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# Phosphinidene Addition to Conjugated Allenes

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Dedicated to Professor Armin de Meijere on the occasion of his 70th birthday.

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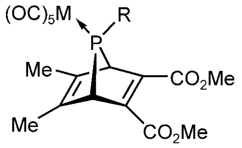
**Abstract:** Generating the transient electrophilic tungsten pentacarbonyl-phenylphosphinidene complex PhP=W(CO)$_5$ in the presence of 2,7-dimethylocta-2,3,5,6-tetraene leads to the formation of a 3,4-disubstituted phosphole or a complexed phospholene, depending on the reaction conditions. The formation of the phospholene results from the reaction of PhP=W(CO)$_5$ with the diallene, while the formation of the phosphole arises from reaction with 3,4-diisopropylidene-cyclobutene, which is formed *in situ* from the isomerization of the conjugated allene.

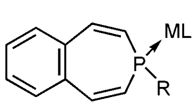
**Keywords:** cycloaddition; diallenes; phosphinidenes; reaction mechanisms; rearrangement

## Introduction

Electrophilic phosphinidene complexes RP=ML$_n$ are the phosphorus analogues of the extensively studied Fischer-type carbenes and can be generated as transient intermediates from appropriate precursors. The intriguing reactivity of such species makes them valuable building blocks for the synthesis of novel organophosphorus compounds that can be used for a plethora of applications, which has been the subject of several reviews.[1] The most employed method to generate neutral electrophilic phosphinidene complexes, developed in the early 1980s by Mathey and Marinetti, consists of the cheletropic elimination from 7-phosphanorbornadiene complexes **1** (M = Cr, Mo, W).[2] Spectroscopic evidence for the transient carbene-like species is still elusive, but its formation is inferred from trapping reactions.[1] Recently, 3*H*-3-benzophosphepine complexes **2** [R = Ph, ML$_n$ = W(CO)$_5$, Mo(CO)$_5$, MnCp(CO)$_2$, Cr(CO)$_5$; R = Me, *t*-Bu, NEt$_2$, ML$_n$ = W(CO)$_5$] were developed in our group as an alternative phosphinidene precursor that offers advantages.[3] These are its simpler synthesis, the variety of allowable transition metal complexing groups is larger, and the by-product of the cheletropic elimination, naphthalene, can be removed easier, by sublimation, than the benzene derivative that results from **1**.[1] Of further importance is that liberating phosphinidenes from **1** occurs thermally at 110 °C, or 55 °C using CuCl as catalyst, whereas only ~65 °C and no catalyst is needed for the benzophosphepine complexes **2**. This means that thermally unstable species cannot be synthesized from **1** at 110 °C, while the lower temperature Cu-catalyzed process is postulated to give the less reactive and bulkier RP(Cl)M(CO)$_5$-CuS (S = toluene or alkene) that is more sensitive to steric hindrance.[4] Hence, the synthetic pathways might differ depending on whether **1** or **2** is used.

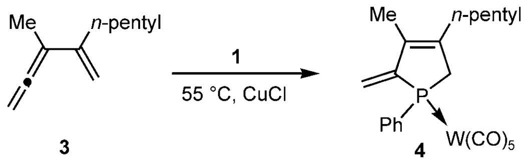


**1**



**2**

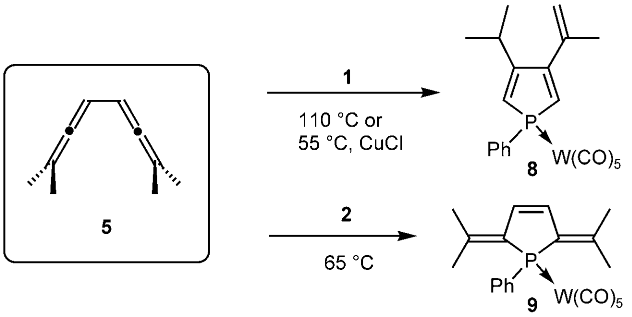
Electrophilic phosphinidenes react with C=C bonds even when they are conjugated.[1] Typically, the *in* *situ*-generated phosphinidene complex performs concerted [1+2] cycloadditions to π-bonds with full retention of configuration, forming three-membered phosphiranes that can be surprisingly stable[5] or rearrange into other products.[1,6] The retention of configuration observed in all cycloaddition products[6] of both (*E*)- and (*Z*)-double bonds underlines the concerted reactivity expected for singlet species. Five-membered phospholenes can result from the reaction with conjugated dienes, either by a [1,3]-sigmatropic shift of the initial [1+2] adduct[6,7] or from the less common direct [1+4] cycloaddition.[8] Earlier, we found that reaction of allenene **3** with PhP=W(CO)$_5$, generated from **1** with CuCl at 55 °C, gave two phosphirane intermediates with characteristic $^{31}$P NMR resonances at −128 and −131 ppm that were not isolable due to their rapid conversion to phospholene **4** *via* a [1,3]-sigmatropic shift (Scheme 1).[9]



**Scheme 1.**

The reactivity towards conjugated allenes has been investigated for the iron-complexed phosphinidene ($i$-Pr)$_2$NP=Fe(CO)$_4$, which is generated *in situ* from the reduction of ($i$-Pr)$_2$NPCl$_2$ with Na$_2$Fe(CO)$_4$ at −30 °C.[10] It was suggested that ($i$-Pr)$_2$NP=Fe(CO)$_4$ undergoes [1+2] cycloaddition to one of the less hindered double bonds of 2,7-dimethylocta-2,3,5,6-tetraene (**5**), yielding intermediate vinylphosphirane **6**, which upon heating undergoes a [1,3]-sigmatropic shift[11] to 2,5-diisopropylidene-phospholene **7** (Scheme 2).

