Chapter 5

Phosphinidene Addition to Conjugated Allenes


Abstract: Generating transient electrophilic phosphinidene 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-diisopropylidenecyclobutene, which is formed in situ from the isomerization of the conjugated allene.

5.1. Introduction

Electrophilic phosphinidene complexes $\text{RP}=\text{ML}_n$ 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 $\textbf{1}$ ($M = \text{Cr, Mo, W}$).\(^2\) Spectroscopic evidence for the transient carbene-like species is still elusive, but its formation is inferred from trapping reactions.\(^1\) Recently, $3H$-3-benzophosphine complexes $\textbf{2}$ ($R = \text{Ph, ML}_n = \text{W(CO)}_5$, Mo(CO)$_5$, MnCp(CO)$_2$, Cr(CO)$_5$; $R = \text{Me, tBu, NEt}_2$, ML$_n = \text{W(CO)}_5$) were developed in our group as an alternative phosphinidene precursor that offers advantages.\(^3\) Namely, 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 $\textbf{1}$.\(^1\) Of further importance is that liberating phosphinidenes from $\textbf{1}$ occurs thermally at 110 °C, or 55 °C using CuCl as catalyst, whereas only ~65 °C and no catalyst is needed for the benzophosphine complexes $\textbf{2}$. This means that thermally unstable species cannot be synthesized from $\textbf{1}$ at 110 °C, while the lower temperature Cu-catalyzed process is postulated to give the less reactive and bulkier $\text{RP(Cl)M(CO)}_5\text{–CuS}$ ($S = \text{toluene or alkene}$) that is more sensitive to steric hindrance.\(^4\) Hence, the synthetic pathways might differ depending on whether $\textbf{1}$ or $\textbf{2}$ is used.

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 $n$-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 $(Z)$-
Phosphinidene Addition to Conjugated Allenes

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 or from the less common direct [1+4]-cycloaddition. Earlier, we found that reaction of allene with PhP=\text{W}(\text{CO})_5, generated
from 1 with CuCl at 55 °C, gave two phosphirane intermediates with characteristic
\text{^31P} NMR resonances at –128 and –131 ppm that were not isolable due to their rapid
conversion to phospholene via a [1,3]-sigmatropic shift (Scheme 1).

Scheme 1. Addition of PhP=W(\text{CO})_5 to allene 3.

The reactivity towards conjugated allenes has been investigated for the iron-complexed
phosphinidene \text{iPr}_2\text{NP}=\text{Fe}(\text{CO})_4, which is generated in situ from the reduction of \text{iPr}_2\text{NPCl}_2 with Na_2\text{Fe}(\text{CO})_4 at –30 °C. It was suggested that \text{iPr}_2\text{NP}=\text{Fe}(\text{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 to 2,5-diisopropylidene-phospholene 7 (Scheme 2).

Scheme 2. Addition of \text{iPr}_2\text{NP}=\text{Fe}(\text{CO})_4 to tetraene 5.

Here we report on the deviating behavior of the tungsten-complexed phosphinidene
PhP=W(\text{CO})_5 that, when generated in situ in the presence of diallene 5, results in the
formation of the unexpected 3,4-di-substituted 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.
5.2. Results & 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 (δ_{31P} = 12.5 ppm; Scheme 3), which was isolated as yellow crystals in respectively 93% and 58% yield. 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 (δ_{31P} = -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 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 iPr$_2$NP=Fe(CO)$_4$ (Scheme 2).$^{10}$ Could the different behavior be due to the difference in reactions conditions? Could it be that the diallene undergoes a modification, a rearrangement, under the reaction conditions? 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. 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 minutes 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 Computational Section, par. 5.4.1.) 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).

**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].
These results indicate that while the phosphinidene addition to diallene 5 leads to the formation of phospholene 9 (Scheme 3), 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 synH 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 presume 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 'i) 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 favored (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, is the next step and generates singlet diradical phosphacyclopentane–1,3–diyl 13 (∆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 (∆E = –30.7, ∆E$^\ddagger$ = 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) suggest these processes to be likely under the reaction conditions.
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.
5.3. Conclusions

In conclusion, generating phosphinidene complex PhP=W(CO)$_5$ in the presence of tetramethyldiallene 5 leads to the formation of two different products, i.e. 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.
Chapter 5

5.4. Computational Section

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

5.4.1. Thermal and Cu-Catalysed Ring-Closure of Tetramethyldiallene (5)

The thermal and Cu-catalyzed ring-closure of tetramethyldiallene (5) were analyzed computationally, at the BT/TZP level of theory. In some selected cases, multi-reference DFT single point energy calculations (BP/TZP//MRDFT(BHLYP)/TZVP) on the BT/TZP optimized structures were also performed.

