Main-Group Chemistry

International Edition: DOI: 10.1002/anie.201507355
German Edition: DOI: 10.1002/ange.201507355

Stepwise Formation of a 1,3-Butadiene Analogue of Mixed Heavier Group 15 Elements

*Michael Seidl, Gábor Balázs, Alexey Y. Timoshkin, and Manfred Scheer**

Dedicated to Professor Gernot Frenking on the occasion of his 70th birthday

Abstract: *The reaction of the phosphinidene complex [Cp*P{W(CO)$_5$}$_2$] (**1a**) with di-tert-butylcarboimidophosphene leads to the P−C cage compound **6** and the Lewis acid–base adduct [Cp*P{W(CO)$_5$}$_2$(CNtBu)] (**2a**). In contrast, the arsinidene complex shows a different reactivity. At low temperatures, the arsaphosphene complex [{W(CO)$_5$}{η^2-(Cp*)As=P(tBu)}{W(CO)$_5$}] (**3**) is formed. At these temperatures, **3** reacts further with a second equivalent of carboimidophosphene to form [{W(CO)$_5$}{η^2-{(Cp*)(tBu)P}As=P(tBu)}{W(CO)$_5$}] (**5**), probably by the insertion of a phosphinidene unit (tBuP) into an As−C bond. In contrast, at room temperature **3** reacts further by a radical-type reaction to form [{(tBu)P=As−As=P(tBu)}{W(CO)$_5$}$_4$] (**4**). Compound **4** is the first example of a neutral, 1,3-butadiene analogue containing only mixed heavier Group 15 elements. It consists of two P=As double bonds connected by arsenic atoms.*

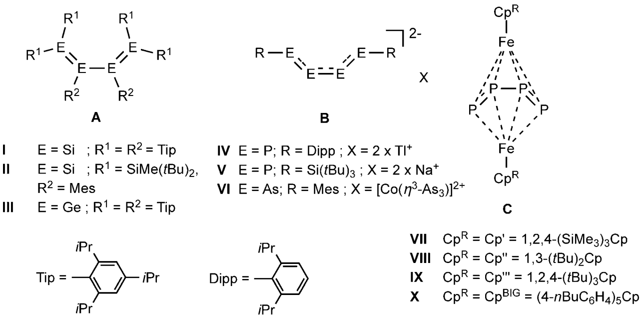

Figure 1. Examples of homonuclear butadiene analogues of heavier main-group elements.

Multiple bonds between heavier main-group elements have been of great interest. In 1981, the first examples of a stable diphosphene ArP=PAr (Ar = 2,4,6-tri-*tert*-butylphenyl),[1] a stable silene $(Me_3Si)_2Si{=}C(Ad)OSiMe_3$ (Ad = adamantyl)[2] and a stable disilene $(Mes)_2Si{=}Si(Mes)_2$ (Mes = 2,4,6-trimethylphenyl)[3] were published. Since then numerous compounds with isolated double and triple bonds were reported.[4] In contrast, for 1,3-butadiene-like conjugated systems consisting of two double bonds between heavier elements, only few examples are known. Weidenbruch et al. reported the first tetrasilabuta-1,3-diene (**I**) in 1997[5] and three years later the first tetragermabuta-1,3-diene (**III**) (Figure 1).[6] In 2004, Sekiguchi reported another tetrasila-1,3-butadiene (**II**).[7] For heavier Group 15 elements, only the three examples of dianionic organic substituted butadienediide analogues are known (Figure 1). Compound **IV** is a thallium salt of the diaryltetraphosphabutadienediide,[8] **V** is a sodium salt of a tri-*tert*-butylsilylated tetraphosphabutadienediide,[9] and **VI** is a cobalt complex with a diaryltetraarsabutadienediide ligand.[10] Moreover, there are sandwich complexes of type **C** $[\{Cp^RFe\}_2(\mu,\eta^{4:4}\text{-}P_4]$ (Figure 1)[11] and some coordinated Co homologues[12] known, which represents formal ionic P_4^{2-} chains. In contrast, neutral or mixed heavier Group 15 analogues of 1,3-butadiene are so far unknown.

