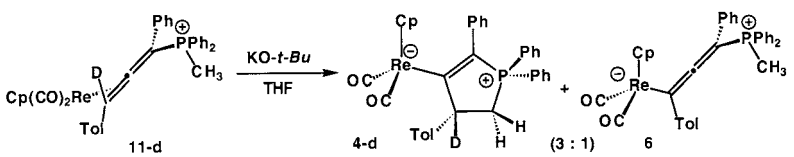
Deuteration of **6** with TfOD at -78°C followed by warming to r.t. produced {$Cp(CO)_2$Re[η^2-2,3-(Tol)DC=C=C(Ph)(PPh_2CH_3)}OTf, **11-d** (Scheme 10). In the ^{2}H-NMR spectrum, a single resonance was observed at δ 4.50 for the allenyl deuterium. Crystallization of **11-d** was accomplished by diffusing pentane into a CH_2Cl_2 solution.



Scheme 9.

Table 2
Selected ^{1}H-, ^{13}C- and ^{31}P-NMR shifts (ppm) and C-P coupling constants (Hz) of compounds **6-$^{13}C_2$**, **10-$^{13}C_2$**, and **11-$^{13}C_2$**

	δ H	δ $^{13}C_\gamma$	δ $^{13}C_\beta$	$^1J_{C\gamma C\beta}$	$^1J_{C\gamma P}$	$^2J_{C\beta P}$	δ ^{13}P
6-$^{13}C_2$		59.2	185.4	93.8	104.7	7.0	19.5
10-$^{13}C_2$	−8.57	72.6	201.4	97 Hz	97 Hz	7.6	22.0
11-$^{13}C_2$	4.40	111.35	182.6	86.1	74.1	8.7	17.5



Scheme 10.

2.9. Deprotonation of **11-d** with KO-t-Bu

When KO-*t*-Bu was added to a colorless solution of **11-d** at −78°C, the solution turned bright yellow instantaneously. The ^{1}H-NMR spectrum taken at −91°C provided evidence for the immediate conversion to a 3:1 mixture of **4-d** and undeuterated **6** (Scheme 10). Resonances for the CH_2 group of **4-d** at δ 3.13 and 3.35 displayed a strong geminal coupling ($^2J = 16.6$ Hz) but no vicinal coupling due to the absence of a neighboring proton [9]. A broad peak at δ 5.40 assigned to C(Tol)D of **4-d** was observed in the ^{2}H-NMR spectrum. The formation of **6** was established by ^{1}H, ^{13}C, and ^{31}P-NMR spectroscopy.

3. Discussion

3.1. Structure and bonding of dihydrophospholium complexes

There are two reasonable resonance structures for rhenium dihydrophospholium complex **4**: zwitterionic structure **I** and rhenium carbene-phosphorane structure **II** (Scheme 11). Spectroscopy and X-ray crystallography indicate that **I** is the major contributor. The low frequency IR bands of **4** at 1878 and 1802 cm^{-1} are consistent with an anionic $Re(CO)_2$ unit. The 2.120(3) Å Re–C distance in **4** is 0.116(6) Å longer than the Re=C double bond distance in alkynyl carbene complex **1c** and is similar to the Re–C single bond length in Gladysz' σ-vinyl complex $Cp(NO)(PPh_3)ReCH{=}CHCH_2Ph$ [2.129(10) Å] [10]. The 0.116(6) Å difference between the Re=C double bond and the Re–C single bond in **1a** and **4** is significantly less than the 0.180(11) Å difference between that in Gladysz' $Cp(NO)(PPh_3)Re{=}CHPh$ and his σ-vinyl-complex; this supports some contribution from resonance structure **II**. The 1.383(4) Å carbon-carbon distance in **4** is longer than most C=C bonds (1.32–1.33 Å) [11] and provides additional evidence for some contribution from **II**. The small $^{13}C{=}^{13}C$ coupling constant ($^1J_{CC} = 48.9$ Hz) for the ring C=C in **8-$^{13}C_2$** is outside the range of typical $^{13}C{=}^{13}C$ couplings (65–80 Hz) [12,13] and again supports some contribution from resonance structure **II**.

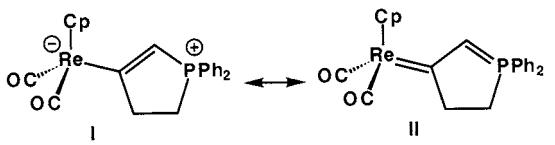
3.2. Regiochemistry of phosphine addition to alkynyl carbene complexes

Kinetic addition of phosphines to the carbene carbon and thermodynamic addition to the remote alkynyl carbon of alkynyl carbene complexes were observed. Addition of PPh_2CH_3 to the carbene carbon of alkynyl carbene complex **1a** occurred at −78°C to produce **5** (Scheme 4). The formation of **5** was reversible, and interestingly, the equilibrium shifted to starting materials at −40°C in an entropy driven process. Upon warming to −20°C, conjugate addition of PPh_2CH_3 to the remote alkynyl carbon of **1a** occurred to give a more stable σ-allenyl rhenium complex **6**. The greater stability of **6** might be related to the loss of a relatively weak π-bond of an alkyne upon addition. The conjugate addition of PPh_3 to **1a** produced σ-allenyl rhenium complex **7**; at least in this case, conjugate phosphine addition was reversible.

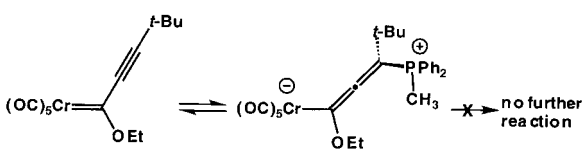
Fischer reported that the addition of dimethylamine to the carbene carbon of $(CO)_5Cr{=}C(OEt)(C{\equiv}CPh)$ with the subsequent elimination of EtOH is a kinetically controlled process at −115°C [14]. At −20°C, the amine undergoes a thermodynamically controlled conjugate addition to the remote alkynyl carbon. Nucleophilic addition of phosphines to carbene complexes is often reversible [15]. Conjugate additions of Ph_2PCH_3 to chromium and tungsten alkynyl carbene complexes were reported by Aumann [16]. Interestingly, these σ-allenyl adducts failed to undergo further transformations similar to the conversion of **6** to dihydrophospholium complex **4** (see Scheme 12).

3.3. Mechanism of conversion of σ-allenyl rhenium intermediates to dihydrophospholium products

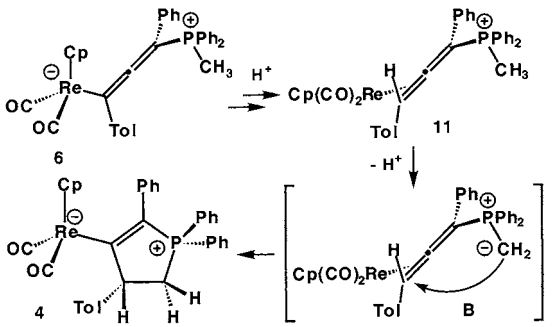
Two mechanisms can explain the overall transformation of σ-allenyl rhenium complexes to the dihydrophospholium products. One involves a 'free carbene' intermediate formed by a 1,2-rhenium shift of the σ-allenyl rhenium complex (Scheme 5). The other involves acid-base chemistry and carbon-carbon bond formation via attack of a phosphorane on an allene complex (Scheme 13). Nucleophilic attack on allene complexes is well documented, including intramolecular examples leading to 5-membered rings [17,18]. The mechanism in Scheme 13 is strongly supported by the observations that protonation of σ-allenyl intermediate **6** produces the allene complex **11** and that deprotonation of **11** produces the dihydrophospholium complex **4**.



