Group 15 Heterocycles

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Reaction of Tungsten–Phosphinidene and –Arsinidene Complexes with Carbodiimides and Alkyl Azides: A Straightforward Way to Four-Membered Heterocycles**

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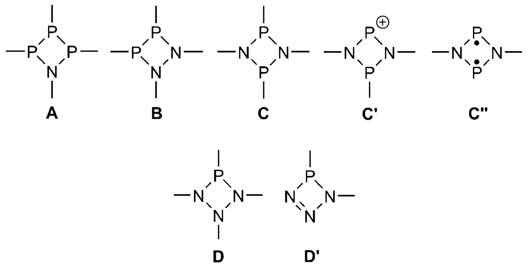
Dedicated to Professor Gerhard Roewer on the occasion of his 75th birthday

***Abstract:** The reaction of the phosphinidene and arsinidene complexes $[Cp^*E\{W(CO)_5\}_2]$ (E = P (**1a**), As (**1b**); $Cp^* = C_5Me_5$) with carbodiimides leads to the new four-membered heterocycles of the type $[Cp^*C(NR)_2E\{W(CO)_5\}_2]$ (E = P: R = iPr (**2a**), Cy (**3a**); E = As: R = iPr (**2b**), Cy (**3b**)). The reaction of phosphinidene complex **1a** with alkyl azides yields the triazaphosphete derivatives $[Cp^*P\{W(CO)_5\}N(R)NN\{W(CO)_5\}]$ (R = Hex, Cy) (**4**). These unprecedented N_3P four-membered triazaphosphete complexes can be regarded as stabilized intermediates of the Staudinger reaction, which have not been previously isolated. All of the isolated products were characterized by NMR, IR spectroscopy, mass spectrometry, and by single-crystal X-ray diffraction analysis.*



Scheme 1. Representations of four-membered PN heterocycles.

EN heterocycles (E = Group 15 element) are an interesting class of compounds.[1] Recently, a series of new binary five-membered PN and AsN heterocycles was reported by Schulz et al.[2] Of special importance are four-membered EN heterocycles of which PN heterocycles of the types **A**–**C** are known (Scheme 1). Whereas only few examples of structurally characterized azatriphosphetidines (**A**)[3] and 1,2-diaza-3,4-diphosphetidines (**B**)[4] exist, the 1,3-diaza-2,4-diphosphetidines (**C**) are more common[1,5] and of increasing interest for subsequent reactivity. For example, Weigand et al. showed that the cyclic phosphenium cations **C′** are able to activate P_4 to form cationic P_5 scaffolds.[6] Another example of four-membered ring compounds are the biradicaloids $[P(\mu\text{-}NR)]_2$ (**C″**),[7] which are a Group 15 element-based extension of the large family of stable biradicaloids.[8] In contrast, stable heterocycles revealing the PNNN four-membered ring **D** are as yet unknown and, interestingly, the triazaphosphetes **D′** have only been mentioned to date as an intermediate of the Staudinger reaction.[9]

Recently, we reported the reaction of the tungsten–Group 15 complexes $[Cp^*E\{W(CO)_5\}_2]$ (E = P, As) with isonitriles to form new four- and five-membered heterocycles, such as the first 2,3-dihydro-1,3-azarsete complex.[10] As the nucleophilic attack is the initial reaction step, the use of other nucleophiles with special atom sequences and functionalities came into the focus of our interest. Owing to the nucleophilic nitrogen atoms and the cumulated double-bond system, the use of heterocumulenes such as carbodiimides or alkyl azides could lead to compounds with unknown structural motifs, even in one-step reactions. Herein we report such one-step syntheses, resulting for example in unprecedented stable triazaphosphetes of type **D′**, which have been discussed as possible intermediates of the Staudinger reaction.[11]