Here we report on the deviating behaviour of the tungsten-complexed phosphinidene PhP=W(CO)$_5$ that, when generated *in situ* in the presence of diallene **5**, results in the formation of the unexpected 3,4-disubstituted phosphole **8** or phospholene complex **9**, depending on the reaction conditions (Scheme 3). The mechanism for the formation of the two products will be examined with experimental and computational methods.

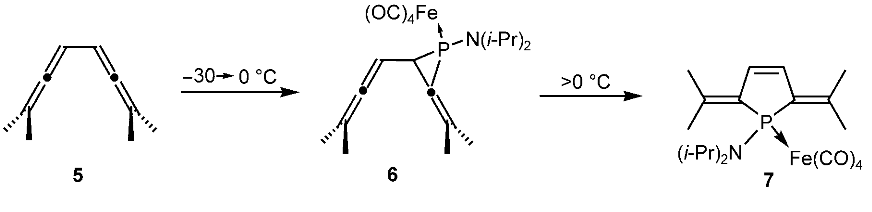


**Scheme 3.** Reaction of PhP=W(CO)$_5$ with tetraene **5**.

## Results and Discussion

Cheletropic elimination of phosphanorbornadiene **1**, either at 110 °C or at 55 °C using CuCl, in the presence of tetraene **5** resulted in the formation of phosphole **8** as sole product ($\delta^{31}$P = 12.5 ppm; Scheme 3), which was isolated as yellow crystals in, respectively, 93% and 58% yields. The assignment of structure **8** is readily made due to the presence of the characteristic absorptions of the isopropyl and isopropylene groups in the $^{1}$H and $^{13}$C NMR spectra and established unequivocally by a single-crystal X-ray structure determination (Figure 1). In contrast, when transient PhP=W(CO)$_5$ was generated in the presence of **5** at 65 °C, using benzophosphepine **2** as precursor, 2,5-diisopropylidene-phospholene **9** ($\delta^{31}$P = −0.5 ppm) was obtained as major product (>90%) with a small amount of **8** in a 10:1 ratio. Phospholene **9** was isolated after column chromatography as yellow crystals in 61% yield. The $^{1}$H, $^{13}$C, and $^{31}$P NMR characteristics are in accord with those reported for the Fe(CO)$_4$ complex **7**.

The formation of **8** is surprising since we expected PhP=W(CO)$_5$ to generate phospholene **9** in all cases, in analogy to the reaction of diallene **5** with ($i$-Pr)$_2$NP=Fe(CO)$_4$ (Scheme 2).[10] Could the different behaviour be due to the difference in reactions conditions? Could it be that the diallene undergoes a modification, a rearrangement, under the reaction condi-



**Scheme 2.** Addition of ($i$-Pr)$_2$NP=Fe(CO)$_4$ to tetraene **5**.

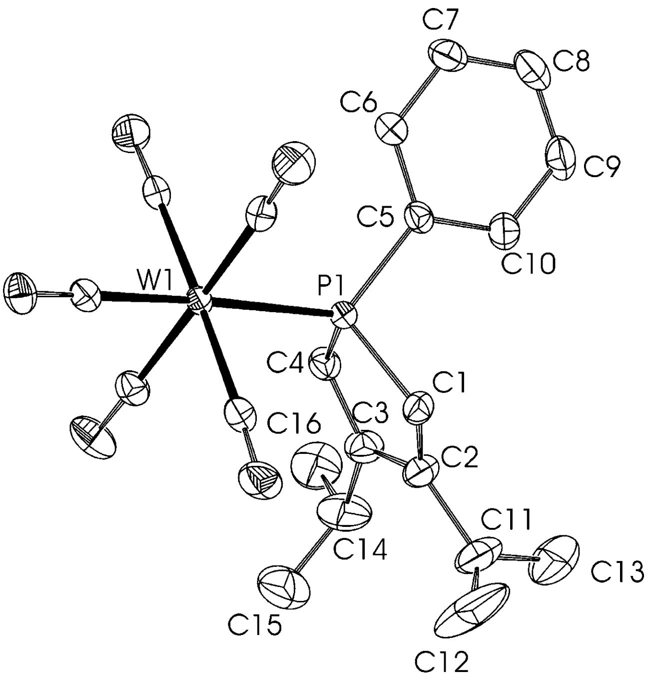


**Figure 1.** Displacement ellipsoid plot (50% probability level) of **8**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles and torsion angles [°]: P1−W1 2.5081(5), P1−C5 1.8234(19), P1−C1 1.794(2), P1−C4 1.788(2), C1−C2 1.337(3), C2−C3 1.490(3), C3−C4 1.344(3), C2−C11 1.493(3), C11−C12 1.368(4), C11−C13 1.442(4), C3−C14 1.510(3), C14−C15 1.477(4), C14−C16 1.495(4); C1−P1−C4 90.96(10), P1−C1−C2 110.96(16), C1−C2−C3 113.50(19), C2−C3−C4 113.21(19), C3−C4−P1 110.94(17); P1−C1−C2−C3 1.6(2), C1−C2−C3−C4 3.3(3), C2−C3−C4−P1 −6.5(2), C3−C4−P1−C1 6.21(17).

tions? For example, it is known that diallenes are prone to isomerizations and that **5** can undergo thermal isomerization to 3,4-diisopropylidene-cyclobutene (**10**)[12] and that CuCl can catalyze this process, thereby facilitating the conrotatory electrocyclic ring closure.[13,14] Therefore, the stability of substrate **5** was investigated under the phosphinidene reaction conditions. Heating a solution of **5** in toluene at 110 °C or at 55 °C in the presence of CuCl for 15 min resulted in both cases in the quantitative conversion into cyclobutene **10**. On the contrary, the electrocyclic ring-closure (without CuCl) is far slower at 65 °C and completes in ~40 h. These observations are supported by DFT calculations at BP/TZP that revealed a concerted, closed-shell ring closure of **5** that requires 26.4 kcal mol$^{-1}$ and is exothermic by $-9.7$ kcal mol$^{-1}$ (Figure 2).