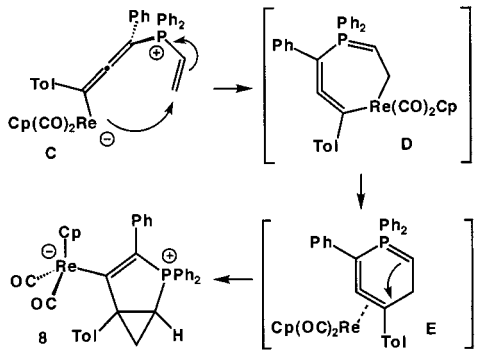
Scheme 11.



Scheme 12.



Scheme 13.



Scheme 14.

For the 'free carbene' mechanism to be correct, we need to postulate that deuterium incorporation occurs via acid-base chemistry in a side reaction unrelated to carbon–carbon bond formation. Moreover, we need to postulate that cyclopropanation would occur for the vinyl phosphine but not for the allyl phosphine even though both cyclopropane products would be expected to have comparable stability. Metal catalyzed intramolecular cyclopropanations to form bicyclo[4.1.0]heptanones from alkenyl diazo carbonyl precursors have been reported [19]. In some cases, allylic CH insertions were found to be a competitive side reaction [20] or the exclusive reaction [21]. Since no cyclopropane formation was observed from the allyl phosphine, a 'free carbene' mechanism seems unlikely.

For the mechanism proceeding via attack of a phosphorane on an allene rhenium complex, we need to explain why cyclopropane is formed only from the vinyl phosphine. We believe that the unique electrophilic nature of a vinyl phosphonium intermediate can explain this difference (Scheme 14). Addition of C, O, S, and N nucleophiles to vinyl phosphonium salts are well documented [22]. The ability of the metal center of $Cp(CO)_2Re(\sigma$-vinyl) anions to act as a nucleophile has also been observed [23]. Nucleophilic attack of rhenium on the vinyl phosphonium unit would produce metallacycle **D** [24], which could reductively eliminate to give the strained cyclic allene complex **E**. Related η^2-1,2-cyclohexadiene complexes of platinum and iron have been isolated previously [25]. An intramolecular attack of the ylide carbon on the π-complexed double bond would then form cyclopropane **8**. This mechanism explains how cyclopropane formation is limited to vinyl phosphines, allyl phosphines cannot react by similar pathways.

We have found experimental support for the acid base chemistry leading to allenyl phosphonium complex **11** in Scheme 13. The complete deuteration of the ring hydrogens of **4** when the reaction of **1a** and Ph_2PCH_3 was run in a CH_3OD solution (Scheme 8) is proposed to occur via reversible deprotonation of the phosphonium methyl group of intermediate **6**. Deuterium exchange via reversible deprotonation of methyl phosphonium salts is well precedented. $Ph_3PCH_3^+$ undergoes rapid and complete H-D exchange of the methyl hydrogens in the presence of excess D_2O and catalytic amounts of Na_2CO_3. $(CH_3)_3P{=}CH_2$ undergoes rapid exchange of methyl and methylene protons in the presence of traces of water via reversible formation of $(CH_3)_4P^+$ [26].

The conversion of σ-allenyl intermediate **6** to allene complex **11** via intermediate rhenium hydride **10** provides support for the proposed intermediacy of an allene complex in the formation of dihydrophospholium compounds. Related protonations of σ-vinyl metal anions have been reported [27,28]. Reductive elimination from vinyl hydride complexes have been thoroughly investigated [29]; with a few exceptions [30], vinyl hydride complexes are thermodynamically unstable relative to the resulting alkene complexes [31]. When allene complex **11** was treated with KO-*t*-Bu, some deprotonation to regenerate σ-allenyl rhenium complex **6** was seen in addition to predominant conversion to the dihydrophospholium complex **4**. Similar deprotonation of a vinylic hydrogen of $Cp(NO)(PPh_3)Re(\eta^2$-$CH_2{=}C{=}CH_2)$ produced a σ-allenyl complex [32,33] and deprotonation of $Cp(NO)(PPh_3)Re(\eta^2$-$CH_2 = CHPh)$ produced a σ-vinyl complex [34]. Based on the principle of microscopic reversibility, we postulate that the deprotonation of **11** occurs via initial CH bond activation to give rhenium hydride intermediate **10**, followed by deprotonation of the rhenium hydride. A related CH activation mechanism in conjunction with a deprotonation-reprotonation sequence was postulated by Oro to account for deuterium incorporation into an iridium ethylene complex [35,36].

4. Experimental

4.1. General considerations

All manipulations were performed either in a nitrogen atmosphere glovebox or by standard high vacuum line techniques. Compounds **1a**, **1a-^{13}C**, **1a-$^{13}C_2$** and **1c**

were synthesized as described earlier [2]. Hexane, pentane, THF, THF-d_8, C_6H_6, C_6D_6 and diethyl ether were distilled from sodium and benzophenone. $C_6D_5CD_3$ was distilled from Na–K. CH_2Cl_2 and CD_2Cl_2 were distilled from CaH_2. $CHCl_3$ and $CDCl_3$ were distilled from Na_2SO_4. ^{1}H-NMR spectra were obtained on a Bruker AC 250, AC 300, AM 500 or a Varian Unity 500 spectrometer. $^{13}C\{^1H\}$-NMR spectra were obtained on a Bruker AM 500 or a Varian Unity 500 spectrometer operating at 126 MHz. $^{31}P\{^1H\}$-NMR spectra were obtained on a Bruker AM 500 or a Varian Unity 500 spectrometer operating at 202.5 MHz. Infrared spectra were recorded on a Mattson Polaris FT IR spectrometer.

4.2. $\{Cp(CO)_2Re[C{=}C(Tol)PPh_2CHCH(Tol)]\}_2$ (3)

Addition of bis(diphenylphosphino)ethane (DIPHOS) (5.0 mg, 0.013 mmol) to a black solution of $Cp(CO)_2Re{=}C(Tol)(C{\equiv}CTol)$ (**1c**) (15 mg, 0.029 mmol) in 0.4 ml benzene produced an orange solution after 30 min. After 48 h, orange crystals suitable for X-ray crystallography had precipitated. The solid was washed with very little benzene to yield **3**·(3.5 C_6H_6) (18 mg, 72%). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 2.17 (s, CH_3), 2.49 (s, CH_3), 3.51 (d, $^2J_{PH} = 10.1$ Hz, CHP), 4.22 (s, C_5H_5), 5.91 (d, $^3J_{PH} = 3.7$ Hz, C*H*Tol), 7.0–7.6 (m, aromatic). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 125 MHz) δ 21.16 (CH_3), 21.32 (CH_3), 45.07 (d, $^1J_{CP} = 57.6$ Hz, PCH), 75.31 [d, $^2J_{CP} = 11.8$ Hz, *C*(Tol)CH], 83.44 (C_5H_5), 116.51 (d, $^1J_{CP} = 67.8$ Hz, C=CP), 120–144 (aromatic signals), 207.81 (CO), 208.27 (CO), 218.85 (broad, ReC=C). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 202.5 MHz) δ 44.4. IR (CH_2Cl_2) 1879, 1802 cm^{-1}. MS(FAB) m/z Calc. for $C_{74}H_{62}O_4P_2Re_2$ ($M^+ - 1$) 1449, found 1449.

