Main-Group Chemistry

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Reaction of Pentelidene Complexes with Diazoalkanes: Stabilization of Parent 2,3-Dipnictabutadienes

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Dedicated to Professor Gerhard Erker on the occasion of his 70th birthday

Abstract: *The reaction of the phosphinidene complex* $[Cp^*P\{W(CO)_5\}_2]$ (**1a**) *with diphenyldiazomethane leads to* $[\{W(CO)_5\}Cp^*P{=}NN\{W(CO)_5\}{=}CPh_2]$ (**2**). *Compound* **2** *is a rare example of a phosphadiazadiene ligand* ($R\text{-}P{=}N{-}N{=}CR'R''$) *complex. At temperatures above 0 °C,* **2** *decomposes into the complex* $[\{W(CO)_5\}PCp^*\{N(H)N{=}CPh_2\}_2]$ (**3**), *among other species. The reaction of the pentelidene complexes* $[Cp^*E\{W(CO)_5\}_2]$ ($E = P$, As) *with diazomethane* (CH_2NN) *proceeds differently. For the arsinidene complex* (**1b**), *only the arsaalkene complex* **4b** $[\{W(CO)_5\}_2\{\eta^{1:2}\text{-}(Cp^*)As{=}CH_2\}]$ *is formed. The reaction with the phosphinidene complex* (**1a**) *results in three products, the two phosphaalkene complexes* $[\{W(CO)_5\}_2\{\eta^{1:2}\text{-}(R)P{=}CH_2\}]$ (**4a**: $R = Cp^*$, **5**: $R = H$) *and the triazaphosphole derivative* $[\{W(CO)_5\}P(Cp^*)\text{-}CH_2\text{-}N\{W(CO)_5\}{=}N\text{-}N(N{=}CH_2)]$ (**6a**). *The phosphaalkene complex* (**4a**) *and the arsaalkene complex* (**4b**) *are not stable at room temperature and decompose to the complexes* $[\{W(CO)_5\}_4(CH_2{=}E{-}E{=}CH_2)]$ (**7a**: $E = P$, **7b**: $E = As$), *which are the first examples of complexes with parent 2,3-diphospha-1,3-butadiene and 2,3-diarsa-1,3-butadiene ligands.*

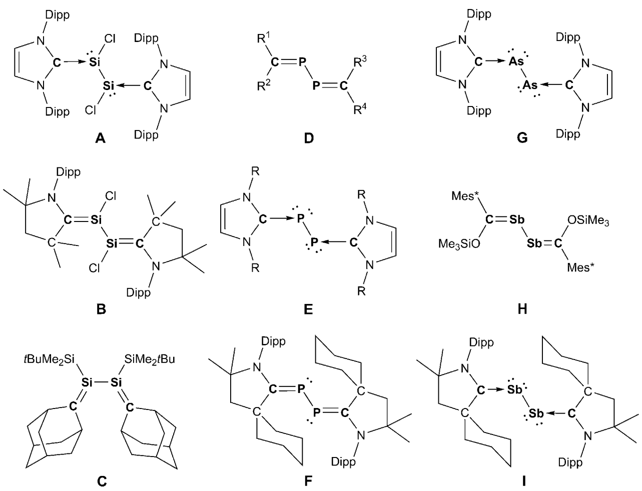

Figure 1. Examples of known 2,3-disila-1,3-butadienes, 2,3-dipnicta-1,3-butadienes, and related compounds.[12]