For the Cu-catalyzed process, four different CuCl adducts of diallene **5** were found of similar stability (see the Supporting Information) of which only the least stable one ($\Delta E = 6.6$ kcal mol$^{-1}$) leads to the formation of **10**[CuCl] ($\Delta E = -15.1$ kcal mol$^{-1}$) with a barrier of only 3.8 kcal mol$^{-1}$ (Figure 3).

These results indicate that while the phosphinidene addition to diallene **5** leads to the formation of phospholene **9** (Scheme 2), the formation of phosphole **8** arises from the reaction of PhP=W(CO)$_5$ with the *in situ* formed 3,4-bis(isopropylidene)cyclobutene (**10**). Indeed, reaction of cyclobutene **10** with PhP=W(CO)$_5$, generated from **1** at 110 °C or 55 °C using CuCl, resulted in the quantitative formation of **8**. Monitoring instead the reaction of **10** with benzophosphepine complex **2** at 65 °C by $^{31}$P NMR spectroscopy showed besides the formation of **8**, two side-products with $^{31}$P resonances at $-118.3$ and $-124.9$ ppm (ratio 10:1.2:1.0) that were identified as *syn*- and *anti*-**12** (Scheme 4). Prolonged heating of **12** at 65 °C resulted in the quantitative formation of **8**. Phosphinidene addition to the less hindered endocyclic double bond of **10** should yield **11**, which we pre-

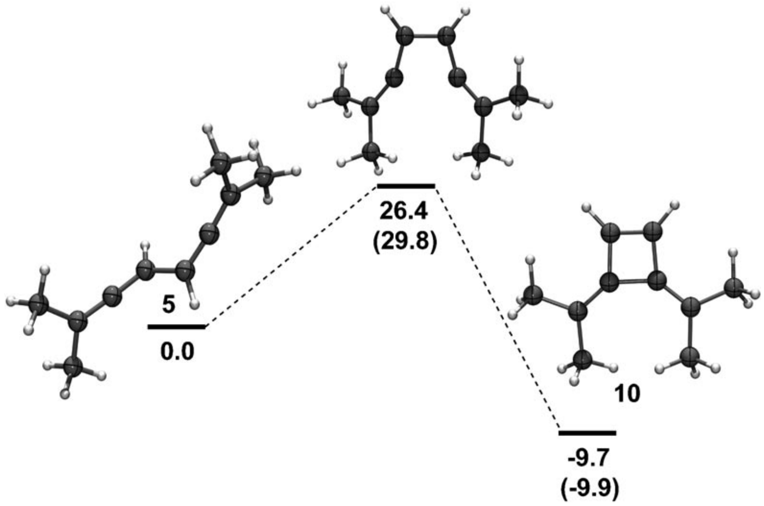


**Figure 2.** Relative BP/TZP energies in kcal mol$^{-1}$ for the thermal ring-closure of 2,7-dimethylocta-2,3,5,6-tetraene (**5**) to 3,4-diisopropylidene-cyclobutene (**10**). The relative MRDFT(BHLYP)/TZVP//BP/TZP energies are given in parentheses.