4.3. $Cp(CO)_2Re[C{=}C(Ph)PPh_2CH_2CH(Tol)]$ (4)

Addition of Ph_2PCH_3 (45.5 mg, 0.227 mmol) to a solution of 14.3 mg (0.0280 mmol) $Cp(CO)_2Re{=}C(Tol)$-($C{\equiv}C$–Ph) (**1a**) in 1 ml CH_2Cl_2 produced an orange color after 1 min. After 48 h, hexane was added to precipitate a yellow solid which was redissolved in a few drops of CH_2Cl_2. Slow addition of 1 ml diethyl ether led to the formation of orange needles of **4** (18.1 mg, 91% yield) suitable for X-ray crystallography. ^{1}H-NMR (CD_2Cl_2, 500 MHz) δ 2.33 (s, CH_3), 2.95 (ddd, $^2J = 16.0$, $^3J = 2.8$ Hz, $^2J_{PH} = 8.3$ Hz, CHCHH_{trans}), 3.19 (ddd, $^2J = 15.9$ Hz, $^3J = 9.0$ Hz, $^2J_{PH} = 11.7$ Hz, CHCH_{cis}H), 4.35 (s, C_5H_5), 5.41 (ddd, $^3J = 8.9$ Hz, $^3J = 2.8$ Hz, $^3J_{PH} = 12.1$ Hz, CHTol), 7.09 (d, $^3J = 8.2$ Hz, aromatic), 7.12 (d, $^3J = 8.2$ Hz, aromatic), 7.19–7.30 (m, aromatic), 7.44 (dd, $^3J = 8.0$ Hz, $^3J_{PH} = 11.6$ Hz, aromatic), 7.50 (td, $^3J = 8.0$ Hz, $^3J_{PH} = 3.1$ Hz, aromatic), 7.52–7.57 (m, aromatic), 7.61–7.69 (m, aromatic). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 125 MHz) δ 21.71(CH_3), 34.92 (d, $^1J_{CP} = 61.0$ Hz, PCH_2), 71.08 (d, $^2J_{CP} = 14.7$ Hz, CTol), 83.75 (C_5H_5), 117.08 (d, $^1J_{CP} = 64.4$ Hz, C=CP), 123.60 (d, $^1J_{CP} = 73.4$ Hz, C_{ipso}), 126.06 ($^1J_{CP} = 75.5$ Hz, C_{ipso}), 126.86 ($^4J_{CP} = 2.6$ Hz, aromatic), 128.32 (aromatic), 128.80 (aromatic), 129.01 (aromatic), 129.70 (d, $^3J_{CP} = 11.3$ Hz, aromatic), 129.89 (d, $^3J_{CP} = 12.0$ Hz, aromatic), 132.67 (aromatic), 132.74 (aromatic), 132.75 (aromatic), 133.53 (d, $^4J_{CP} = 2.9$ Hz, aromatic), 136.04 (aromatic), 140.37 (d, $^2J_{CP} = 20.4$ Hz, aromatic), 144.42 (aromatic), 208.77 (CO), 209.16 (CO), 218.94 (d, $^2J_{CP} = 6.4$ Hz, ReC=C). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 202.5 MHz) δ 34.0. IR (CH_2Cl_2) 1878, 1802 cm^{-1}. HRMS(EI) m/z Calc. for $C_{36}H_{30}O_2PRe$ (M^+) 712.1542, found 712.1549.

4.4. $Cp(CO)_2Re[C{=}^{13}C(Ph)PPh_2CH_2CH(Tol)]$ (4-^{13}C)

Compound **4-^{13}C** (13 mg, 80% yield) was prepared from $Cp(CO)_2Re{=}C(Tol)(C{\equiv}^{13}CPh)$ (**1a-^{13}C**) (12 mg, 0.023 mmol) and Ph_2PCH_3 (12 mg, 0.060 mmol). ^{1}H-NMR (CD_2Cl_2, 500 MHz) δ 2.33 (s, CH_3), 2.95 (dddd, $^2J = 16.2$ Hz, $^3J = 2.8$ Hz, $^2J_{PH} = 8.4$ Hz, $^3J_{CH} = 8.4$ Hz, CHCHH_{trans}), 3.18 (dddd, $^2J = 15.1$ Hz, $^3J = 8.8$ Hz, $^2J_{PH} = 11.7$ Hz, $^3J_{CH} = 0.4$ Hz, CHCH_{cis}H), 4.35 (s, C_5H_5), 5.40 (dddd, $^3J = 9.0$ Hz, $^3J = 2.8$ Hz, $^3J_{PH} = 12.0$ Hz, $^4J_{CH} = 1.9$ Hz, CHTol), 7.0–7.7 (m, aromatic). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 125 MHz) δ 21.19 (CH_3), 34.94 (dd, $^1J_{CP} = 61.0$ Hz, $^2J_{CC} = 8.3$ Hz, PCH_2),), 71.08 (d, $^2J_{CP} = 15.2$ Hz, CTol), 83.75 (C_5H_5), 117.08 (d, $^1J_{CP} = 64.4$ Hz C = ^{13}CP), 123.60–144.42 (aromatic signals), 208.75 (CO), 209.14 (CO), 218.12 (d, $^2J_{CP} = 7.0$ Hz, $^1J_{CC} = 48.1$ Hz, ReC=C). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 202.5 MHz) δ 34.0 (d, $^1J_{CP} = 64.6$ Hz). IR (CH_2Cl_2) 1878, 1802 cm^{-1}. HRMS(EI) m/z Calc. for $C_{35}^{13}CH_{30}O_2PRe$ (M^+) 713.1575, found 713.1545.

4.5. $Cp(CO)_2Re[C{=}C(Ph)PPh_2CD_2CD(Tol)]$ (4-d_3)

Compound **4-d_3** (12 mg, 88% yield) was prepared from $Cp(CO)_2Re{=}C(Tol)(C{\equiv}CPh)$ (**1a**) (10 mg, 0.019 mmol) and Ph_2PCD_3 (5 mg, 0.03 mmol). ^{1}H-NMR (CD_2Cl_2, 500 MHz) δ 2.33 (s, CH_3), 4.36 (s, C_5H_5), 7.0–7.75 (m, aromatic). ^{2}H-NMR (CH_2Cl_2, 77 MHz) δ 2.95 (s, br, CDCDD_{trans}), 3.18 (s, br, CDCD_{cis}D), 5.39 (s, br, C*D*CDD). IR (CH_2Cl_2) 1878, 1802 cm^{-1}. HRMS(EI) m/z Calc. for $C_{36}H_{27}D_3O_2PRe$ (M^+) 715.1730, found 715.1745.

4.6. Reaction of (1a) and Ph_2PCH_3 in CH_3OD

Addition of Ph_2PCH_3 (8 mg, 0.04 mmol) to a solution of $Cp(CO)_2Re{=}C(Tol)(C{\equiv}CPh)$ (**1a**) (12 mg, 0.023 mmol) in CH_3OD (360 mg, 10.9 mmol) produced an orange color after 1 min. After 24 h, hexane was added to precipitate a yellow solid which was redissolved in a few drops of CH_2Cl_2. Slow addition of 1ml diethyl

ether led to the formation of orange needles of **4-d$_3$** (14 mg, 85% yield). ^{1}H and ^{2}H-NMR were identical with those from an authentic sample of **4-d$_3$** obtained in the previous experiment. Residual ^{1}H-NMR signals for each ring hydrogen amounted to less than 5%.