At room temperature, the complexes $[Cp^*E\{W(CO)_5\}_2]$ (E = P, As; $Cp^* = C_5Me_5$) show no reaction with *N,N′*-dicyclohexylcarbodiimide (DCC) or *N,N′*-diisopropylcarbodiimide (DIC). The reaction only takes place in boiling toluene, and a mixture of the new products **2a/b** and **3a/b** (Scheme 2), together with the thermolysis products of **1a/b**, are obtained.[12] Owing to both competing reactions and the need for thin-layer chromatographic workup of the reaction mixtures, the yields of isolated product are moderate (6–22 %). Compounds **2a/b** and **3a/b** are diazaphosphete and novel diazaarsete complexes that are formed after the initial nucleophilic attack of the carbodiimide at the E atom and by subsequent migration of the Cp* ligand from the phosphorus atom to the carbon atom of the former carbodiimide, leading to a chelating amidinate substituent. Insertion reactions of

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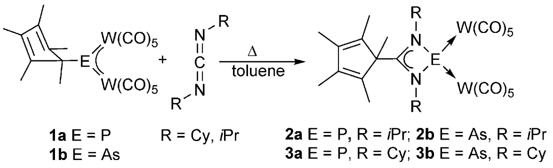


Scheme 2. Reaction of **1 a/b** with carbodiimides.

carbodiimides are known for transition-metal complexes, and especially for lanthanides[13] and early transition metals.[14] For main-group elements, only a few examples have been reported; for example, the insertion into an Al–R or Ga–R bond.[15] The only example of the insertion of a carbodiimide into a P–X bond was reported by the reaction of $(CF_3)_2PCl_3$ with carbodiimides to form a neutral hexacoordinated phosphorus compound.[16] However, there are no examples reported for the insertion of a carbodiimide into an As–R bond as now found for **2b** and **3b**.

The ^{31}P NMR spectra of **2a** and **3a** show singlets at $\delta =$ 297.7 and 298.8 ppm, respectively, both with a $^1J(P,W)$ coupling constant of 188 Hz. The molecular structures of the isostructural diazaphosphete or diazaarsete complexes **2a/b** and **3a/b**, respectively, are shown in Figure 1. In the following, the structural parameters of **2a/b** will be discussed (for **3a/b**, see the Supporting Information).[9] Both E–N1 and E–N2 (E = P/As) distances (1.804(4)/1.959(4) Å and 1.792(4)/1.934(3) Å) are in the range between a dative bond (N→P = 1.885(4) Å,[17] N→As = 2.014 Å[18]) and a single bond (1.78/1.90 Å from covalent radii[19]). The C11–N1 and the C11–N2 bonds (1.344(6)/1.334(4) Å and 1.349(6)/1.335(5) Å) are very similar and also between a single and a double bond. This indicates the presence of a delocalized double bond within the N-C-N ring system. The overall four-membered ring is almost planar, with the Group 15 atom being slightly out of the plane formed by the N-C-N ring fragment (0.06 Å for **2a** and 0.09 Å for **2b**).

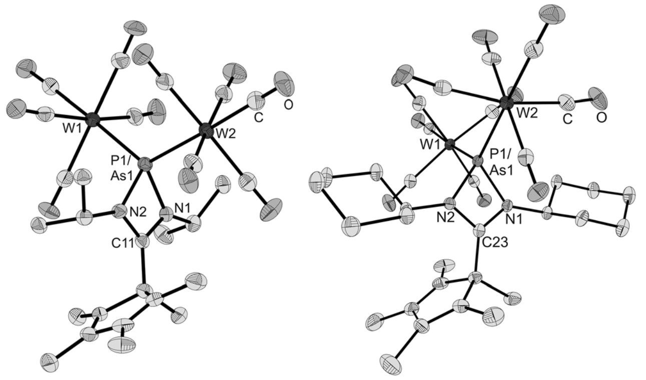
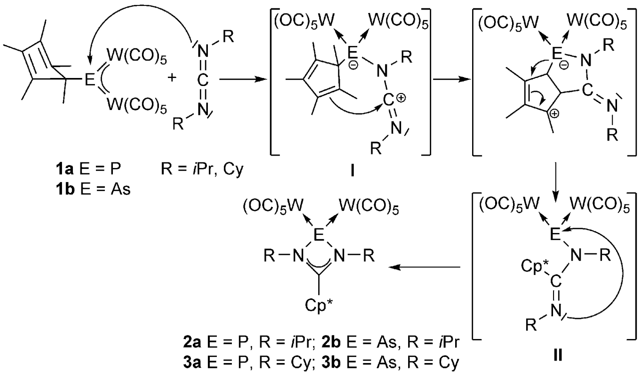


Figure 1. Molecular structure of **2a** (E = P)/**2b** (E = As) (left) and **3a** (E = P)/**3b** (E = As) (right) (ellipsoids are set at 50% probability). All hydrogen atoms have been omitted for clarity.