Armstrong and Miller first isolated 1,3-butadiene in 1886 from the pyrolysis products of petroleum.[1] Since then, it has been used in many applications, including for the formation of copolymers. It took, however, until 1983 that the first 1,3-butadiene derivative with two phosphorus atoms in 2,3-position was reported by Appel et al. (**D**; Figure 1).[2] Over the following 10 years, further 2,3-diphospha-1,3-butadienes with sterically demanding substituents at the carbon atom were synthesized.[3] In 2008, Robinson et al. reported a diphosphorus unit stabilized by two NHCs (**E**; Figure 1), which can also be regarded as a butadiene derivative with respect to at least one of its resonance structures.[4] One year later, Bertrand et al. reported the reaction of white phosphorus with the cyclic(alkyl)(amino)carbenes (CAACs) forming the butadiene derivative **F** (Figure 1). The 2,3-diphosphabutadiene structure is more favorable for **F** than for **E** because of the higher electrophilicity of the CAACs as compared to the NHCs.[5] For other butadiene derivatives with heteroatoms such as Si (**A**, **B**, **C**; Figure 1),[6] As (**G**),[7] and Sb (**H**, **I**)[8] in the 2,3-position, only a few examples are known (Figure 1). However, all of them have NHCs, CAACs, or sterically demanding substituents in common. The parent compounds ($H_2C{=}E{-}E{=}CH_2$; $E = SiH$, P, As, Sb) are as yet unknown.

Recently, we have shown that the pentelidene complexes $[Cp^*E\{W(CO)_5\}_2]$ ($E = P$, As) are unique starting materials for the formation of new four-membered heterocycles, such as a first triazaphosphete complex.[9] In the reaction with carboimidophosphene, a singular complex with a 1,3-butadiene ligand was obtained, composed exclusively of mixed heavier Group 15 elements.[10,11]

In view of the open quest for parent 2,3-dipnictabutadienes, these results prompted us to use diazoalkanes in the reaction with pentelidene complexes to get further access to this unknown class of compounds and/or to build up new nitrogen-rich pentel heterocycles. Herein, we report on these results, which led, among other products, to complexes containing the as yet unknown parent 2,3-diphospha-1,3-butadiene and 2,3-diarsa-1,3-butadiene ($CH_2{=}E{-}E{=}CH_2$; $E = P$, As) as ligands. Moreover, by using diazomethane, unprecedented triazaphosphole heterocycles as well as parent pnictaalkene complexes are achievable.

After the addition of the diphenyldiazomethane at low temperature (−78 °C) to the phosphinidene complex **1a**,

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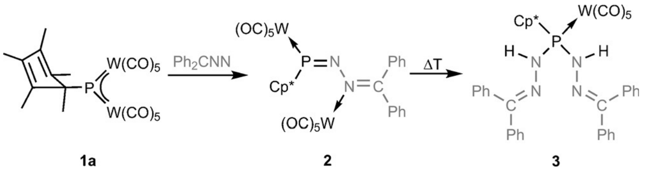
the reaction occurs immediately and the formed $[\{W(CO)_5\}Cp^*P{=}NN\{W(CO)_5\}{=}CPh_2]$ (**2**) can be isolated in good yields (60 %) at −40 °C as a yellow precipitate (Scheme 1). Compound **2** is one of the few examples of a phosphadiazadiene ligand (R-P=N−N=CR′R″) in which the phosphorus atom is in the oxidation state +3.[13] The two tungsten pentacarbonyl fragments are coordinated by the phosphorus atom and the β-nitrogen atom, respectively. At temperatures above −20 °C, **2** shows decomposition. This decomposition was monitored by a temperature dependent ^{31}P NMR from −40 °C to 80 °C (Supporting Information), which showed that two products are formed. However, only the minor product of this decomposition, compound **3** $[\{W(CO)_5\}PCp^*\{N(H)N{=}CPh_2\}_2]$, could be isolated and structurally characterized (Scheme 1).[14]



Scheme 1. Reaction of the phosphinidene complex **1a** with diphenyldiazomethane.

The molecular structure of **2** is shown in Figure 2. The main structural motif is the phosphadiazadiene unit, which consists of the atoms P1, N1, N2, and C21. The bond distances are with 1.580(3) Å (P1−N1), 1.418(4) Å (N1−N2), and 1.305(5) Å (N2−C21), in the typical range for such compounds.[13c]