Recently, we reported on the reaction of the complexes $[Cp^*E\{W(CO)_5\}_2]$ (E = P, As) with heterocumulenes, such as carbodiimides and alkylazides, leading to four-membered heterocycles. For the alkylazides, the first example of a triazaphosphete complex was obtained.[13] These reactions proceed via a 1,3-cycloaddition, and the sequence of the heterocycle obtained is defined by the heterocumulene used. Therefore, we searched for suitable heterocumulenes to approach rare or unknown heterocycles. Thus, carboimidophosphenes (R−P=C=N−R) raise the question as to which atom, N or P, would serve as nucleophile to attack the electrophilic E center. Subsequently, we expected to obtain four-membered heterocycles of the sequence EPCN (E = P, As). For E = P only few examples are known,[14] whereas AsPCN heterocycles are so far unknown. Herein we report the reaction of the complexes $[Cp^*E\{W(CO)_5\}_2]$ (E = P, As) with carboimidophosphenes, which result in the unprecedented formation of a mixed butadiene derivative via an arsaphosphene intermediate.

The reaction of the arsinidene complex and the carboimidophosphene in a 2:1 stoichiometry takes place at low temperatures (−78 °C), which was accompanied by a color change from deep blue to orange. After warming the reaction mixture to room temperature, the products **2b** and **4** (Scheme 1) were isolated. The proposed 1,3-cycloaddition did not take place. Rather, the carboimidophosphene acted as a transfer agent of a phosphinidene unit (*t*BuP) to the arsinidene **1b**, thus inducing a reaction sequence, yielding **4** as the final product. The concomitantly released *t*BuNC also reacts with **1b** to form the Lewis acid–base adduct [Cp*As-

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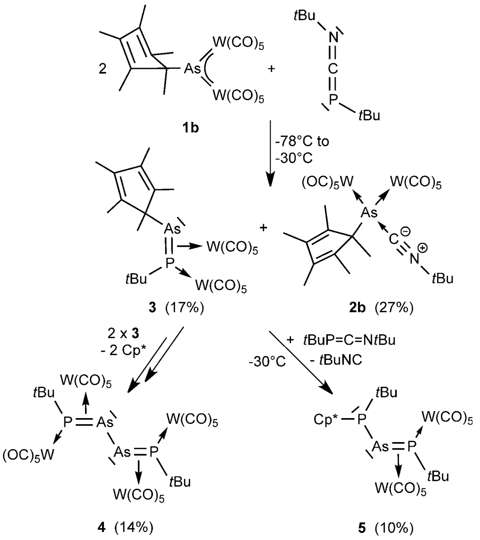
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201507355.



Scheme 1. Reaction of **1 b** with di-*tert*-butylcarboimidophosphene. Isolated yields in parenthesis.[20]

$\{W(CO)_5\}_2(t$BuNC)] (**2b**). There are only few reports that carboimidophosphenes can act as phosphinidene transfer agents such as the reaction of $F_3C{-}P{=}C{=}N{-}t$Bu with Me_3P or DMB (DMB = 2,3-dimethylbutadiene).[15] For phosphaketenes, which represent, like carboimidophosphenes, also phosphacumulenes, this kind of reactivity is more common.[16] Compound **2b** was obtained previously by the reaction of the arsinidene complex (**1b**) with *tert*-butylisonitrile (*t*BuNC).[17] In contrast, **4** is the first example of a neutral 1,3-butadiene analogue of mixed heavier Group 15 elements.[18] Compound **4** consists of two arsaphosphene units that are connected through the two arsenic atoms. One $W(CO)_5$ fragment is coordinated by a phosphorus atom and the other two $W(CO)_5$ fragments are side-on coordinated by the two As=P double bonds. In the ^{31}P NMR spectrum, **4** shows a singlet at $\delta = 77.7$ ppm with an ABX-type spectrum for the ^{183}W satellite signals (^3J(P,P) = 16.7 Hz, ^1J(P,W) = 37.5 Hz, ^1J(P,W) = 223 Hz). [19] To better understand the reaction pathway, the reaction was monitored by ^{31}P NMR spectroscopy at −80 °C, where a singlet at $\delta = 47.5$ ppm (^1J(P,W) = 48 Hz, ^1J(P,W) = 202 Hz) was observed. To identify the observed species, the reaction was carried out at low temperatures (from −78 °C to −30 °C). After chromatographic work-up at −30 °C, compound **3** and the Lewis acid–base adduct **2b** could be isolated (Scheme 1). Compound **3** is an arsaphosphene bearing a Cp* substituent at the arsenic atom and a *tert*-butyl group at the phosphorus atom, which coordinates η^1 to a $W(CO)_5$ fragment. The P=As double bond coordinates side-on to a second $W(CO)_5$ fragment. The mass spectrum (LIFD) of **3** shows two peaks, a weak peak at $m/z = 946.3$ for the molecular ion and a second intense peak at $m/z = 811.2$ for a fragment of **3** that has lost the Cp* substituent.