The computed BT/TZP and BP/TZP//MRDFT(BHLYP)/TZVP energies for the thermal ring closure of tetramethyldiallene 5, reported in Table 1, are given in atomic units. Relative energies are given in kcal·mol\(^{-1}\).

<table>
<thead>
<tr>
<th></th>
<th>(E) (a.u.)</th>
<th>(\Delta E) (kcal·mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>-5.028651</td>
<td>0.0</td>
</tr>
<tr>
<td>TS5-10</td>
<td>-4.986580 (-389.221282)</td>
<td>26.4 (29.8)</td>
</tr>
<tr>
<td>10</td>
<td>-5.044047 (-389.284605)</td>
<td>-9.7 (-9.9)</td>
</tr>
</tbody>
</table>

Table 1. BT/TZP energies for the thermal ring closure of tetramethyldiallene 5. BP/TZP//MRDFT(BHLYP)/TZVP energies are in parenthesis.

For the Cu-catalysed ring-closure of tetramethyldiallene (5), we computed four different CuCl-adducts of tetramethyldiallene 5, which are shown below (Figure 5).

Figure 5. Computed CuCl-adducts of tetramethyldiallene 5.
Phosphinidene Addition to Conjugated Allenes

One of these adducts (#4), can rearrange into $10\text{[CuCl]}$ ($\Delta E = -15.1$ kcal·mol$^{-1}$) via transition state $\text{TS5-10[CuCl]}$ ($\Delta E^\ddagger = 3.8$ kcal·mol$^{-1}$) (as shown in Figure 3, par. 5.2.). The computed BT/TZP energies (in a.u.) and relative energies (in kcal·mol$^{-1}$) for the CuCl-adducts of tetrametyldiallene 5 and for the Cu-catalysed ring closure of tetramethyldiallene 5 are reported in Table 2.

<table>
<thead>
<tr>
<th></th>
<th>$E$ (a.u.)</th>
<th>$\Delta E$ (kcal·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5[CuCl] #1</td>
<td>-5.231389</td>
<td>0.0</td>
</tr>
<tr>
<td>5[CuCl] #2</td>
<td>-5.230239</td>
<td>0.7</td>
</tr>
<tr>
<td>5[CuCl] #3</td>
<td>-5.219872</td>
<td>7.2</td>
</tr>
<tr>
<td>5[CuCl] #4</td>
<td>-5.220852</td>
<td>6.6</td>
</tr>
<tr>
<td>$\text{TS5-10[CuCl]}$</td>
<td>-5.214762</td>
<td>10.4</td>
</tr>
<tr>
<td>$10\text{[CuCl]}$</td>
<td>-5.244789</td>
<td>-8.5</td>
</tr>
</tbody>
</table>

Table 2. BT/TZP energies for the CuCl-adducts of tetrametyldiallene 5 and for the Cu-catalysed ring closure of tetramethyldiallene 5.

5.4.2. Phosphinidene Addition to 3,4-diisopropylidene-cyclobutene (10)

In our computational analysis, we have considered that the transient phosphinidene complex can react either with the endocyclic double bond of 10, to give 11, or to the exocyclic double bond of 10 to give 12.

The computed BT/TZP energies for the syn and anti isomers of $11'$ and $12'$ are reported in Table 3. The computed structures for the syn and anti isomers of $11'$ and $12'$ are shown in Figure 6 and Figure 7, respectively.

<table>
<thead>
<tr>
<th></th>
<th>$E$ (a.u.)</th>
<th>$\Delta E$ (kcal·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPCr(CO)$_5$</td>
<td>-3.431114</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>-5.044047 (-389.284605)</td>
<td></td>
</tr>
<tr>
<td>Syn-$11'$</td>
<td>-8.542838 (-2342.293388)</td>
<td>-42.5</td>
</tr>
<tr>
<td>Anti-$11'$</td>
<td>-8.543456 (-2342.292104)</td>
<td>-42.9</td>
</tr>
<tr>
<td>Syn-$12'$</td>
<td>-8.530541</td>
<td>-34.8</td>
</tr>
<tr>
<td>Anti-$12'$</td>
<td>-8.527384</td>
<td>-32.8</td>
</tr>
</tbody>
</table>