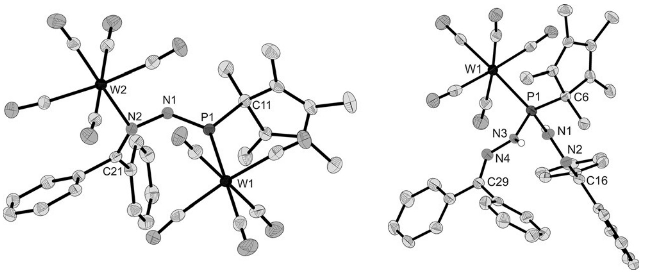
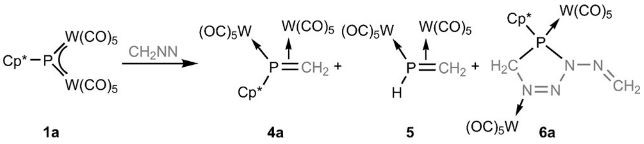


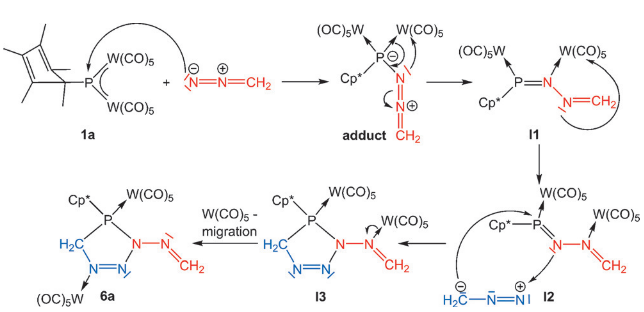
Figure 2. Molecular structure of **2** (left) and **3** (right) with ellipsoids at 50 % probability level. The hydrogen atoms at the carbon atoms are omitted for clarity.

To investigate the influence of the substituents on the diazomethane, the phosphinidene complex **1a** was reacted with a solution of freshly prepared CH_2NN. The reaction takes place at low temperatures (−78 °C) and after workup by chromatography, the compounds **4a**, **5**, and **6a** can be isolated (Scheme 2). **4a** and **5** are only obtained together in the same fraction. They are phosphaalkenes, which are coordinated by $[W(CO)_5]$ groups in a η^1 and η^2 fashion. **4a** is very likely formed by the reaction of **1a** with the CH_2 carbene, which is generated by N_2 elimination from the diazomethane. On the other hand, **5** is probably formed out of **4a**, by the elimination of tetramethylfulvene or by homolytic bond cleavage of the P−C bond in **4a**, followed by abstraction of a proton from the solvent or a Cp* substituent by the initially formed $[\{W(CO)_5\}_2\{\eta^{1:2}\text{-}P{=}CH_2\}]$ radical.[15] Both compounds show a singlet in the $^{31}P\{^1H\}$ NMR spectrum with characteristic tungsten satellite signals. The ^{1}H NMR spectrum of **4a** reveals three signals for the CH_3 groups of the Cp* substituent and two signals for the CH_2 group. In the ^{1}H NMR spectrum of **5**, three signals are detected, two for the CH_2 group and one for the hydrogen at the phosphorus atom.[16]



Scheme 2. Reaction of **1a** with diazomethane.

Compound **6a** is the first triazaphosphole derivative bearing a methanimine group at the α-nitrogen atom. **6a** is formally formed by the reaction of **1a** with two diazomethane molecules, without the elimination of N_2. Scheme 3 shows a possible reaction pathway for its formation, which was confirmed by DFT computations at the B3LYP/def2-SVP level of theory. The thermodynamic parameters for the considered reactions, the optimized structures of the compounds and a Gibbs energy diagram for the gas phase reaction are given in the Supporting Information. The first reaction step is the adduct formation, which leads to the phosphadiazadiene (**I2**), similar to **2**, after migration of a $[W(CO)_5]$ group. This phosphadiazadiene reacts with a second diazomethane by a [2+3] cycloaddition and the migration of a $[W(CO)_5]$ group to **6a**. In general, triazaphospholes are obtained by the reaction of phosphaalkenes[17] or phosphaalkynes[18] with an azide (RN_3). However, Niecke et al. reported the formation of a triazaphosphole by a [2+3] cycloaddition between a diazomethane and an iminophosphane.[19] This procedure is related to the predicted [2+3] cycloaddition in Scheme 3.



Scheme 3. Proposed reaction pathway for the formation of **6a**.