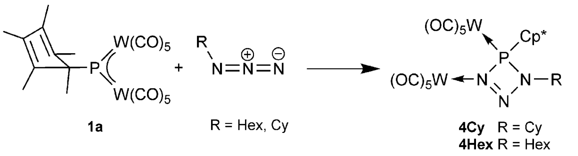
Scheme 3. Proposed reaction pathway for the reaction of **1 a/b** with carbodiimides.

A proposed reaction pathway for the reaction of **1a/b** with carbodiimides is given in Scheme 3. First, the nucleophilic attack of the lone-pair of one nitrogen atom of the carbodiimide at the Group 15 atom occurs to form adduct **I**. The formation of adducts was observed in some reactions of μ-phosphinidene complexes with Lewis bases,[10,20] but they could be isolated in only a few cases. The second step is the migration of the Cp* substituent from the Group 15 atom to the carbon atom at the carbodiimide to give intermediate **II**, representing an aminophosphinidene or aminoarsinidene complex. In the last step, the attack of the second nitrogen atom of the carbodiimide at the Group 15 atom occurs, resulting in the formation of the final products. A comparable reaction pathway was calculated by Barry et al. for the insertion of a carbodiimide into an Al–Me or an Al–NMe_2 bond.[21]

The reaction of organic azides (RN_3) with phosphines (R_3P) leads to phosphazenes ($R_3P{=}NR'$) and N_2, which were first reported by Staudinger.[22] The applications of this reaction in organic synthesis are manifold, as exemplified by the formation of new C=N bonds by the aza-Wittig reaction.[23] For a long time, the reaction mechanism was uncertain, but by theoretical calculations it was possible to provide insight into the occurring transition states and intermediates.[9,,11,24] It is predicted that the Staudinger reaction proceeds by a nucleophilic attack of the phosphorus lone pair on the terminal nitrogen atom of the azide, leading to the formation of a phosphazide intermediate in pseudo-*cis* configuration. Only some examples of such *cis* phosphazides are known,[25] whereas phosphazides with *trans* configuration are more common. The second step is the cyclization of the *cis* phosphazide to a four-membered cyclic intermediate. This intermediate subsequently extrudes dinitrogen with almost no energy barrier,[11] which is probably the reason why the latter intermediate had not been isolated until now.

In this context, we have been interested in investigating how the phosphinidene and arsinidene complexes will react with organoazides. Interestingly, only three of such examples starting from phosphinidene complexes have been reported.[26] Whereas all proceed with N_2 elimination, for $[Fe_2Cp_2(\mu\text{-}PCy)\text{-}(\mu\text{-}CO)(CO)_2]$ a phosphatriazadiene ligand was isolated at room temperature, which eliminates dinitrogen only after heating to form a phosphaimine complex.[26c]

In contrast to the thermolysis reaction with carbodiimide described above, the phosphinidene complex **1a** already reacts at temperatures below 0 °C with alkyl azides. No reaction was observed for the arsinidene complex (**1b**). The hexyl azide (HexN$_3$) reacts at −20 °C with the phosphinidene complex (**1a**), as indicated by a change of color from dark blue to yellow. However, the product, which shows a singlet in the ^{31}P{^{1}H} NMR at $\delta = 279.6$ ppm (^{1}J(P,W) = 290 Hz), decomposes slowly at room temperature into several species that could not be isolated or further characterized.[9] In contrast, the reaction of cyclohexyl azide (CyN$_3$) with the phosphinidene complex (**1a**) occurred at slightly higher temperature (−15 °C) and resulted in a single product **4Cy** (Scheme 4). The ^{31}P{^{1}H} NMR spectrum of **4Cy** shows a singlet at the same chemical shift recorded for the reaction with HexN$_3$ ($\delta = 280.4$ ppm, ^{1}J(P,W) = 290 Hz). Because of this similarity, the formation of a triazaphosphete complex (**D′**-like) can be assumed in both reactions at low temperature. In contrast to **4Hex**, complex **4Cy** is stable at room temperature and was isolated in good yields (53 %). Heating **4Cy** to 110 °C in toluene results in a complete decomposition into several products, which could not be further characterized.