Table 3. BT/TZP energies for $11'$ and $12'$. BP/TZP//MRDFT(BHLYP)/TZVP energies are in parenthesis.
5.4.3. Formation of (1-phenyl-3-isopropenyl-4-isopropyl-1H-phosphole)penta-carbonyltungsten (8)

As described in the previous paragraph (par 5.2.), the formation of phosphole 8 was also investigated computationally. In particular, we investigated the phosphinidene addition (using HP=Cr(CO)$_5$ as simplified model for PhP=W(CO)$_5$) to cyclobutene 10, and the subsequent rearrangement of the most favored addition product (11’) which leads to the formation of 8. The computed BT/TZP and BP/TZP//MRDFT(BHLYP)/TZVP energies (in parentheses) for the formation of 8 are reported in Table 4.
Table 4. BT/TZP and BP/TZP/MRDFT(BHLYP)/TZVP energies (in brackets) for the formation of phosphole 8.

<table>
<thead>
<tr>
<th></th>
<th>E (a.u.)</th>
<th>ΔE (kcal·mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPCr(CO)₅</td>
<td>-3.431114</td>
<td></td>
</tr>
<tr>
<td>Anti-11'</td>
<td>-8.543456468</td>
<td>(-2342.292104)</td>
</tr>
<tr>
<td>Syn-11'</td>
<td>-8.542837772</td>
<td>(-2342.293388)</td>
</tr>
<tr>
<td>TS-anti-11'−13'</td>
<td>-8.505101329</td>
<td>(-2342.272848)</td>
</tr>
<tr>
<td>TS-syn-11'−13'</td>
<td>-8.501769515</td>
<td>(-2342.246675)</td>
</tr>
<tr>
<td>13'</td>
<td>-8.531197483</td>
<td>(-2342.264407)</td>
</tr>
<tr>
<td>TS13'−8'</td>
<td>-8.495111830</td>
<td>(-2342.272232)</td>
</tr>
<tr>
<td>8'</td>
<td>-8.580224792</td>
<td>(-2342.338795)</td>
</tr>
</tbody>
</table>

5.4.4. Formation of (2,5-diisopropylidene-1-phenyl-2,5-dihydro-1H-phosphole)-pentacarbonyltungsten (9)

In our computational analysis, we also investigated the mechanism for the expected formation of phospholene 9' (again using HP=Cr(CO)₅ as simplified model for PhP=W(CO)₅). The reaction mechanism for the formation of 9', which has not been described in the previous paragraphs, is illustrated in Figure 8. The computed BT/TZP energies (in a.u.) and the relative energies (in kcal·mol⁻¹) for the formation of 9' are reported in Table 5.

Figure 8. Relative BP/TZP energies in kcal·mol⁻¹ for the formation of phospholene 9'.
<table>
<thead>
<tr>
<th></th>
<th>E (a.u.)</th>
<th>$\Delta E$ (kcal·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPCr(CO)$_5$</td>
<td>-3.431114</td>
<td></td>
</tr>
<tr>
<td>Phosphirane</td>
<td>-8.526795441</td>
<td>0.0</td>
</tr>
<tr>
<td>TSphosphirane-9'</td>
<td>-8.486944834</td>
<td>17.1</td>
</tr>
<tr>
<td>9'</td>
<td>-8.596397433</td>
<td>-1.6</td>
</tr>
</tbody>
</table>

**Table 5.** BT/TZP energies in a.u. for the formation of phospholene 9.
5.5. Experimental Section

**General.** All syntheses were performed with the use of Schlenk techniques under 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 (\(^1\text{H}, \^{13}\text{C}, \^{31}\text{P}; \) 85% \(\text{H}_3\text{PO}_4\)) or a Bruker Advance 400 (\(^1\text{H}, \^{13}\text{C}\)) and referenced internally to residual solvent resonances (CDCl\(_3\): \(^1\text{H}: \delta 7.26, \^{13}\text{C}({}^1\text{H}) : \delta 77.0\)). 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 3KeV. 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 \(^5\) and \(^{18}\) 3,4-bis(isopropylidene)cyclobutene \(^10\) phospha-norbornadiene complex \(^1\) \(^2\) and \(^3\)H-benzophosphepine complex \(^2\) were synthesized according to literature procedures.