We also investigated the influence of the stoichiometry on the reaction of the arsinidene complex with the carboimidophosphene by using an excess of carboimidophosphene (stoichiometry 1:2). If the reaction mixture is warmed from −78 °C to room temperature, compounds **2b** and **4** are obtained. Keeping the reaction mixture at −28 °C for several days resulted in the new product **5**. Compound **5** is likely to be formed by the insertion of a phosphinidene unit (*t*BuP) into the As−C bond of **3**. The ^{31}P NMR spectrum (−30 °C) of the crystals of **5**, dissolved in CD_2Cl_2 at −30 °C, resulted in two sets of signals (see the Supporting Information) with a ratio of 9:1, which are likely isomers. Note that the molecular structure of **5** shows a ratio of disorder (96:4) in the crystal that could be a hint of the other isomer. Because of the low percentage of disorder in the second component, only the heavy atom framework consisting of AsP_2W_2 could be refined (see the Supporting Information). Warming the solution to room temperature gave an isomeric ratio of 7:3 (isomer 1 (70 %): $\delta = 76.6$ (d, ^2J(P,P) = 95 Hz, ^1J(P,W) = 210 Hz, ^1J(P,W) = 30 Hz), 77.4 ppm (d, ^2J(P,P) = 95 Hz); isomer 2 (30 %): $\delta = 67.9$ (^2J(P,P) = 110 Hz), 81.4 ppm (^2J(P,P) = 110 Hz, ^1J(P,W) = 223 Hz, ^1J(P,W) = 33 Hz)).

The molecular structures of **3**, **4**, and **5** (Figure 2) show the rare structural motive of an arsaphosphene coordinated η^2 at a transition-metal fragment,[21] consisting of the atoms P1, As1, and W1. The P1−As1 distances are 2.2663(7) Å (**3**), 2.258(1) Å (**4**), and 2.265(1) Å (**5**). If these distances are compared with the As−P bonds of [Mes*P=AsCH(SiMe$_3$)$_2$] (As−P 2.125(1) Å)[22] and [tBu$_6$As$_2$P$_6$] (As-P2 2.361(2) Å),[23]

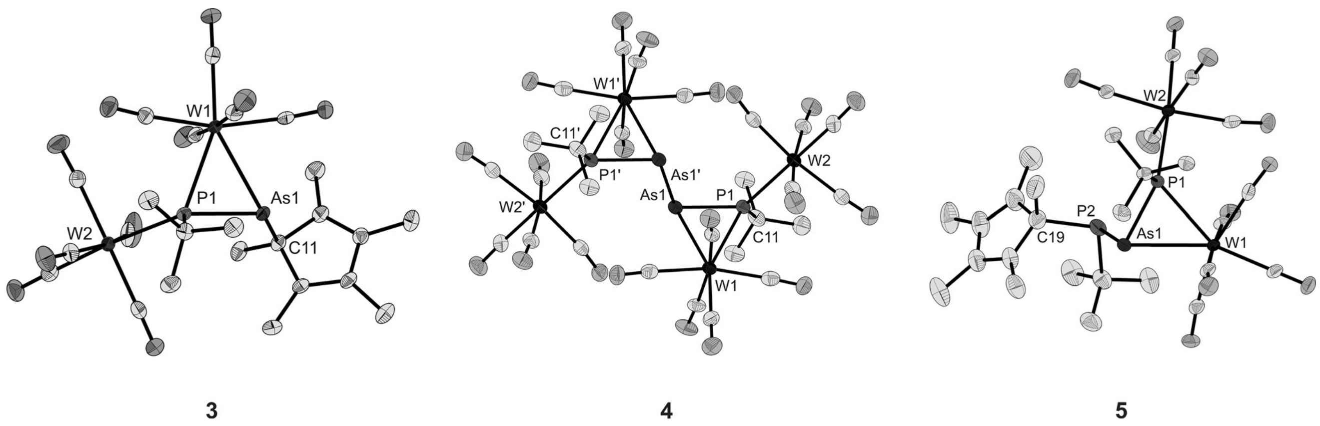
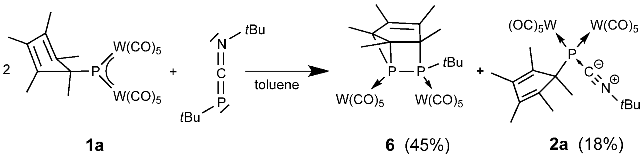