Scheme 4. Reaction of **1a/b** with alkyl azides.

The molecular structure of **4Cy** (Figure 2) reveals a main structural motif the four-membered binary PNNN ring (type **D′**). The P1−N1 distance is with 1.760(5) Å in the range of a single bond, whereas the P1-N3 distance (1.801(5) Å) lies between a single and a dative bond. Both N−N distances are between a single and a double bond (1.330(7) Å for N1−N2 and 1.298(7) Å for N2−N3), indicating an electron delocalization through the NNN system. The ring system is almost planar, and the P atom is 0.15 Å out of the plane formed by the three nitrogen atoms. The P atom reveals a distorted tetrahedral environment with an N1-P1-N3 angle of 71.3(2)° and a W1-P1-C11 angle of 124.4(2)°. The P1−C11 distance (1.855(5) Å) is in the range of a lengthened single bond.

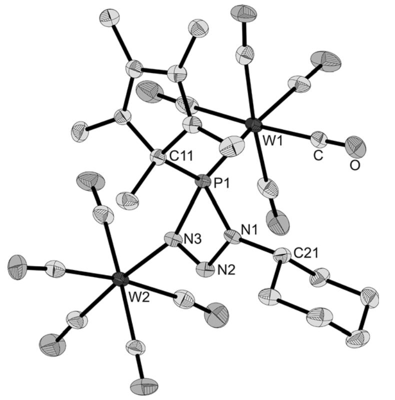
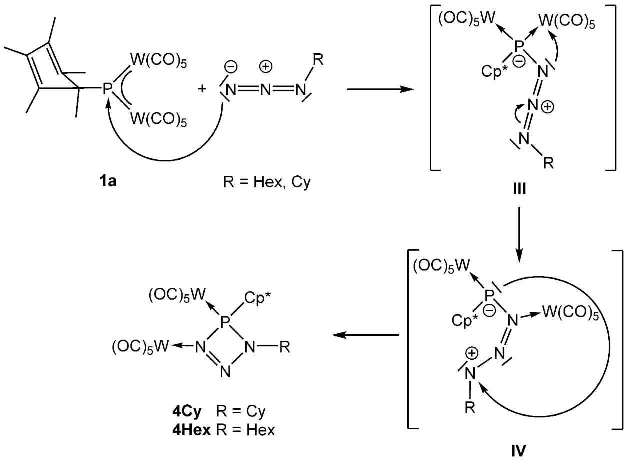


Figure 2. Molecular structure of **4Cy** (ellipsoids are set at 50 % probability). All hydrogen atoms have been omitted for clarity.



Scheme 5. Proposed reaction pathway for the reaction of **1a** with RN$_3$.

The proposed reaction pathway of the reaction of **1a** with RN$_3$ is depicted in Scheme 5. First, a nucleophilic attack of the alkyl azide occurs at the electrophilic phosphorus atom, which was confirmed experimentally by the disappearance of the blue color of the starting materials in solution. In a second step, a tungsten pentacarbonyl fragment migrates from the phosphorus atom to the N$_\alpha$ atom of the azide and a phosphatriazadiene ligand (**IV**) is formed. In the last step, a new P−N bond is formed between the P atom and the N$_\gamma$ atom, which results in the triazaphosphete products **4**. During this reaction, the oxidation state at the phosphorus atom formally changes from phosphorus(I) to phosphorus(III), which is comparable with the change of the oxidation state from P$^{\mathrm{III}}$ to P$^{\mathrm{V}}$ of the Staudinger reaction.