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

**Procedure A:** A solution of 2,7-dimethylocta-2,3,5,6-tetraene \(^5\) (0.041 g, 0.30 mmol), phosphonorbornadiene \(^1\) (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 (0.066 g, 58% yield). **Procedure B:** A solution of \(^5\) (0.040 g, 0.30 mmol) and phosphonorbornadiene \(^1\) (0.131 g, 0.20 mmol) in toluene (10 mL) was heated at 110 °C until \(^{31}\text{P}\) 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 (0.105 g, 93% yield). **Procedure C:** A solution of 3,4-bis(isopropylidene)-cyclobutene \(^10\) (0.134 g, 1.00 mmol), phosphonorbornadiene \(^1\) (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 eluent
afforded 8 as a yellow oil (0.080 g, 71% yield). Procedure D: A solution of 3,4-bis(isopropylidene)-cyclobutene 10 (0.134 g, 1.00 mmol), phosphorbornadiene 1 (0.130 g, 0.20 mmol) in toluene (2 mL) was heated at 110 ºC for 22 h. Evaporation of the volatiles followed by column chromatography over aluminum oxide with pentane as eluent yielded 8 as a yellow oil (0.056 g, 50% yield). Mp. 61.7–61.8 ºC; 1H NMR (CDCl3): δ 1.15 (d, 3J(H,H) = 6.7 Hz, 3H, CH–C(CH3)2), 1.22 (d, 3J(H,H) = 6.7 Hz, 3H, CH–CH3), 2.02 (s, 3H, =C–CH3), 2.91 (d, 3J(H,H) = 6.8 Hz, 4J(H,P) = 0.9 Hz, 1H, CH–CH3), 5.01 (s, 1H, =C–PH3), 5.19 (s, 1H, =C–CH3), 6.54 (m, 1H, PCH), 6.67 (m, 1H, PCH), 7.37–7.55 (m, 5H, PhH); 13C(1H) NMR (CDCl3): δ 22.6 (s, CH–C(CH3)2), 23.2 (s, CH–C(CH3)2), 24.0 (s, =C–CH3), 29.2 (d, 3J(C,P) = 9.4 Hz, CH–CH3), 116.2 (s, =C–CH3), 127.3 (d, 1J(C,P) = 43.5 Hz, PCH=C–Pr), 129.0 (d, 3J(C,P) = 10.1 Hz, m–Ph), 129.7 (d, 1J(C,P) = 41.3 Hz, ipso–Ph), 130.6 (d, 3J(C,P) = 2.5 Hz, p–Ph), 131.5 (d, 3J(C,P) = 11.9 Hz, o–Ph), 131.9 (d, 1J(C,P) = 41.5 Hz, PCH=C–C(CH3)=CH2), 140.9 (d, 3J(C,P) = 11.3 Hz, =C–Pr), 155.7 (d, 3J(C,P) = 9.4 Hz, =C–C(CH3)=CH2), 160.9 (d, 3J(C,P) = 6.9 Hz, C(CH3)=CH2), 196.1 (d, 1J(C,P) = 6.3 Hz, COw), 198.7 (d, 3J(C,P) = 18.2 Hz, COw); 31P(1H) NMR (CDCl3): δ 12.5 (d, 1J(P,W) = 135.5 Hz); IR: ν = 1871–1885 (s/br, COeq); HR–MS: calcd for C21H19O5PW: 566.0480, found: 566.0483; m/z (%): 566 (54) [M]+, 510 (44) [M –2CO]+, 482 (41) [M –3CO]+, 426 (86) [M –SCO]+; Anal. Found: C, 44.57; H, 3.42; P 5.10; Calcd for C21H19O5PW: C, 44.54; H, 3.38; P, 5.47.