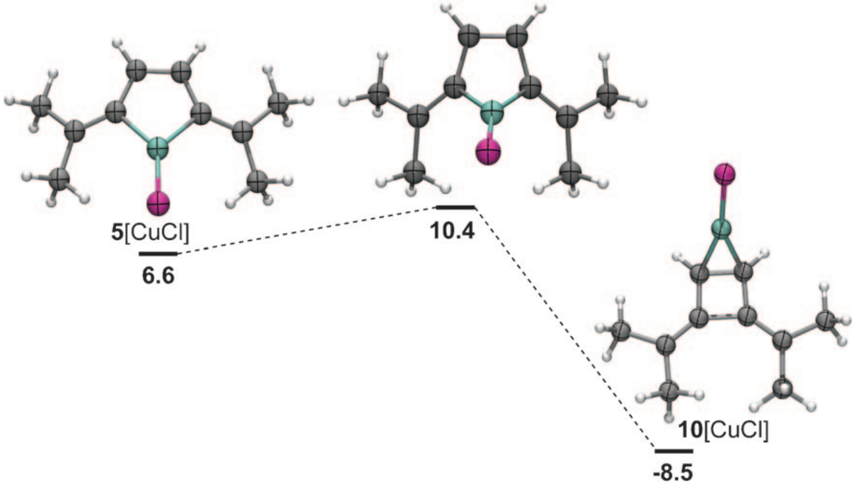


**Figure 3.** Relative BP/TZP energies in kcal mol$^{-1}$ for the conversion of **5**[CuCl] into **10**[CuCl].

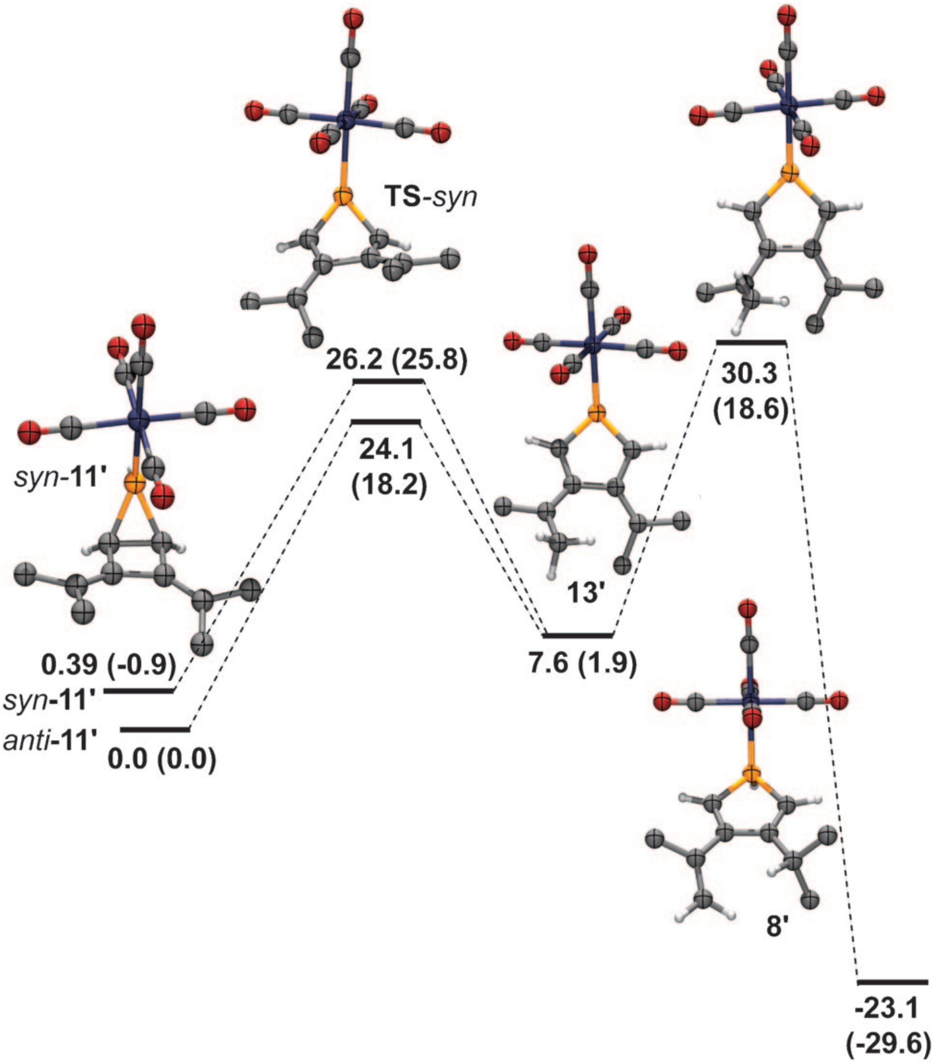
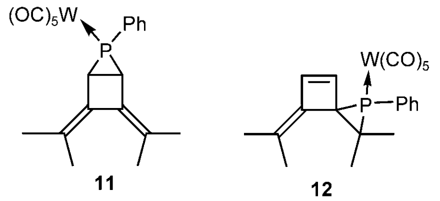


**Figure 4.** Relative BP/TZP energies in kcal mol$^{-1}$ for the formation of phosphole **8′**. The relative MRDFT(BHLYP)/TZVP//BP/TZP energies are given in parentheses.



**Scheme 4.** Phosphinidene adducts of cyclobutene **10**.

sume to be more reactive than **12**, and rearrange to the same phosphole product **8**.

To bring about an understanding into the unexpected formation of **8**, we resorted again to density functional theory by addressing the reaction of **10** with $HP{=}Cr(CO)_5$ as simplified model (labeled with a prime ′) for $PhP{=}W(CO)_5$. The phosphinidene addition to the endocyclic double bond of **10**, resulting in *syn* and *anti* phosphiranes **11**′, is exothermic by, respectively, 32.8 and 33.2 kcal mol$^{-1}$ and favoured (by ~8–10 kcal mol$^{-1}$) over the addition to the exocyclic double bond of **10** that gives *syn*- and *anti*-**12**’ (Figure 4; all energies are relative to *anti*-**11**′).

Homolytic C–C bond cleavage of phosphabicyclo-[2.1.0]pentane **11**′, in analogy to the all-carbon bicyclo[2.1.0]pentanes,[15] is the next step and generates singlet diradical phosphacyclopentane-1,3-diyl **13**′ ($\Delta E = 7.6$ kcal mol$^{-1}$) which is stabilized by allylic resonance. The reaction barriers for its formation from *anti*- and *syn*-**11**’ are, respectively, 24.1 and 25.8 kcal mol$^{-1}$. Expectedly, phosphole **8**′ is the global minimum and can be formed directly from **13**′ *via* a [1,7]-H-shift ($\Delta E = -30.7$, $\Delta E^{\neq} = 22.7$ kcal mol$^{-1}$). Due to the diradical character of the intermediates **13**, we performed single point energy multi-reference (MR-DFT) calculations (BHLYP/TZVP) on the DFT (BP/TZP) optimized structures. The significant reduction in reaction barriers for *anti*-**11**′ and **13**′ by 5.9 and 6.0 kcal mol$^{-1}$, respectively, (see Figure 4) suggests these processes to be likely under the reaction conditions.