Figure 2. Molecular structure of **3**, **4**, and **5**.[25] Ellipsoids are set at 50% probability; all hydrogen atoms have been omitted for clarity.

it is obvious that they are in the range between a single and a double bond. Compound **3** also shows a long As–C bond with 2.061(3) Å between the arsenic atom and the Cp* substituent. This long As–C bond indicates the weakness of this bond and its easy cleavage, which presumably facilitates the formation of **4**. Instead of this As–C bond, **4** possesses an As–As bond with 2.424(1) Å, which is in the range of a single bond. Apart from the coordinated As1–P1 double bond (2.265(1) Å), compound **5** also has an As1–P2 single bond (2.351(1) Å).

The reaction of two equivalents of the phosphinidene complex with one equivalent of the di-*tert*-butylcarboimidophosphene takes also place at low temperatures, and the compounds **2a** and **6** are formed in the ratio 1:1 (confirmed by ^{31}P NMR of the reaction mixture; Scheme 2). Compound **6** is a polycyclic P–C cage complex. By using an excess of the carboimidophosphene (stoichiometry 1:2), it is possible to increase the amount of **6** formed. However, it is not possible to suppress the formation of **2a** completely. A separation of the products can be accomplished by column chromatography. Compound **6** reveals in the ^{31}P NMR spectrum two signals characteristic for an AM spin system at $\delta = 51.9$ ppm (^{1}J(P,P) = 146 Hz, ^{1}J(P,W) = 229 Hz) and −115.8 ppm (^{1}J(P,P) = 146 Hz, ^{1}J(P,W) = 229 Hz).



Scheme 2. Reaction of **1a** with di-*tert*-butylcarboimidophosphene. Isolated yields in parenthesis.[20]

The molecular structure of **6** is shown in Figure 3. The P–P distance is 2.195(1) Å. The P–C distances are slightly elongated (1.895(3) Å, 1.934(3) Å, and 1.940(3) Å, respectively). This elongation is especially distinct at the P2–C15 bond, which can be attributed to the steric demand of the *t*Bu substituent. A similar complex, bearing instead of the *t*Bu group a second Cp* substituent, was reported by the Streubel group.[24]

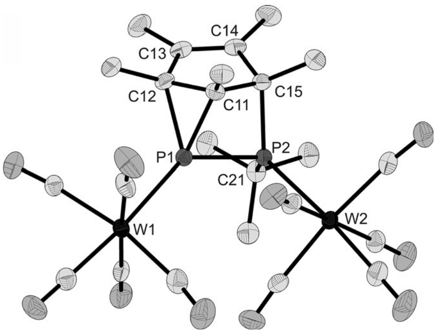
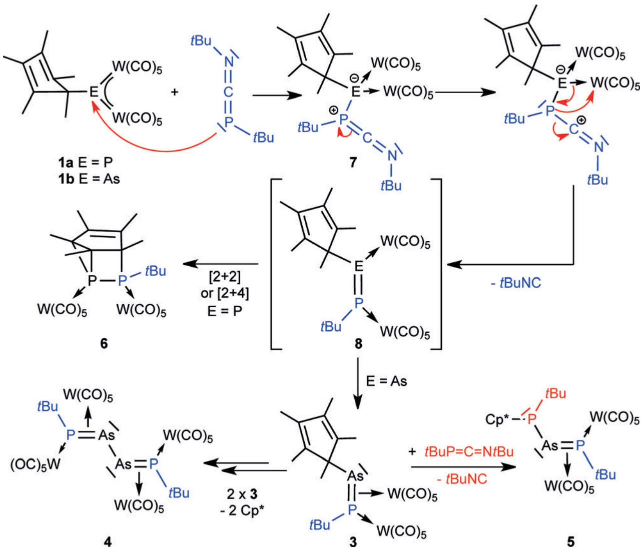