The central structural motif of **6a** (Figure 3) is the five-membered ring formed by the atoms P1-C21-N1-N2-N3. This ring is not completely planar and the phosphorus atom projects 0.3 Å out of the plane, formed by the other four atoms. The bonds P1−N3 (1.749(4) Å), P1−C21 (1.828(4) Å),

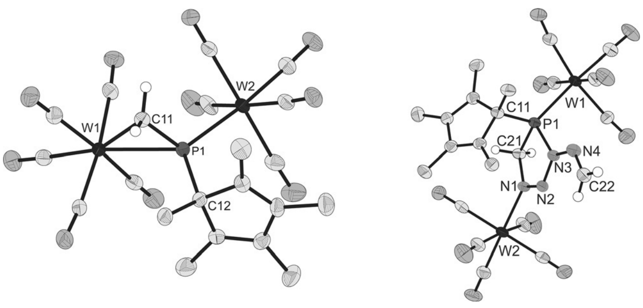
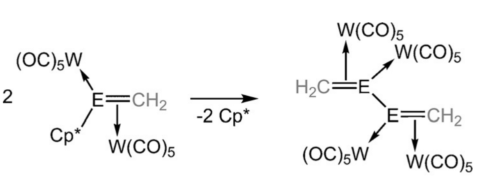


Figure 3. Molecular structure of **4a** (left) and **6a** (right) with ellipsoids at a 50% probability level. Except for the hydrogen atoms at C11 (**4a**), C21, and C22 (**6a**), all other hydrogen atoms adjoined to carbon atoms are omitted for clarity. (The molecular structure of **4b**, which is isostructural to **4a**, is depicted in the Supporting Information.)

and C21–N1 (1.504(5) Å) are single bonds. The bond distance of N1–N2 (1.259(5) Å) is in the range of a double bond and that of N2–N3 (1.360(5) Å) lies between a single and a double bond.[20]

Interestingly, the reaction of the arsinidene complex **1b** with both diazomethanes gives different results. For the diphenyldiazomethane, no reaction takes place. On the other hand, the diazomethane reacts readily with **1b** at low temperatures by the elimination of N_2 to form **4b**, which can be isolated after chromatographic workup. However, the formation of a triazaarsol derivate similar to **6a** was not observed, although our theoretical calculations predict the formation of **6b** out of **1b** and two equivalents of diazomethane to be exergonic by $-45.7\,kJ\,mol^{-1}$.[21] Compound **4b** is an arsaalkene coordinated to two tungsten pentacarbonyl fragments and is isostructural with **4a** (Figure 3). For both compounds, the C11–E1 bond is in the range of an elongated double bond (E=P: 1.736(3) Å; E=As: 1.865(3) Å), which is very likely caused by coordination to a $[W(CO)_5]$ fragment.[20]