In conclusion, generating phosphinidene complex $PhP{=}W(CO)_5$ in the presence of tetramethyldiallene **5** leads to the formation of two different products, that is, phosphole **8** or phospholene **9**, depending on the reaction conditions. Whereas the expected phospholene **9** is formed *via* a 1,3-sigmatropic shift of the initial vinylphosphirane product, phosphole **8** arises from the phosphinidene addition to the *in situ* generated diisopropylidenecyclobutene **10**, followed by homolytic rupture of the intracyclic C–C bond of the intermediate phosphabicyclopentane **11** and a subsequent [1,7]-H-shift.

# Experimental Section

## Computational Methods

All DFT calculations were performed with the Amsterdam Density Functional (ADF) program,[16] using the Perdew correlation functional (BP86) and a triple-ξ basis set with one polarization function (TZP). Multi-reference DFT single point energy calculations were performed using the TURBOMOLE suite of programs,[17]with the BHLYP functional and TZVP basis set on BP86/TZP optimized geometries.

## General Experimental Remarks

All syntheses were performed with the use of Schlenk techniques under an atmosphere of dry nitrogen. Toluene was freshly distilled under nitrogen from sodium. Other solvents were used as purchased. Since the phosphinidene complex bears a transition metal group with carbonyl ligands, the reaction mixtures need to be protected from light. NMR spectra were recorded at 300.2 K on a Bruker Advance 250 ($^1$H, $^{13}$C, $^{31}$P; 85% $H_3PO_4$) or a Bruker Advance 400 spectrometer ($^1$H, $^{13}$C) and referenced internally to residual solvent resonances ($CDCl_3$: $^1$H: $\delta = 7.26$, $^{13}$C{$^1$H}: $\delta = 77.0$). IR spectra were recorded on a Shimadzu FTIR-8400S spectrophotometer. Fast atom bombardment (FAB) mass spectrometry was carried out using a JEOL JMS SX/SX 102A four-sector mass spectrometer, coupled to a JEOL MS-MP9021D/UPD system program. Samples were loaded in a matrix solution (3-nitrobenzyl alcohol) on to a stainless steel probe and bombarded with xenon atoms with an energy of 3 keV. During the high resolution FAB-MS measurements a resolving power of 10,000 (10% valley definition) was used. The elemental analysis of **8** was performed by the Microanalytischer Labor Pascher, Remagen-Bandorf (Germany). Melting points were measured on samples in unsealed capillaries and are uncorrected. 2,7-Dimethylocta-2,3,5,6-tetraene (**5**),[18] 3,4-bis(isopropylidene)cyclobutene (**10**),[19] phosphanorbornadiene complex **1**[2] and 3*H*-benzophosphepine complex **2**[3] were synthesized according to literature procedures.

## (1-Phenyl-3-isopropenyl-4-isopropyl-1*H*-phosphole)pentacarbonyltungsten (8)

***Procedure A:*** A solution of 2,7-dimethylocta-2,3,5,6-tetraene **5** (0.041 g, 0.30 mmol), phosphanorbornadiene **1** (0.137 g, 0.20 mmol) and a catalytic amount of CuCl (~10 mol%) in toluene (10 mL) was heated at 55 °C for 6.5 h. After evaporation of the volatiles, the crude product was purified by column chromatography over aluminum oxide with pentane as eluent. Crystallization from pentane at −75 °C afforded **8** as yellow crystals; yield: 0.066 g (58%).

***Procedure B:*** A solution of **5** (0.040 g, 0.30 mmol) and phosphanorbornadiene **1** (0.131 g, 0.20 mmol) in toluene (10 mL) was heated at 110 °C until $^{31}$P NMR spectroscopy showed complete consumption of **1** (18 h). Evaporation of the volatiles and subsequent column chromatography over aluminum oxide with pentane as eluent yielded **8** as a yellow oil. Crystallization from pentane at −75 °C afforded **8** as yellow crystals; Yield: 0.105 g (93%).

***Procedure C:*** A solution of 3,4-bis(isopropylidene)-cyclobutene **10** (0.134 g, 1.00 mmol), phosphanorbornadiene **1**

(0.131 g, 0.20 mmol) and CuCl (~20 mg) in toluene (2 mL) was heated at 55 °C for 9.5 h. Evaporation of the volatiles and column chromatography over aluminum oxide with pentane as eluens afforded **8** as a yellow oil; yield: 0.080 g (71%).