To shed light into the reaction pathway of complexes **1a/b** with carbodiimides and alkyl azides, DFT calculations have been carried out. The Gibbs energy profiles for these reactions are depicted in Figure 3. The thermodynamic parameters for the considered reactions and the optimized structures of the compounds are given in the Supporting Information. For the reaction of the phosphinidene and arsinidene complexes with the carbodiimides it was only possible to obtain the high-energy starting species **Ia** for the phosphinidene complex (131 kJ mol^{-1}). The calculated species of the arsinidene complex is not stable. High-energy species require larger activation energies, and thus high-temperature conditions, which is in accordance with experiment (110 °C). The reactions of **1a** and **1b** with carbodiimides

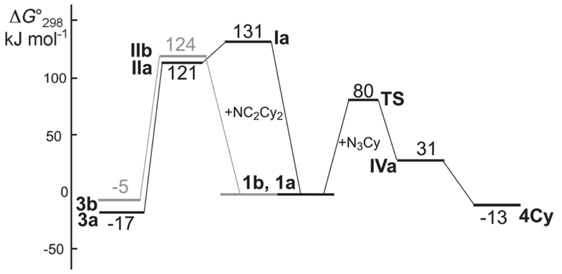


Figure 3. Gibbs energy profile for reactions of **1a** (black) and **1b** (gray) with carbodiimides (left) and alkyl azides (right).

to give finally the cyclic products **2a**, **2b**, **3a**, and **3b**, respectively, are exergonic by 5–19 kJ mol^{-1}. The reactions of **1a** with alkyl azides are exergonic by only 13–23 kJ mol^{-1}. At first glance, this is contradictory to the high-temperature requirements for the reaction in the first case and the low-temperature reactivity in the latter. However, if the formation of chain-like intermediates is considered, remarkable effects are observed. The reaction of **1a** and **1b** with carbodiimides, which leads to the chain-like (acyclic) intermediates **IIa***i*Pr, **IIb***i*Pr, **IIa**Cy, and **IIb**Cy, is slightly endothermic (by 12–32 kJ mol^{-1}). In contrast, for the reaction with alkyl azides, the formation of such chain-like (acyclic) intermediates **IV**Cy and **IV**Hex is slightly exothermic (by 16–39 kJ mol^{-1}). This may explain why the reaction with carbodiimides requires heating (formation of intermediates is endothermic), whereas the reaction with alkyl azides proceeds rapidly even at low (−20 and −15 °C) temperatures (formation of intermediates is exothermic).

It was also of interest to investigate why only the migration of the $W(CO)_5$ group is observed for the reaction of **1a** with alkyl azides and not the migration of the Cp* substituent, as was found for the reaction of **1** with carbodiimides. For the formation of **4**, the Cp* migration is energetically less favorable than the $W(CO)_5$ migration by about 35–41 kJ mol^{-1}. In the gas phase, the interaction of **1a** with N_3R and the additional migration of Cp* is endergonic, but the migration of the $W(CO)_5$ group is exergonic. These data explain that only the $W(CO)_5$ migration product is formed experimentally. The energetic differences between the substituents Cy and Hex are small; therefore, similar reactivity is expected from the thermodynamic point of view.

In conclusion, we showed that it is possible for carbodiimides to insert into the E−R bonds (E = P, As) of phospinidene and arsinidene complexes, resulting in novel four-membered heterocycles stabilized by $W(CO)_5$ units. For the arsinidene complex, it is the first example of an insertion of a carbodiimide into an As−R bond. Moreover, the reaction of the phosphinidene complex with alkyl azides leads to the formation of unprecedented triazaphosphete complexes, which is stable at ambient temperatures for the cyclohexyl derivative **4Cy**. This product can be regarded as a $W(CO)_5$-stabilized derivative for a theoretically predicted intermediate of the Staudinger reaction. Additionally, the influence of the substituent at the azide on the stability of the novel triazaphosphete complexes was explored. By changing from *n*-hexyl to cyclohexyl, an increased stability of these products was found.

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