(2,5-Diisopropylidene-1-phenyl-2,5-dihydro-1H-phosphe)Pentacarbonyltungsten (9): A solution of 2,7-dimethylocta-2,3,5,6-tetraene 5 (40 mg, 0.30 mmol) and benzophosphine complex 2 (112 mg, 0.20 mmol) in toluene (3 mL) was heated at 65 ºC until complete fragmentation of 2 (48 h). The crude product was purified by column chromatography over silica with pentane as eluens and crystallized from pentane at ~20 ºC to afford phospholene 9 as yellow crystals (66 mg, 61% yield). Mp. 113 ºC; 1H NMR (CDCl3): δ 1.63 (s, 6H, CH3), 1.94 (s, 6H, CH3), 6.68 (d, 3J(H,P) = 15.4 Hz, 2H, PCCCH3), 7.40–7.42 (m, 3H, p–PhH, m–PhH), 7.63–7.71 (m, 2H, o–PhH); 13C(1H) NMR (CDCl3): δ 21.3 (d, 3J(C,P) = 9.2 Hz, CH3), 24.7 (d, 3J(C,P) = 10.0 Hz, CH3), 128.6 (d, 3J(C,P) = 10.4 Hz, m–PhH), 130.1 (d, 3J(C,P) = 14.4 Hz, o–PhH), 130.3 (d, 3J(C,P) = 3.5 Hz, p–PhH), 132.9 (d, 3J(C,P) = 33.1 Hz, ipso–PhH), 132.0 (d, 3J(C,P) = 13.5 Hz, PCC=C), 137.5 (d, 3J(C,P) = 10.7 Hz, (CH3)3C=C), 138.5 (d, 3J(C,P) = 47.1 Hz, PCC), 197.1 (d, 3J(C,P) = 6.7 Hz, COw), 199.2 (d, 3J(C,P) = 21.0 Hz, COw); 31P(1H) NMR (CDCl3): δ –0.5 (d, 1J(P,W) = 235.1 Hz); IR: ν = 1878–1885 (s/br, COw), 1991 (w, COw), 2067 (m, COw); HR–MS: calcd for C21H19O5PW: 566.0480, found: 566.0475; m/z (%): 566 (98) [M]+, 510 (100) [M –2CO]+, 426 (55) [M –SCO]+.
Phosphinidene Addition to Conjugated Allenes

(6-Isopropylidene-2,2-dimethyl-1-phenyl-1-phospha-spiro[2.3]hex-4-ene)-pentacarbonyltungsten(0) (12): A solution of 10 (1.433 g, 10.7 mmol) and benzophosphine 2 (0.500 g, 0.90 mmol) in toluene (10 mL) was heated at 65 ºC until complete decomposition the 2 (35 h), when the $^{31}$P NMR showed only three resonances at 12.5 ($^{31}$P) and –118.3 ($^{12}$a) and –124.9 ($^{12}$b) ppm in a 1:0.12:0.10 ratio, respectively. The reaction mixture was then concentrated and filtered over short column of silica gel with pentane as eluent. Fractional crystallization from pentane at –80 ºC yielded $^{12}$a as a white solid (40 mg, 8%).

$^{1}H$ NMR (CDCl$_3$): $\delta$ 0.72 (s, 3H, CH$_3$C=), 1.50 (d, J(H,P) = 19.0 Hz, CH$_3$CP), 1.60 (d, J(H,P) = 11.6 Hz, CH$_3$CP), 1.74 (s, 3H, CH$_3$C=), 6.44 (br s, 1H, H=CHCP), 6.86 (d, J(H,P) = 3.1 Hz, =C=CHCP), 7.30–7.55 (m, 3H, p–PhH, m–PhH), 7.70–7.80 (m, 2H, o–PhH); $^{13}$C($^{1}H$) NMR: 20.8 (s, CH$_3$C=), 21.6 (s, CH$_3$C=), 22.8 (d, $^{2}$J(C,P) = 3.6 Hz, CH$_3$CP), 26.3 (d, $^{2}$J(C,P) = 7.8 Hz, CH$_3$CP), 32.0 (br. s, CH$_3$C=), 56.8 (br. s, CPC(CH$_3$)$_2$), 119.0 (s, (CH$_3$)$_2$C=), 134.4 (s, (CH$_3$)$_2$C=C), 138.7 (br. s, PCCH=CH), 139.8 (d, $^{2}$J(C,P) = 11.4 Hz, PCCH=CH), 196.0 (d, $^{1}$J(C,W) = 8.0 Hz, CO$_{ax}$), 198.1 (d, $^{2}$J(C,P) = 29.5 Hz, CO$_{eq}$), 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$_5$PW, Fw = 566.18, yellow block, 0.54 x 0.42 x 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 = 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. Scaling and absorption correction based on multiple measured reflections was performed with the program SADAB$_{21}$ (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 using Direct Methods and refined with SHELXL–97 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 slight disorder, which has not been resolved. 256 Parameters were refined with no restraints. R1/wR2 [I > 2$\sigma$(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
Chapter 5

\(e/\text{Å}^3\). Geometry calculations and checking for higher symmetry was performed with the PLATON program.\(^{23}\)
5.6. References


Chapter 5