***Procedure D:*** A solution of 3,4-bis(isopropylidene)-cyclobutene **10** (0.134 g, 1.00 mmol), phosphanorbornadiene **1** (0.130 g, 0.20 mmol) in toluene (2 mL) was heated at 110 °C for 22 h. Evaporation of the volatiles followed by column chromatography over aluminum oxide with pentane as eluens yielded **8** as a yellow oil; yield: 0.056 g (50%); mp 61.7–61.8 °C; $^{1}$H NMR (CDCl$_3$): $\delta = 1.15$ (d, $^{3}J_{H,H} = 6.7$ Hz, 3 H, CH-C$H_3$), 1.22 (d, $^{3}J_{H,H} = 6.7$ Hz, 3 H, CH-C$H_3$), 2.02 (s, 3 H, =C-C$H_3$), 2.91 (dsept, $^{3}J_{H,H} = 6.8$ Hz, $^{4}J_{H,P} = 0.9$ Hz, 1 H, C$H$-CH$_3$), 5.01 (s, 1 H, =C$H_2$), 5.19 (s, 1 H, =C$H_2$), 6.54 (m, 1 H, PC$H$), 6.67 (m, 1 H, PC$H$), 7.37–7.55 (m, 5 H, Ph$H$); $^{13}$C{$^{1}$H} NMR (CDCl$_3$): $\delta = 22.6$ (s, CH-$C$H$_3$), 23.2 (s, CH-$C$H$_3$), 24.0 (s, =C-$C$H$_3$), 29.2 (d, $^{3}J_{C,P} = 9.4$ Hz, $C$H-CH$_3$), 116.2 (s, =$C$H$_2$), 127.3 (d, $^{1}J_{C,P} = 43.5$ Hz, P$C$H=C-*i*-Pr), 129.0 (d, $^{3}J_{C,P} = 10.1$ Hz, *m*-Ph), 129.7 (d, $^{1}J_{C,P} = 41.3$ Hz, *ipso*-Ph), 130.6 (d, $^{4}J_{C,P} = 2.5$ Hz, *p*-Ph), 131.5 (d, $^{2}J_{C,P} = 11.9$ Hz, *o*-Ph), 131.9 [d, $^{1}J_{C,P} = 41.5$ Hz, P$C$H=C-C(CH$_3$)=CH$_2$], 140.9 (d, $^{2}J_{C,P} = 11.3$ Hz, =$C$-*i*-Pr), 155.7 [d, $^{2}J_{C,P} = 9.4$ Hz, =$C$-C-(CH$_3$)=CH$_2$], 160.9 [d, $^{3}J_{C,P} = 6.9$ Hz, $C$(CH$_3$)=CH$_2$], 196.1 (d, $^{2}J_{C,P} = 6.3$ Hz, $C$O$_{eq}$), 198.7 (d, $^{2}J_{C,P} = 18.2$ Hz, $C$O$_{ax}$); $^{31}$P{$^{1}$H} NMR (CDCl$_3$): $\delta = 12.5$ ($^{1}J_{P,W} = 211.6$ Hz); IR: $\nu =$ 1871–1905 (s/br, CO$_{eq}$), 1984 (w, CO$_{eq}$), 2071 cm$^{-1}$ (m, CO$_{ax}$); HR-MS: m/z = 566.0483, calcd. for $C_{21}H_{19}O_5PW$: 566.0480; MS: *m/z* (%) = 566 (54) [M]$^+$, 510 (44) [M−2 CO]$^+$, 482 (41) [M−3 CO]$^+$, 426 (86) [M−5 CO]$^+$; anal. found: C 44.57, H 3.42, P 5.10; calcd. for $C_{21}H_{19}O_5PW$: C 44.54, H, 3.38, P 5.47.

### (2,5-Diisopropylidene-1-phenyl-2,5-dihydro-1*H*-phosphole)Pentacarbonyltungsten(0) (9)

A solution of 2,7-dimethylocta-2,3,5,6-tetraene **5** (40 mg, 0.30 mmol) and benzophosphepine complex **2** (112 mg, 0.20 mmol) in toluene (3 mL) was heated at 65 °C until complete fragmentation of **2** (48 h). The crude product was purified by column chromatography over silica with pentane as eluent and crystallized from pentane at −20 °C to afford phospholene **9** as yellow crystals; yield: 66 mg (61%); mp 113 °C; $^{1}$H NMR (CDCl$_3$): $\delta = 1.63$ (s, 6 H, C$H_3$), 1.94 (s, 6 H, C$H_3$), 6.68 (d, $^{3}J_{H,P} = 15.4$ Hz, 2 H, PCC$H$), 7.40–7.42 (m, 3 H, *p*-Ph$H$, *m*-Ph$H$), 7,63–7.71 (m, 2 H, *o*-Ph$H$); $^{13}$C{$^{1}$H} NMR (CDCl$_3$): $\delta = 21.3$ (d, $^{3}J_{C,P} = 9.2$ Hz, $C$H$_3$), 24.7 (d, $^{3}J_{C,P} = 10.0$ Hz, $C$H$_3$), 128.6 (d, $^{3}J_{C,P} = 10.4$ Hz, *m*-Ph), 130.1 (d, $^{2}J_{C,P} = 14.4$ Hz, *o*-Ph), 130.3 (d, $^{4}J_{C,P} = 3.5$ Hz, *p*-Ph), 132.9 (d, $^{1}J_{C,P} = 33.1$ Hz, *ipso*-Ph), 132.0 (d, $^{2}J_{C,P} = 13.5$ Hz, PC$C$=), 137.5 (d, $^{2}J_{C,P} = 10.7$ Hz, (CH$_3$)$_2$$C$=C), 138.5 (d, $^{1}J_{C,P} =$ 47.1 Hz, P$C$=), 197.1 (d, $^{2}J_{C,P} = 6.7$ Hz, $C$O$_{eq}$), 199.2 (d, $^{2}J_{C,P} = 21.0$ Hz, $C$O$_{ax}$); $^{31}$P{$^{1}$H} NMR (CDCl$_3$): $\delta = -0.5$ ($^{1}J_{P,W} = 235.1$ Hz); IR: $\nu = 1878$–1885 (s/br, CO$_{eq}$), 1991 (w, CO$_{eq}$), 2067 $^{cm-1}$ (m, CO$_{ax}$); HR-MS: *m/z* = 566.0475, calcd. for $C_{21}H_{19}O_5PW$: 566.0480; MS: *m/z* (%) = 566 (98) [M]$^+$, 510 (100) [M−2 CO]$^+$, 426 (55) [M−5 CO]$^+$.