4.7. Reaction of $Cp(CO)_2Re{=}C(Tol)(C{\equiv}CPh)$ with Ph_2PCH_3 (variable temperature-NMR experiment)

Addition of Ph_2PCH_3 (19 mg, 0.095 mmol) to a black solution of $Cp(CO)_2Re{=}C(Tol)(C{\equiv}CPh)$ (**1a**) (7.5 mg, 0.015 mmol) in 0.4 ml CD_2Cl_2 at −78°C produced a yellow color after 3 h. Spectra of $Cp(CO)_2ReC(PPh_2CH_3)(Tol)[CC{\equiv}CPh]$ (**5**) were recorded without isolation. ^{1}H-NMR (CD_2Cl_2, 500 MHz, −80°C) δ 2.25 (s, CH_3), 2.70 (d, $^2J_{PH} = 12.2$ Hz, PCH_3), 4.64 (C_5H_5), 6.93–7.90 (m, partly obscured by excess Ph_2PCH_3, aromatic). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 125 MHz) δ 1.42 (broad signal, $\omega_{1/2} = 97$ Hz, ReCP), 15.75 d, $^1J_{CP} = 74.5$ Hz, PCH_3), 20.36 (CH_3), 85.76 (broad, $\omega_{1/2} = 22$ Hz, C_5H_5), 91.66 (d, $^3J_{CP} = 9.0$ Hz, C≡*C*Ph), 95.00 (d, $^2J_{CP} = 9.0$ Hz, *C*≡CPh), 124-142 (aromatic, partly obscured by signals from excess Ph_2PCH_3), 207.71 (broad, $\omega_{1/2} = 58$ Hz, CO), 211.77 (broad, $\omega_{1/2} = 58$ Hz, CO). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 202.5 MHz, −80°C) δ 27.5.

The sample was warmed to −20°C for 1 h to form $Cp(CO)_2ReC(Tol){=}C{=}C(Ph)(PPh_2CH_3)$ (**6**). ^{1}H-NMR (CD_2Cl_2, 500 MHz, −20°C) δ 2.28 (s, CH_3), 2.41 (d, 3H, $^2J_{PH} = 12.8$, PCH_3), 4.98 (C_5H_5), 7.0–7.8 (m, aromatic). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 125 MHz, −20°C) δ 12.47 (d, $^1J_{CP} = 67.8$ Hz, PCH_3), 20.87 (CH_3), 59.58 (d, $^1J_{CP} = 105.0$ Hz, C=CP), 86.83 (C_5H_5), 96.82 (d, $^3J_{CP} = 12.9$ Hz, ReC=C), 124–140 (aromatic, partly obscured by signals from excess Ph_2PCH_3), 185.15 (d, $^2J_{CP} = 9.0$ Hz, C=C=C), 208.85 (CO). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 202.5 MHz, −20°C) δ 20.0.

Upon warming to 24°C $Cp(CO)_2Re[C{=}C(Ph)PPh_2CH_2CH(Tol)]$ (**4**) formed slowly. No intermediates were detected.

4.8. Reaction of $Cp(CO)_2Re{=}C(Tol)(C{\equiv}{}^{13}CPh)$ (**1a-^{13}C**) with Ph_2PCH_3 (variable temperature-NMR experiment)

Addition of Ph_2PCH_3 (12 mg, 0.060 mmol) to a black solution of $Cp(CO)_2Re{=}C(Tol)(C{\equiv}{}^{13}CPh)$ (**1a-^{13}C**) (12 mg, 0.023 mmol) in 0.4 ml CD_2Cl_2 at −78°C produced a yellow solution after 3 h. Spectra of $Cp(CO)_2ReC(PPh_2CH_3)(Tol)[CC{\equiv}{}^{13}CPh]$ (**5-C^{13}**) were recorded without isolation. ^{1}H-NMR (CD_2Cl_2, 500 MHz, −80°C) δ 2.29 (s, CH_3), 2.74 (d, $^2J_{PH} = 12.2$ Hz, PCH_3), 4.65 (C_5H_5), 6.93–7.90 (m, aromatic). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 125 MHz) label at δ 91.5 (d, $^3J_{CP} = 9.5$ Hz, C≡*^{13}C*Ph). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 202.5 MHz) δ 27.5 (d, $^3J_{CP} = 10.0$ Hz).

The sample was warmed to −20°C for 1 h to form $Cp(CO)_2ReC(Tol){=}C{=}{}^{13}C(Ph)(PPh_2CH_3)$ (**6-^{13}C**). ^{1}H-NMR (CD_2Cl_2, 500 MHz) δ 2.28 (s, CH_3), 2.41 (dd, $^2J_{PH} = 12.8$, $^3J_{CH} = 2.2$ Hz, PCH_3), 4.98 (C_5H_5), 6.93–7.90 (m, aromatic). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 125 MHz) δ 59.4 (d, $^1J_{CP} = 104$ Hz, C = *^{13}C*P). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 202.5 MHz) δ 20.0 (d, $^1J_{CP} = 105$ Hz).

The sample was warmed to 24°C and $Cp(CO)_2Re[C{=}{}^{13}C(Ph)PPh_2CH_2CH(Tol)]$ (**4-^{13}C**) formed slowly. No intermediates were detected by ^{1}H-NMR.

4.9. Reaction of $Cp(CO)_2Re{=}C(Tol)(^{13}C{\equiv}{}^{13}CPh)$ (**1a-$^{13}C_2$**) with Ph_2PCH_3 at −20°C to form $Cp(CO)_2Re[C(Tol){=}{}^{13}C{=}{}^{13}C(Ph)(PPh_2CH_3)$ (**6-$^{13}C_2$**)

Addition of Ph_2PCH_3 (10 mg, 0.050 mmol) to a black solution of $Cp(CO)_2Re{=}C(Tol)(^{13}C{\equiv}{}^{13}CPh)$ (**1a-$^{13}C_2$**) (7.3 mg, 0.014 mmol) in 0.4 ml CD_2Cl_2 at −20°C produced an orange color after 15 min. Spectra of **6-$^{13}C_2$** were recorded without isolation. ^{1}H-NMR (CD_2Cl_2, 500 MHz, −80°C) δ 2.28 (s, CH_3), 2.41 (d, $^2J_{PH} = 12.8$ Hz, PCH_3), 4.98 (C_5H_5), 7.0–7.8 (m, aromatic). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 125 MHz, −80°C) label at δ 59.2 (dd, $^1J_{CC} = 93.7$, $^1J_{CP} = 104.7$ Hz, $P^{13}C{=}{}^{13}C$), 185.4 (dd, $^1J_{CC} = 93.8$, $^2J_{CP} = 7.0$ Hz, $C{=}{}^3C{=}{}^{13}C$). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 202.5 MHz, −80°C) δ 19.5 (dd, $^1J_{CP} = 105.3$, $^2J_{CP} = 6.1$ Hz).