Figure 3. Molecular structure of **6**.[25] Ellipsoids are set at 50% probability; all hydrogen atoms have been omitted for clarity.

A possible pathway for the reaction of **1a/b** with di-*tert*-butylcarboimidophosphene is shown in Scheme 3. The first reaction step is the nucleophilic attack by the phosphorus atom of the carboimidophosphene at the Group 15 atom, leading to a Lewis acid–base adduct (**7a/b**). However, it was not possible to monitor this adduct formation by ^{31}P NMR spectroscopy. Even at −80 °C, the signals of compounds **2a**, **3**, and **6** were already observed. Therefore, immediately after the adduct formation, a migration of a W(CO)$_5$ fragment takes place followed by the elimination of a *t*BuNC unit. This released *t*BuNC unit reacts with free **1a/b** to form **2a/b**. After the elimination of the isonitrile, intermediate **8** is formed. Compound **8** is an unstable diphosphene (**8a**) or an arsaphosphene (**8b**). For the diphosphene, a [2+2] or a [2+4] cycloaddition of the P=P double bond with the diene system of the Cp* substituent takes place, forming the cage compound **6**. For the arsaphosphene such a cycloaddition is not observed; instead, a change of the coordination mode of a W(CO)$_5$ fragment from η^1 at the arsenic atom to η^2 at the As=P bond takes place. This leads to compound **3**, which is only stable at low temperatures. At temperatures over −20 °C or under the influence of light, **3** transforms to **4**. The formation of **4** can be explained by a radical reaction step, at which the As–C bond in **3** is homolytically cleaved and an arsaphosphene radical is formed. Subsequently, two of these arsaphosphene radicals combine to form **4**. To confirm this radical reaction step, a sample of **3** was analyzed by EPR spectroscopy. At room temperature, no EPR signal was detected whether the sample was irradiated with UV light or not. By cooling the solution of **3** to 77 K and upon irradiation with UV light, it was possible to detect an EPR signal (Supporting Information, Figure S16). The appearance of the signal supports the proposed radical reaction process. For the reaction of **3** with a second unit of carboimidophosphene at low temperatures, it is likely that again a *t*BuNC entity is



Scheme 3. Proposed reaction pathway for the reaction of **1a/b** with di-*tert*-butylcarboimidophosphene.

eliminated and an insertion of a “free” phosphinidene (*t*BuP) into the As–C bond of compound **3** occurs, leading to compound **5**.

To confirm the thermodynamic favorability of the proposed reaction pathway of the complexes **1a**/**b** with carboimidophosphenes, DFT calculations have been conducted. The Gibbs energy diagram is shown in Figure 4. The thermodynamic parameters for the considered reactions and the optimized structures of the compounds are given in the Supporting Information. At the first step of the reaction, the adduct formation, two high-energy species (**7a**: 115.0 kJ mol^{-1}; **7b**: 96.0 kJ mol^{-1}) at which the phosphorus atom of the carboimidophosphene is bound to the Group 15 atom of **1a**/**b** could be obtained. Optimization of the isomers in which the nitrogen atoms of the carboimidophosphene are bond to the Group 15 atom results in isolated fragments. From these data, P coordination is preferred. The transformation of **7a**/**b** to the compounds **8a**/**b** and a *t*BuNC unit is favored by −74.4 kJ mol^{-1} (**7a**) and −44.1 kJ mol^{-1} (**7b**), respectively. The conversion of **8a**/**b** into the compounds **3** and **6** is also favored (**3**: −33.4 kJ mol^{-1}; **6**: −25.4 kJ mol^{-1}), but only the reaction of a generated *t*BuNC unit with a second equivalent of **1a**/**b** causes the overall reaction to be exergonic. The formation of a Cp* radical and a [{W(CO)$_5$}{η^2-As=P(*t*Bu)}{W(CO)$_5$}] radical, by the homolytic bond cleavage of the As–C bond of compound **3**, is endergonic by 14.4 kJ mol^{-1} at 25 °C and by 30.6 kJ mol^{-1} at −30 °C. The larger Gibbs energy value of the homolytic bond cleavage at −30 °C is the reason why the formation of **4** is only observed at room temperature or upon irradiation with UV light at −30 °C. The reaction of **3** with a second equivalent of di-*tert*-butylcarboimidophosphene and **1b** to form **5** and **2b** is endergonic by 1.7 kJ mol^{-1} at 25 °C and exergonic by −9.9 kJ mol^{-1} at −30 °C.