### (6-Isopropylidene-2,2-dimethyl-1-phenyl-1-phosphaspiro[2.3]hex-4-ene)pentacarbonyltungsten(0) (12)

A solution of **10** (1.433 g, 10.7 mmol) and benzophosphepine **2** (0.500 g, 0.90 mmol) in toluene (10 mL) was heated at 65 °C until complete decomposition the **2** (35 h), when the $^{31}$P NMR showed only three resonances at 12.5 (**8**), −118.3 (**12a**) and −124.9 (**12b**) ppm in a 1:0.12:0.10 ratio, respectively. The reaction mixture was then concentrated and filtered over a short column of silica gel with pentane as eluent. Fractional crystallization from pentane at −80 °C yielded **12a** as a white solid; yield: 40 mg (8%). $^{1}$H NMR (CDCl$_3$): $\delta = 0.72$ (s, 3 H, C$H_3$C=), 1.50 (d, 3 H, $^{3}J_{H,P} =$ 19.0 Hz, C$H_3$CP), 1.60 (d, 3 H, $^{3}J_{H,P} = 11.6$ Hz, C$H_3$CP), 1.74 (s, 3 H, C$H_3$C=), 6.44 (br s, 1 H, $H$C=CHCP), 6.86 (d, 1 H, $^{3}J_{H,P} = 3.1$ Hz, =C$H$CP), 7.30–7.38 (m, 3 H, *p*-Ph$H$, *m*-Ph$H$), 7.40–7.55 (m, 2 H, *o*-Ph$H$); $^{13}$C{$^{1}$H} NMR: $\delta = 20.8$ (s, $C$H$_3$C=), 21.6 (s, $C$H$_3$C=), 22.8 (d, $^{2}J_{C,P} = 3.6$ Hz, $C$H$_3$CP), 26.3 (d, $^{2}J_{C,P} = 7.8$ Hz, $C$H$_3$CP), 32.0 [br. s, (CH$_3$)$_2$$C$P], 56.8 [br. s, $C$PC(CH$_3$)$_2$], 119.0 [s, (CH$_3$)$_2$$C$=], 134.4 [s, (CH$_3$)$_2$C=$C$], 138.7 (br. s, PCCH=$C$H), 139.8 (d, $^{2}J_{C,P} = 11.4$ Hz, PC$C$H=), 196.0 (d, $^{1}J_{C,W} = 8.0$ Hz, $C$O$_{eq}$), 198.1 (d, $^{2}J_{C,P} =$ 29.5 Hz, $C$O$_{ax}$), the resonances of the phenyl ring are unresolved. The $^{13}$C resonances at 32.0 and 56.8 ppm were observed with HMBC NMR spectroscopy; $^{31}$P{$^{1}$H} NMR (CDCl$_3$): $\delta = -118.3$ ($^{1}J_{P,W} = 250.9$ Hz).

### X-Ray Crystal Structure Determination of 8

$C_{21}H_{19}O_5PW$, Fw = 566.18, yellow block, 0.54 × 0.42 × 0.36 mm$^3$, monoclinic, $P2_1/c$ (no. 14), $a = 14.0275(4)$, $b =$ 9.5551(4), $c = 20.2053(7)$ Å, $\beta = 126.480(2)°$, $V =$ 2177.56(13) Å$^3$, $Z = 4$, $D_x = 1.727$ g cm$^{-3}$, $\mu = 5.405$ mm$^{-1}$. 43575 Reflections were measured on a Nonius KappaCCD diffractometer with rotating anode (graphite monochromator, $\lambda = 0.71073$ Å) at a temperature of 150 K up to a resolution of $(\sin\theta/\lambda)_{max} = 0.65$ Å$^{-1}$. The reflections were integrated using the program EvalCCD.[20] Scaling and absorption correction based on multiple measured reflections was performed with the program SADABS[21] (0.07–0.14 correction range). 5003 Reflections were unique ($R_{int} = 0.0228$) of which 4512 were observed [$I > 2\sigma(I)$]. The structure was solved with the program SHELXS-97[22] using direct methods and refined with SHELXL-97[22] against F$^2$ of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined with a riding model. The carbon atoms of the isopropyl groups have large displacement parameters indicating a slight disorder, which has not been resolved. 256 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0138/0.0302. R1/wR2 [all refl.]: 0.0186/0.0318. S = 1.105. Residual electron density between −0.58 and 1.06 e Å$^3$. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[23]

CCDC 713887 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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## References

[1] a) J. C. Slootweg, K. Lammertsma, in: *Science of Synthesis* Vol. 42, (Eds.: B. M. Trost, F. Mathey), Georg Thieme Verlag: Stuttgart, **2009**, pp 15–36; b) K. Lammertsma, *Top. Curr. Chem.* **2003**, *229*, 95–119; c) K. Lammertsma, M. J. M. Vlaar, *Eur. J. Org. Chem.* **2002**, 1127–1138; d) F. Mathey, N. H. T. Huy, A. Marinetti, *Helv. Chim. Acta* **2001**, *84*, 2938–2957; e) F. Mathey, *Dalton Trans.* **2007**, 1861–1868.

[2] a) A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, *J. Am. Chem. Soc.* **1982**, *104*, 4484–4485; b) A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, *J. Chem. Soc. Chem. Commun.* **1982**, 667–668; c) A. Marinetti, F. Mathey, *Organometallics* **1982**, *1*, 1488–1492.

[3] a) M. L. G. Borst, R. E. Bulo, C. W Winkel, D. J. Gibney, A. W. Ehlers, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, *J. Am. Chem. Soc.* **2005**, *127*, 5800–5801; b) M. L. G. Borst, R. E. Bulo, D. J. Gibney, Y. Alem, F. J. J. de Kanter, A. W. Ehlers, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, *J. Am. Chem. Soc.* **2005**, *127*, 16985–16999.