4.10. $Cp(CO)_2ReC(Tol){=}C{=}C(Ph)PPh_3$ (**7**)

Addition of PPh_3 (31.5 mg, 0.120 mmol) to a solution of $CpRe(CO)_2{=}C(Tol)(C{\equiv}CPh)$ (**1a**) (12.1 mg, 0.0237 mmol) in 0.4 ml $CDCl_3$ in an NMR tube produced an orange color after 15 min. Spectroscopic charcterization was performed without isolation. ^{1}H and ^{31}P-NMR spectra indicated clean formation of **7**. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 2.25 (s, CH_3), 4.82 (s, C_5H_5), 7.09–7.75 (m aromatic). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 125 MHz) δ 21.02(CH_3), 58.57 (d, $^1J_{CP} = 107.3$ Hz, C=CP), 83.22 (C_5H_5), 98.19 (d, $^3J_{CP} = 13.5$ Hz, ReC=C), 119.30 (d, $^1J_{CP} = 84.7$ Hz, C_{ipso}), 123.60 (d, $^1J_{CP} = 73.4$ Hz, C_{ipso}), 128.17 (aromatic), 128.21 (aromatic), 128.87 (aromatic), 131.87 (aromatic), 132.06 (d, $^3J_{CP} = 10.2$ Hz, aromatic), 133.49 (aromatic), 134.58 (d, $^3J_{CP} = 9.0$ Hz, aromatic), 137.14 (d, $^2J_{CP} = 11.3$ Hz, aromatic), 139.26 (aromatic), 140.96 (d, $^2J_{CP} = 6.8$ Hz, aromatic), 144.73 (aromatic), 185.15 (d, $^2J_{CP} = 9.0$ Hz, C=C=C), 208.85 (CO). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 202.5 MHz) δ 20.2. IR (CH_2Cl_2) 1878, 1802 cm^{-1}.

4.11. $Cp(CO)_2ReC(Tol){=}C{=}{}^{13}C(Ph)PPh_3$ (**7-^{13}C**)

Compound **7-^{13}C** was prepared from $Cp(CO)_2Re{=}C(Tol)(C{\equiv}{}^{13}CPh)$ (**1a-^{13}C**) (10 mg, 0.020 mmol) and PPh_3 (15 mg, 0.057 mmol) in 0.4 ml CD_2Cl_2. ^{1}H-NMR (CD_2Cl_2, 500 MHz) δ 2.25 (s, CH_3), 4.82 (s, C_5H_5), 7.09–7.75 (m aromatic). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 125 MHz) label at δ 59.4 (d, $^1J_{CP} = 106.9$ Hz, C = *^{13}C*P). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 202.5 MHz) δ 20.2 (d, $^1J_{CP} = 106.9$ Hz).

*4.12. $Cp(CO)_2ReC(Tol)=^{13}C=^{13}C(Ph)PPh_3$ (**7-$^{13}C_2$**)*

Compound **7-$^{13}C_2$** was prepared from $Cp(CO)_2Re{=}C(Tol)(^{13}C{\equiv}^{13}CPh)$ (**1a-$^{13}C_2$**) (7.6 mg, 0.015 mmol) and PPh_3 (28.4 mg, 0.108 mmol) in 0.4 ml CD_2Cl_2. ^{1}H-NMR (CD_2Cl_2, 500 MHz, −40°C) δ 2.19 (s, CH_3), 2.23 (s, CH_3), 4.72 (s, C_5H_5), 7.09–7.75 (m aromatic). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 125 MHz, −40°C) δ 20.61 (CH_3), 20.80 (CH_3), 58.79 (dd, $^1J_{CC}=94.9$ Hz, $^1J_{CP}=107.3$ Hz, $^{13}C{=}^{13}CP$), 83.17 (C_5H_5), 97.77 (ddd, $^1J_{CC}=93.8$ Hz, $^2J_{CC}=4.7$ Hz $^3J_{CP}=13.6$ Hz, Re*C*=^{13}C), 123–145 (12 aromatic peaks), 187.04 (labeled, dd, $^1J_{CC}=94.9$ Hz, $^2J_{CP}=10.2$ Hz, C=^{13}C=^{13}C), 208.61 (CO), 209.69 (CO). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 202.5 MHz) δ 21.7 at −40°C, 20.2 at 24°C.

*4.13. $Cp(CO)_2Re[C{=}C(Ph)PPh_2CHCH_2C(Tol)]$ (**8**)*

Addition of $Ph_2PCH{=}CH_2$ (18 mg, 0.084 mmol) to a solution of $Cp(CO)_2Re{=}C(Tol)(C{\equiv}CPh)$ (**1a**) (22 mg, 0.043 mmol) in 1 ml CH_2Cl_2 produced a yellow orange solution after 10 min. After 48 h, pentane was added to precipitate a yellow solid. The crude product was redissolved in a few drops of CH_2Cl_2 and 1 ml hexane was slowly added to give **8** (28 mg, 90%) as orange crystals suitable for X-ray crystallography. ^{1}H-NMR (CD_2Cl_2, 500 MHz) δ 1.71 (dt, $^{2,3}J=5.4$ Hz, $^3J_{PH}=11.5$ Hz, CHH_{trans}CH), 1.83 (ddd, $^3J=8.6$ Hz, $^2J=5.8$ Hz, $^3J_{PH}=15.6$ Hz, CH_{cis}HCH), 2.36 (s, CH_3), 2.71 (ddd, $^3J=8.8$ Hz, $^3J=5.3$ Hz, $^2J_{PH}=9.3$ Hz, CHP), 4.49 (s, C_5H_5), 7.11 (d, $^3J=7.1$ Hz, aromatic), 7.16 (d, $^3J=7.9$ Hz, aromatic), 7.20–7.27 (m, aromatic), 7.33 (d, $^3J=8.0$ Hz, aromatic), 7.40–7.51 (m, aromatic), 7.53–7.72 (m, aromatic). ^{13}C-NMR (CD_2Cl_2, 125 MHz) δ 21.24 (q, $^1J_{CH}=126.5$ Hz, CH_3), 22.50 (ddt, $^1J_{CH}=176.3$ Hz, $^{2,2'}J_{CH}=3.3$ Hz, $^1J_{CP}=97.1$ Hz, PCH), 26.11 (dddd, $^1J_{CH}=176.4$ Hz, $^1J_{CH}=162.2$ Hz, $^2J_{CH}=5.9$ Hz, $^2J_{CP}=5.6$ Hz, CH_2), 61.72 (d, $^2J_{CP}=14.7$ Hz, CTol), 83.72 (dp, $^1J_{CH}=177.3$ Hz, $^{2,3}J_{CH}=5.9$ Hz, C_5H_5), 114.65 (dt, $^{3,3'}J_{CH}=3.5$ Hz, $^1J_{CP}=68.9$ Hz, C=CP), 121.96 (dt, $^{3,3'}J_{CH}=8.5$ Hz, $^1J_{CP}=82.9$ Hz, C_{ipso}), 126.45 (dt, $^{3,3'}J_{CH}=7.9$ Hz, $^1J_{CP}=76.3$ Hz, C_{ipso}), 126.97 (dtd, $^1J_{CH}=159.1$ Hz $^{3,3'}J_{CH}=7.1$ Hz, $^4J_{CP}=2.2$ Hz, aromatic), 128.20 (dtd, $^1J_{CH}=160.0$ Hz $^{3,3'}J_{CH}=6.2$ Hz, $^4J_{CP}=2.2$ Hz, aromatic), 128.71 (dt, $^1J_{CH}=155.7$ Hz $^{3,3'}J_{CH}=5.7$ Hz, aromatic), 129.57 (dd, $^1J_{CH}=155.6$ Hz, $^3J_{CH}=4.8$ Hz, aromatic), 129.69 (ddd, $^1J_{CH}=163.6$ Hz, $^3J_{CH}=7.2$ Hz, $^3J_{CP}=50.8$ Hz, aromatic), 129.99 (dd, $^1J_{CH}=163.5$ Hz, $^3J_{CH}=7.1$ Hz, aromatic), 132.69 (ddt, $^1J_{CH}=162.2$ Hz, $^3J_{CH}=8.5$ Hz, $^3J_{CP}=10.1$ Hz, aromatic), 133.08 (dt, $^1J_{CH}=162.7$ Hz, $^{3,3'}J_{CH}=7.0$ Hz, aromatic), 133.10 (dd, $^1J_{CH}=161.8$ Hz, $^3J_{CH}=7.6$ Hz, $^3J_{CP}=12.4$ Hz, aromatic), 133.54 (dtd, $^1J_{CH}=162.8$ Hz, $^3J_{CH}=5.6$ Hz, $^4J_{CP}=3.4$ Hz, aromatic), 133.7 (dtd, $^1J_{CH}=162.4$ Hz, $^3J_{CH}=7.1$ Hz, $^4J_{CP}=3.4$ Hz, aromatic), 136.29 (q, $^2J_{CH}=6.5$ Hz, aromatic), 139.23 (dt, $^{3,3'}J_{CH}=6.7$ Hz, $^2J_{CP}=20.3$ Hz, aromatic), 140.51 (s, broad), 207.82 (s, CO), 207.94 (s, CO), 215.57 (s, ReC=C). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 202.5 MHz) δ 39.5. IR (CH_2Cl_2) 1878, 1806 cm^{-1}.