During the attempt to recrystallize **4a** at +4 °C from CH_2Cl_2, crystals of **7a** $[\{W(CO)_5\}_4(CH_2{=}P{-}P{=}CH_2)]$ were obtained (Scheme 4). **7a** is the first example of a 2,3-diphosphabutadiene stabilized by four $[W(CO)_5]$ moieties. DFT computations showed that, at 25 °C, reactions leading to **7a**/**7b** with evolution of two Cp* radicals are endergonic, both in the gas phase and in CH_2Cl_2 solution. However, such reactions under formation of HCp* and fulvene in CH_2Cl_2 solution are predicted to be exergonic by 25.5 and $47.3\,kJ\,mol^{-1}$ for **7a** and **7b**, respectively.[22] Therefore, we were confident that it might be possible to obtain **7b** as the first 2,3-diarsabutadiene, without sterically demanding substituents on the carbon atoms. And in fact, keeping a solution of **4b** in CH_2Cl_2 for several days at room temperature resulted in the desired 2,3-diarsabutadiene (**7b**) as an orange crystalline solid in moderate yields of 30%. For the formation of **7a**/**b**, we expected a radical reaction pathway similar to the formation of the complex $[\{W(CO)_5\}_4(t\mathrm{Bu})P{=}As{-}As{=}P(t\mathrm{Bu})]$.[10] Therefore, we performed EPR experiments with the compounds **4a**, **4b**, and **7b** under different conditions.[23] Unfortunately, these experiments showed no EPR signals. Hence, no concrete predictions of the reaction pathway can be made. Figure 4 shows the molecular structure of **7b** (for **7a** see the Supporting Information). The As1–C41 (1.877(7) Å) and As2–C42 (1.879(7) Å) bond lengths in **7b** are very similar to the As1–C11 bond of **4b** (1.865(3) Å), and they are in the range of elongated double bonds. The formed As1–As2 bond (2.4261(10) Å) is in the range of a typical As–As single bond (compare the sum of arsenic single-bonded covalent radii (2.42 Å)).[24] 2,3-Diphosphabutadienes without sterically demanding substituents are, like phosphaalkenes, known to dimerize fast. For **7a**/**b**, this dimerization is prevented by the coordination to the four $W(CO)_5$ groups. There are some theoretical studies on the unsubstituted 2,3-diphosphabutadiene, which predict that the planar *trans* isomer is the global minimum and that a minor conformer (gauche) also exists with a dihedral angle of 60°.[25] For the compounds **7a**/**b**, we found in the solid state two molecules in the asymmetric unit cell. One molecule shows an almost planar *cis*-conformation with a dihedral angle of 1° (**7a**) and 3° (**7b**). The other molecule is disordered, with one part showing a twisted *cis*-conformation (dihedral angle: **7a**, 11°; **7b**, 18°) and the other part a twisted *trans*-conformation (dihedral angle: **7a**, 141°; **7b**, 144°). We also performed DFT calculations regarding the favorability of the different isomers. These calculations predict that the *cis*-conformations, with a dihedral angle of 3° (**7a**) and 11° (**7b**), are more stable than the *trans*-conformations (dihedral angle: **7a**, 140°; **7b**, 144°) by $4.8\,kJ\,mol^{-1}$ and $2.3\,kJ\,mol^{-1}$, respectively, which is in agreement with the experimentally observed results. This divergence between the calculated planar *trans*-conformation of the free 2,3-diphosphabutadiene and the observed conformations of **7a**/**b** is very likely caused by the steric demand of the four $[W(CO)_5]$ groups.



4a E = P
4b E = As

7a E = P
7b E = As

Scheme 4. Decomposition of **4a**/**b** into **7a**/**b**.

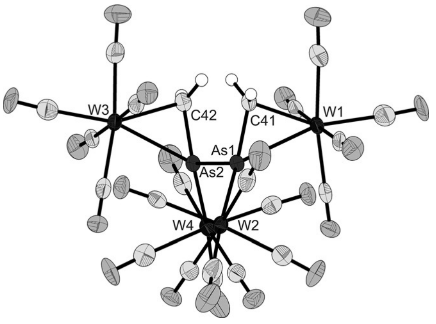


Figure 4. Molecular structure of compound **7b** with ellipsoids at 50% probability level. Most hydrogen atoms at the carbon atoms are omitted for clarity, except for the hydrogen atoms at C41 and C42.

In summary, we reported the reactions of different diazoalkanes with pentelidene complexes of the type

$[Cp^*E\{W(CO)_5\}_2]$ (E = P, As). We succeeded at the unique formation of a rare example of a phosphadiazadiene complex **2**, as well as the synthesis of a nitrogen rich phosphorus heterocycle **6a**, the first triazaphosphole derivative bearing a methanimine group at the α-nitrogen atom. Moreover, after N_2 elimination, phosphaalkene and arsaalkene complexes **4** were obtained, which are, because of the lability of their Cp* substituent, of great value as building blocks for subsequent chemistry; including the formation of the first parent phosphaalkene complex **5**. Finally, we found a synthetic pathway to the unprecedented parent 2,3-diphospha-1,3-butadiene and 2,3-diarsa-1,3-butadiene ligands stabilized in the coordination sphere of tungsten pentacarbonyl moieties (**7a,b**). Such 1,3-butadienes with Group 15 elements in the 2,3-position could so far only be realized if they were bearing bulky substituents such as NHCs or CAACs.

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Keywords: arsenic · 1,3-butadienes · diazomethane · phosphinidenes · phosphorus · tungsten

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