[4] a) K. Lammertsma, A. W. Ehlers, M. L. McKee, *J. Am. Chem. Soc.* 2003, 125, 14750–14759; b) J. C. Slootweg, S. Krill, F. J. J. de Kanter, M. Schakel, A. W. Ehlers, M. Lutz, A. L. Spek, K. Lammertsma, *Angew. Chem.* **2005**, *117*, 6737–6740; *Angew. Chem. Int. Ed.* **2005**, *44*, 6579–6582.

[5] a) J. C. Slootweg, M. Schakel, F. J. J. de Kanter, A. W. Ehlers, S. I. Kozhushkov, A. de Meijere, M. Lutz, A. L. Spek, K. Lammertsma, *J. Am. Chem. Soc.* **2004**, *126*, 3050; b) J. C. Slootweg, F. J. J. de Kanter, M. Schakel, M. Lutz, A. L. Spek, S. I. Kozhushkov, A. de Meijere, K. Lammertsma, *Chem. Eur. J.* **2005**, *11*, 6982–6993.

[6] K. Lammerstma, J. T. Hung, P. Chand, G. M. Gray, *J. Org. Chem.* **1992**, *57*, 6557–6560.

[7] M. J. van Eis, C. M. D. Komen, F. J. J. de Kanter, W. H. de Wolf, K. Lammertsma, F. Bickelhaupt, M. Lutz, A. L. Spek, *Angew. Chem.* **1998**, *110*, 1656–1658; *Angew. Chem. Int. Ed.* **1998**, *37*, 1547–1550.

[8] M. J. van Eis, F. J. J. de Kanter, W. H. de Wolf, K. Lammertsma, F. Bickelhaupt, M. Lutz, A. L. Spek, *Tetrahedron* **2000**, *56*, 129–136.

[9] J. B. M. Wit, *Bottled Phosphinidene Complexes. A Study on their Synthesis and Reactivity, PhD thesis*, Vrije Universiteit Amsterdam, **2001**.

[10] J. B. M. Wit, G. T. van Eijkel, F. J. J. de Kanter, M. Schakel, A. W. Ehlers, M. Lutz, A. L. Spek, K. Lammertsma, *Angew. Chem.* **1999**, *111*, 2716–2719; *Angew. Chem. Int. Ed.* **1999**, *38*, 2596–2599.

[11] a) W. J. Richter, *Chem. Ber.* **1983**, *116*, 3293–3300; b) W. J. Richter, *Chem. Ber.* **1985**, *118*, 1575–1579; c) B. Wang, C. H. Lake, K. Lammertsma, *J. Am. Chem. Soc.* **1996**, *118*, 1690–1695; d) M. J. van Eis, T. Nijbacker, F. J. J. de Kanter, W. H. de Wolf, K. Lammertsma, F. Bickelhaupt, *J. Am. Chem. Soc.* **2000**, *122*, 3033–3036; e) R. E. Bulo, A. W. Ehlers, S. Grimme, K. Lammertsma, *J. Am. Chem. Soc.* **2002**, *124*, 13903–13910.

[12] L. Skattebøl, S. Solomon, *J. Am. Chem. Soc.* **1965**, *87*, 4506–4513.

[13] a) D. J. Pasto, S. H. Yang, *J. Org. Chem.* **1989**, *54*, 3544–3549; b) D. J. Pasto, W. Kong, *J. Org. Chem.* **1989**, *54*, 4028–4033; c) D. J. Pasto, N. Z. Huang, *J. Org. Chem.* **1985**, *50*, 4465–4467.

[14] F. Toda, K. Tanaka, T. Tamashima, M. Kato, *Angew. Chem.* **1998**, *110*, 2852–2855; *Angew. Chem. Int. Ed.* **1998**, *37*, 2724–2727.

[15] a) G. R. Shelton, D. A. Hrovat, W. T. Borden, *J. Org. Chem.* **2006**, *71*, 2982–2986; b) B. K. Carpenter, *Org. Biomol. Chem.* **2004**, *2*, 103–109.

[16] a) G. te Velde, F. M. Bickelhaupt, S. J. A. van Gisbergen, C. Fonseca Guerra, E. J. Baerends, J. G. Snijders, T. Ziegler, 'Chemistry with ADF', *J. Comput. Chem.* **2001**, *22*, 931–967; b) C. Fonseca Guerra, J. G. Snijders, G. te Velde, E. J. Baerends, *Theor. Chem. Acc.* **1998**, *99*, 391–403; c) ADF2007.01, *SCM, Theoretical Chemistry*, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.

[17] a) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *TURBOMOLE V5–3*, *Chem. Phys. Lett.* **1989**, *162*, 165–169; b) O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346–354; c) S. Grimme, M. Waletzke, *J. Chem. Phys.* **1999**, *111*, 5645–5655.

[18] M. S. Sigman, B. E. Eaton, *J. Am. Chem. Soc.* **1996**, *118*, 11783–11788.

[19] D. J. Pasto, D. K. Mitra, *J. Org. Chem.* **1982**, *47*, 1381–1382.

[20] A. J. M. Duisenberg, L. M. J. Kroon-Batenburg, A. M. M. Schreurs, *J. Appl. Crystallogr.* **2003**, *36*, 220–229.

[21] G. M. Sheldrick, *SADABS: Area-Detector Absorption Correction*, v2.10, Universität Göttingen, Germany, **1999**.

[22] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122.

[23] A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13.