*4.14. $Cp(CO)_2Re[C=^{13}C(Ph)PPh_2CHCH_2C(Tol)]$ (**8-^{13}C**)*

Compound **8-^{13}C** (12 mg, 94% yield) was obtained from $Cp(CO)_2Re{=}C(Tol)(C{\equiv}^{13}CPh)$ (**1a-^{13}C**) (9 mg, 0.02 mmol) and $Ph_2PCH{=}CH_2$ (15 mg, 0.070 mmol). ^{1}H-NMR (CD_2Cl_2, 500 MHz) δ 1.71 (dt, $^{2,3}J=5.4$ Hz, $^3J_{PH}=11.5$ Hz, CHH_{trans}CH), 1.83 (dddd, $^3J=8.6$ Hz, $^2J=5.8$ Hz, $^3J_{PH}=15.6$ Hz, $^3J_{CH}=3.5$ Hz, CH_{cis}HCH), 2.36 (s, CH_3), 2.71 (ddd, $^3J=8.8$ Hz, $^3J=5.3$ Hz, $^2J_{PH}=9.3$ Hz, CHP), 4.49 (s, C_5H_5), 7.08–7.12 (m, aromatic), 7.16 (d, $^3J=7.9$ Hz, aromatic), 7.20–7.27 (m, aromatic), 7.30–7.51 (m, aromatic), 7.53–7.72 (m, aromatic). ^{13}C-NMR (CD_2Cl_2, 125 MHz) δ 21.28 (CH_3), 22.50 (dd, $^1J_{CP}=97.1$ Hz, $^2J_{CC}=6.1$ Hz, PCH), 26.18 (CH_2), 61.72 (d, $^2J_{CP}=14.7$ Hz, CTol), 83.74 (C_5H_5), 114.50 (d, $^1J_{CP}=68.5$ Hz, C=^{13}*C*P), 121.96 (d, $^1J_{CP}=82.9$ Hz, C_{ipso}), 126.53 (d$^1J_{CP}=76.3$ Hz, C_{ipso}), 126.96 (aromatic), 128.22 (d, $^4J_{CP}=2.2$ Hz, aromatic), 128.73 (aromatic), 129.57 (aromatic), 129.70 (d, $^3J_{CP}=50.4$ Hz, aromatic), 129.99 (aromatic), 132.69 (d, $^3J_{CP}=10.1$ Hz, aromatic), 133.10 (aromatic), 133.14 (d, $^3J_{CP}=12.4$ Hz, aromatic), 133.54 (broad, aromatic), 133.73 (broad, aromatic), 136.31 (aromatic), 139.29 (dd, $^1J_{CC}=62.8$ Hz, $^2J_{CP}=20.3$ Hz, aromatic), 140.56 (s, broad), 207.77 (s, CO), 207.89 (s, CO), 215.71 (d, $^1J_{CC}=48.8$ Hz, Re*C*=^{13}C). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 202.5 MHz) δ 39.5 (d, $^1J_{CP}=68.7$ Hz). IR (CH_2Cl_2) 1878, 1806 cm^{-1}. HRMS(EI) m/z Calc. for $C_{36}^{13}CH_{30}O_2PRe$ (M^+) 725.1575, found 725.1564.

*4.15. $Cp(CO)_2Re[^{13}C=^{13}C(Ph)PPh_2CHCH_2C(Tol)]$ (**8-$^{13}C_2$**)*

Compound **8-$^{13}C_2$** (6 mg, 85% yield) was obtained from $Cp(CO)_2Re{=}C(Tol)(^{13}C{\equiv}^{13}CPh)$ (**1a-$^{13}C_2$**) (9 mg, 0.01 mmol) and $Ph_2PCH{=}CH_2$ (8 mg, 0.04 mmol). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 125 MHz) δ 114.58 (dd, $^1J_{CC}=48.9$ Hz, $^1J_{CP}=68.1$ Hz, $^{13}C{=}^{13}CP$), 215.5 (d, $^1J_{CC}=48.9$ Hz, $Re^{13}C{=}^{13}C$). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 202.5 MHz) δ 39.5 (d, $^1J_{CP}=68.7$ Hz).

*4.16. $Cp(CO)_2Re[C{=}C(Ph)PPh_2CH(CH{=}CH_2)CH(Tol)]$ (**9a**)*

Reaction of $Cp(CO)_2Re{=}C(Tol)C{\equiv}CPh$ (**1a**) (15 mg, 0.030 mmol) with $Ph_2PCH_2CH{=}CH_2$ (22 mg, 0.097 mmol) gave a 5:1 mixture of **9a**-(*anti*): **9a**-(*syn*) (21 mg, 97%). Pure **9a**-(*anti*) (14 mg, 60%) was isolated as orange crystals by slow evaporation of a CH_2Cl_2/hexane solution.