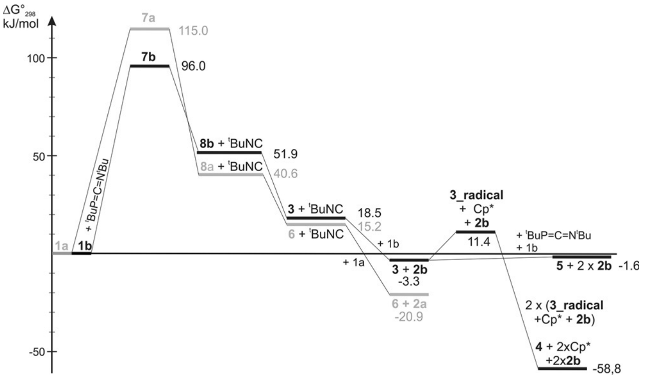


Figure 4. Gibbs energy diagram for the gas phase reactions of **1a**/**b** with di-*tert*-butylcarboimidophosphene at 298.15 K.

In conclusion, we have shown that the complexes **1a**/**b** do not react with the di-*tert*-butylcarboimidophosphene by a 1,3-cycloaddition to form new heterocycles. Rather, the phosphinidene complex reacts by a unique elimination of a *t*BuNC unit followed by a cycloaddition to form the P–C cage compound **6**. The reaction with the arsinidene complex is much more versatile. At low temperatures it leads to the arsaphosphene **3**, which is a rare example of a As=P bond moiety coordinated η^2 to a transition-metal fragment. The increase of the reaction temperature from −30 °C to room temperature leads to **4**, which is the first example of a 1,3-butadiene analogue of mixed heavier Group 15 elements. By the variation of the stoichiometry from the ratio 1:1 of the arsinidene **1b** and di-*tert*-butylcarboimidophosphene to an excess of carboimidophosphene, it is possible at low temperatures to obtain compound **5**, a novel example of a phosphinyl-substituted arsaphosphene complex, as a product of the insertion of a phosphinidene unit (*t*BuP) into the As–C bond of **3**. Moreover, the thermodynamic feasibility of the overall reactions is confirmed by computational studies.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft.

Keywords: 1,3-butadiene analogues · arsenic · phosphinidene · phosphorus · tungsten

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 431–435
Angew. Chem. **2016**, *128*, 442–446

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[18] The sandwich complex $[\{\mathrm{Cp'''Fe}\}_2(\mu,\eta^{4:4}\text{-}\mathrm{P}_n\mathrm{As}_{4-n})]$ with a mixed $\mathrm{P}_n\mathrm{As}_{4-n}$ middle deck, containing unstoichiometric As content in the chain though P is the major component in all positions, is not taken into account, although it is also a 1,3-butadiene analogue of mixed heavier Group 15 elements: C. Schwarzmaier, M. Bodensteiner, A. Y. Timoshkin, M. Scheer, *Angew. Chem. Int. Ed.* **2014**, *53*, 290–293; *Angew. Chem.* **2014**, *126*, 295–299.

[19] The simulated ^{31}P NMR spectrum is shown in the Supporting Information.

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[25] CCDC1405423 (**3**), 1405424 (**4**), 1405426 (**5**), and 1405422 (**6**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Received: August 7, 2015
Revised: September 23, 2015