Compound **9a**-(*anti*): ^{1}H-NMR (CD_2Cl_2, 500 MHz) δ 2.36 (s, CH_3), 3.84 (ddd, $^3J = 9.5$ Hz, $^3J = 5.9$ Hz, $^2J_{PH} = 11.4$ Hz, C*H*CH=), 4.36 (s, C_5H_5), 4.77 (d, $^3J = 5.8$ Hz, CHTol), 5.00 (dd, $^3J = 16.7$ Hz, $^4J_{PH} = 4.0$ Hz, CH=CHH_{trans}), 5.03 (dd, $^3J = 10.0$ Hz, $^4J_{PH} = 2.4$ Hz, CH=CH_{cis}H), 5.36 (dtd, $^3J = 16.8$ Hz, $^{3,3'}J = 10.0$ Hz, $^3J_{PH} = 5.8$ Hz, CH=CH_2), 7.11 (d, $^3J = 8.1$ Hz, tolyl CH), 7.15 (d, $^3J = 8.1$ Hz, tolyl CH), 7.19–7.29 (m, aromatic CH), 7.44 (dd, $^3J = 8.2$ Hz, $^3J_{PH} = 11.2$ Hz, aromatic CH), 7.48 (td, $^3J = 7.8$ Hz, $^4J_{PH} = 3.2$ Hz, aromatic CH), 7.55–7.62 (m, aromatic CH). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 125 MHz) δ 21.25 (CH_3), 52.63 (d, $^1J_{CP} = 57.4$ Hz, PCH), 77.01(d, $^2J_{CP} = 19.0$ Hz, CTol), 83.73 (C_5H_5), 117.14 (d, $^1J_{CP} = 63.2$ Hz, C=CP), 120.14 (d, $^3J_{CP} = 12.1$ Hz, =CH_2), 122.38 (d, $^1J_{CP} = 61.5$ Hz, C_{ipso}), 122.95 (d, $^1J_{CP} = 57.5$ Hz, C_{ipso}), 126.97 (d, $^2J_{CP} = 2.3$ Hz, CH=), 128.33 (aromatic), 128.89 (aromatic), 129.45 (aromatic), 129.81 (d, $^2J_{CP} = 11.4$ Hz, aromatic), 129.95 (d, $^2J_{CP} = 12.35$ Hz, aromatic), 131.90 (d, $^3J_{CP} = 4.5$ Hz, aromatic), 132.46 (d, $^3J_{CP} = 4.6$ Hz, aromatic), 132.51 (aromatic), 133.69 (d, $^4J_{CP} = 2.3$ Hz, aromatic), 133.86 (d, $^4J_{CP} = 2.4$ Hz, aromatic), 134.01 (d, $^3J_{CP} = 10.1$ Hz, aromatic), 136.05 (aromatic), 140.28 (d, $^3J_{CP} = 18.2$ Hz, C_{ipso}-tolyl), 143.27 (d, $^3J_{CP} = 6.7$ Hz, C_{ipso}-phenyl), 208.38 (CO), 208.74 (CO), 216.55 (d, $^2J_{CP} = 4.2$ Hz, ReC=C). ^{31}P{^{1}H}-NMR (CD_2Cl_2, 202.5 MHz) δ 35.9. IR (CH_2Cl_2) 1877, 1804 cm^{-1}. HRMS(EI) m/z Calc. for $C_{38}H_{32}O_2PRe$ (M^+) 738.1698, found 738.1729.

Compound **9a**-(*syn*): ^{1}H-NMR (CD_2Cl_2, 500 MHz) δ 2.28 (s, CH_3), 4.37 (C*H*CH=CH_2, overlap with Cp signal of major isomer) [37],4.51 (s, C_5H_5), 4.72 (ddt, $^3J = 16.8$ Hz, $^3J_{PH} = 4.8$ Hz, $^{3,3'}J = 10.0$ Hz (triplet), CH=CH_2), 4.99 (ddd, CH=CH_{cis}H, overlap with [CH=CHH_{trans}]-signal of major compound) [38] 5.20 (ddd, $^3J = 16.8$ Hz, $^4J = 1.3$ Hz, $^4J_{PH} = 4.0$ Hz, CH=CHH_{trans}), 5.65 (dd, $^3J = 8.6$ Hz, $^3J_{PH} = 21.4$ Hz, CHTol), 7.11 (d, $^3J = 8.1$ Hz, tolyl CH), 7.15 (d, $^3J = 8.1$ Hz, tolyl CH), aromatic signals overlap with major isomer. ^{13}C{^{1}H}-NMR (CD_2Cl_2, 125 MHz) δ 21.25 (CH_3), 50.76 (d, $^1J_{CP} = 59.7$ Hz, PCH), 77.97 (d, $^1J_{CP} = 17.5$ Hz, CTol), 84.27 (C_5H_5), 115.62 (d, $^1J_{CP} = 64.4$ Hz, C=CP), 119.78 (d, $^4J_{CP} = 11.8$ Hz, C=CH_2), aromatic signals and signal of *C*H=CH_2 overlap with peaks of major compound, 208.95 (CO), 209.18 (CO), 220.26 (d, $^2J_{CP} = 7.1$ Hz, ReC=C). ^{31}P{^{1}H}-NMR (CD_2Cl_2, 202.5 MHz) δ 30.5.

NOE studies of **9a**-(*anti*) and **9a**-(*syn*)**.** The stereochemical assignment of **9a**-(*anti*) and **9a**-(*syn*) was established by NOE difference experiments. Irradiation of the benzylic ring hydrogen TolCH (δ 4.77) in **9a**-(*anti*) led to a 2.0% NOE enhancement of the vicinal allylic hydrogen (C*H*CH=CH_2, δ 3.84) and a 3.0% enhancement of the internal vinyl hydrogen (CHCH=CH_2, δ 5.36). By contrast, irradiation of the benzylic ring hydrogen in **9a**-(*syn*) (δ 5.65) resulted in a strong NOE enhancement (4.6%) of the vicinal allylic syn hydrogen at δ 4.37 and no NOE enhancement of the internal vinyl hydrogen (CHCH=CH_2, δ 4.72).

*4.17. Cp(CO)$_2$Re[C=^{13}C(Ph)PPh$_2$CH-(CH=CH$_2$)CH(Tol)] (**9a-^{13}C**)*

Reaction of Cp(CO)$_2$Re=C(Tol)C$\equiv$^{13}CPh (**1a-^{13}C**) (10 mg, 0.020 mmol) with $Ph_2PCH_2CH=CH_2$ (14 mg, 0.062 mmol) gave a 5:1 mixture of **9a-^{13}C**-(*anti*): **9a-^{13}C**-(*syn*) (14 mg, 97%). HRMS(EI) m/z Calc. for $C_{37}^{13}CH_{32}O_2PRe$ (M^+) 739.1732, found 738.1739.

Compound **9a-^{13}C**-(*anti*): ^{13}C{^{1}H}-NMR (CD_2Cl_2, 125 MHz) δ 117.15 (d, $^1J_{CP} = 64.1$ Hz, C=^{13}*C*P). ^{31}P{^{1}H}-NMR (CD_2Cl_2, 202.5 MHz) δ 35.9 (d, $^1J_{CP} = 64.1$ Hz).

Compound **9a-^{13}C**-(*anti*): ^{13}C{^{1}H}-NMR (CD_2Cl_2, 125 MHz) δ 115.57 (d, $^1J_{CP} = 64.1$ Hz, C=^{13}*C*P). ^{31}P{^{1}H}-NMR (CD_2Cl_2, 202.5 MHz) δ 30.5 (d, $^1J_{CP} = 64.1$ Hz).

*4.18. Cp(CO)$_2$Re[C=C(Tol)PPh$_2$CH(CH=CH$_2$)-CH(Tol)] [**9c**-(anti)]*

Compound **9c**-(*anti*) (22 mg, 63% yield) was synthesized from Cp(CO)$_2$Re=C(Tol)C$\equiv$CTol (**1c**) (24 mg, 0.051 mmol) and $Ph_2PCH_2CH=CH_2$ (27 mg, 0.12 mmol). Crystals suitable for X-ray crystallography were obtained by slow evaporation of a 10:10:1 CH_2Cl_2:hexane:THF solution. ^{1}H-NMR (CD_2Cl_2, 500 MHz) δ 2.32 (s, CH_3), 3.82 (ddddd, $^3J = 9.6$ Hz, $^3J = 5.8$ Hz, $^4J = 0.5$ Hz, $^4J = 0.5$ Hz, $^2J_{PH} = 11.3$ Hz, C*H*CH=CH_2), 4.36 (s, C_5H_5), 4.75 (d, $^3J = 6.0$ Hz, CHTol), 4.99 (dddd, $^3J = 16.9$ Hz, $^2J = 1.4$ Hz, $^4J = 0.3$ Hz, $^4J_{PH} = 4.0$ Hz, CH=CHH_{trans}), 5.02 (dddd, $^3J = 10.1$ Hz, $^2J = 1.1$ Hz, $^4J = 0.6$ Hz, $^4J_{PH} = 2.4$ Hz, CH=CH_{cis}H), 5.34 (dddd, $^3J = 16.0$ Hz, $^3J = 10.0$ Hz, $^3J = 9.7$ Hz, $^3J_{PH} = 5.7$ Hz, CH=CH_2), 7.09 (d, $^3J = 8.2$ Hz, tolyl CH), 7.14 (d, $^3J = 8.2$ Hz, tolyl CH), 7.30–7.75 (m, aromatic CH), 7.44 (dd, $^3J = 8.2$ Hz, $^3J_{PH} = 11.2$ Hz, aromatic CH), 7.48 (td, $^3J = 7.8$ Hz, $^4J_{PH} = 3.2$ Hz, aromatic CH), 7.55–7.62 (m, aromatic CH). IR (CH_2Cl_2) 1877, 1802 cm^{-1}. HRMS(EI) m/z Calc. for $C_{39}H_{34}O_2PRe$ (M^+) 752.1855, found 752.1875.

*4.19. Protonation of Cp(CO)$_2$Re[C(Tol)=^{13}C=^{13}C(Ph)-(PPh$_2$CH$_3$) (**6-^{13}C$_2$**) at −80°C*

Compound CF_3SO_3H (1.5 μL, 0.017 mmol) was added to the solution of (**6-^{13}C$_2$**) at −80°C. Spectra of the resulting solution of [Cp(CO)$_2$(H)Re(Tol)-C=^{13}C=^{13}C(Ph)(PPh$_2$CH$_3$)]OTf (**10-^{13}C$_2$**) were recorded at −80°C. ^{1}H-NMR (CD_2Cl_2, 500 MHz, −80°C) δ −8.57 (s, ReH), 2.29 (s, CH_3), 2.49 (d, $^2J_{PH} = 12.8$ Hz, PCH_3), 5.03 (C_5H_5), 7.0–7.8 (m, aromatic). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 125 MHz, −80°C) label at δ 72.6 (dd,

$^1J_{CC} = 97.0$, $^1J_{CP} = 97.0$ Hz, P^{13}C=^{13}C), 201.4 (dd, $^1J_{CC} = 97.0$, $^2J_{CP} = 7.6$ Hz, C=^{13}C=^{13}C). ^{31}P{^{1}H}-NMR (CD_2Cl_2, 202.5 MHz, −80°C) δ 22.0 (dd, $^1J_{CP} = 97.6$, $^2J_{CP} = 6.1$ Hz).

At −80°C, conversion of **10-^{13}C$_2$** to Cp(CO)$_2$Re[η^2-2,3-(Tol)HC=^{13}C=^{13}C(Ph)(PPh_2CH_3)]OTf (**11-^{13}C$_2$**) occurred with a half-life of 30 min. **11-^{13}C$_2$** was stable at r.t. ^{1}H-NMR (CD_2Cl_2, 500 MHz) δ 2.27 (s, CH_3), 2.45 (d, $^2J_{PH} = 13.0$ Hz), 4.4 (br s, =CH), 5.33 (C_5H_5), 7.0–7.8 (m, aromatic). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 125 MHz) δ 111.35 (dd, $^1J_{CC} = 86.1$, $^1J_{CP} = 74.11$ Hz, ^{13}C=^{13}CP), 182.6 (dd, $^1J_{CC} = 86.1$, $^2J_{CP} = 8.7$ Hz, ^{13}C=^{13}CP). ^{31}P{^{1}H}-NMR (CD_2Cl_2, 202.5 MHz) δ 17.5 (dd, $^1J_{CP} = 74.3$, $^2J_{CP} = 8.9$ Hz).

4.20. Cp(CO)$_2$Re[η^2-2,3-(Tol)DC=C=C(Ph)-(PPh_2CH_3)]OTf (**11-d**)

Addition of Ph_2PCH_3 (13 mg, 0.064 mmol) to a black solution of Cp(CO)$_2$Re=C(Tol)(C≡CPh) (**1a**) (28 mg, 0.053 mmol) in 1 ml CH_2Cl_2 at −20°C produced an orange solution after 15 min. The solution was cooled to −78°C and CF_3SO_3D (5 μl, 0.6 mmol) was added by syringe. Solvent was evaporated under vacuum at r.t. and the resulting yellow-brown precipitate was washed with diethyl ether and dissolved in a few drops of CH_2Cl_2. Slow vapor diffusion of pentane into the solution at −35°C gave fine white needles of **11-d** (25 mg, 45%). ^{1}H-NMR (THF-d_8, 500 MHz) δ 2.20 (s, CH_3), 2.61 (d, $^2J_{PH} = 13.5$ Hz, PCH_3), 5.44 (C_5H_5), 6.90 (d, $^3J = 7.9$ Hz, aromatic), 7.31–7.49 (m, aromatic), 7.61–7.64 (m, aromatic), 7.72 (ddd, $^3J = 13.0$, $^4J = 1.2$, $^3J_{PH} = 8.4$ Hz), 7.80 (ddd, $^3J = 13.0$, $^4J = 1.2$, $^3J_{PH} = 8.4$ Hz). ^{31}P{^{1}H}-NMR (THF-d_8, 202.5 MHz, 24°C) δ 14.93. ^{31}P{^{1}H}-NMR (THF-d_8, 202.5 MHz, −93°C) δ 17.14. ^{2}H-NMR (THF-d_8, 76.8 MHz) δ 4.50 (broad).

4.21. Reaction of Cp(CO)$_2$Re[η^2-2,3--(Tol)DC=C=C(Ph)(PPh_2CH_3)]OTf (**11-d**) with KO-*t*-Bu at −78°C

Addition KO-*t*-Bu (17 μL of a 0.50 M solution in THF-d_8, 0.0085 mmol) to a colorless solution of **11-d** (5.7 mg, 0.0056 mmol) in 0.4 ml CD_2Cl_2 at −78°C immediately produced a bright yellow solution of a 3:1 mixture of **4-d**:**6** as shown by ^{1}H-NMR.

Compound **4-d:** ^{1}H-NMR (THF-d_8, 500 MHz, −91°C) δ 2.27 (s, CH_3), 3.13 (dd, $^2J = 16.7$, $^2J_{PH} = 8.1$ Hz, PCH*H*), 3.35 (dd, $^2J = 16.5$, $^2J_{PH} = 12.6$ Hz, PC*H*H), 4.10 (C_5H_5), 7.0–7.8 (aromatic). ^{2}H-NMR (THF, 76.8 MHz, −91°C) δ 5.4 (CH_2CD). ^{31}P{^{1}H}-NMR (THF-d_8, 202.5 MHz, −91°C) δ 34.5.

Compound **6:** ^{1}H-NMR (THF-d_8, 500 MHz, −91°C) δ 2.22 (s, CH_3), 2.47 (d, $^2J_{PH} = 13.0$ Hz, PCH_3), 4.94 (C_5H_5), 7.0–7.8 (aromatic). ^{31}P-NMR (THF-d_8, 202.5 MHz, −91°C) δ 17.7.

5. Supplementary material

Crystallographic data (excluding structure factors) for compounds **3**, **4**, **8**, and **9c** have been deposited with the Cambridge Crystallographic Data Center, CCDC 150167 for compound **3**, CCDC 150164 for compound **4**, CCDC 150166 for compound **8**, and CCDC 150165 for compound **9c**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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