1,2,3-Triphosphole derivatives as reactive intermediates[†][‡]

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The complexes $[Cp*E{W(CO)_5}_2]$ (E = P, As; $Cp* = C_5Me_5$) react with 1,2-diphosphinobenzene to give 1,2,3-triphosphole and 2-arsa-1,3-diphosphole derivatives as reactive intermediates that dimerise to polycyclic phosphorous and arsenic containing cage compounds.

The 1,2,4-triphospholide anion¹⁻³ [A]⁻ is a broadly used ligand in coordination chemistry⁴ and a starting material for the synthesis of organo-substituted 1,2,4-triphospholes [A] $(\mathbf{R} = t\mathbf{B}\mathbf{u}, \mathbf{SiMe}_3)$.⁵ Interestingly, the parent PH compound of [A], the 1H-1,2,4-triphosphole, is only obtained by using the sterically bulky supermesityl substituents.³ Also the radical [A] is only stabilised by these substituents in solution at room temperature.³ In contrast, the isomer of [A], the 1,2,3-triphosphole [B], is so far unknown. Only recently, Russell et al. succeeded in the synthesis of a stable 1,2,3-triphospholide anion $[\mathbf{B}]^{-}$ as well as the arsenic congener $[\mathbf{C}]^{-}$ embedded in an indenyl derivative.⁶ Also, Wright et al. used the permetallated 1,2-diphosphinobenzene as starting material to synthesise the Sb containing anion of $[C]^{-}$ and also $[B]^{-}$.⁷ The aromaticity of these anions is a decisive factor for their stability, for which the subsequent one-electron reduction of the Sb derivative leads to a dimerisation of the radical dianion of [C]^{-,7} Herein we describe the generation of the parent E-H compounds [B] and [C] (E = As) as reactive intermediates and their subsequent reactions by a [2 + 4]-cycloaddition with itself to yield novel hexaphospha- and tetraphospha-diarsa-cage compounds. Furthermore, the trapping reactions of these intermediates with 2,3-dimethylbutadiene are reported.



In the past we have been able to show that the pentelidene complexes $[Cp*E{W(CO)_5}_2] (E = P(1), As(2))^8$ are excellent

starting materials for the *in situ* generation of tungsten element triple-bond intermediates $[Cp^*(CO)_2W \equiv E \rightarrow W(CO)_5]$ [**D**],⁹ which can be trapped by organometallic compounds containing transition metal multiple bonds,¹⁰ alkynes,¹¹ and phosphaalkynes to give novel clusters, metal containing heterocycles, and cage compounds, respectively. In the latter reaction, an unusual opening of the Cp* ligand is additionally observed to form an unprecedented 1,2-diphosphacyclooctatetraene ligand.¹² Yet, we found now that strong nucleophiles can attack the pentel atom (group 15 element atom) and initiate subsequent reactions.

phosphinidene The reaction of the complex $[Cp*P{W(CO)_5}_2]$ (Cp* = C₅Me₅) (1) with the primary phosphine 1,2-diphosphinobenzene in toluene at 60 °C leads to the formation of **3** as the only isolable product (eqn (1)).§ The arsinidene complex $[Cp*As{W(CO)_5}_2]$ (2) reacts readily at room temperature, yielding complex 4 (eqn (1)). The isolated yields of both products are rather low, probably due to oligomerisation and other subsequent reactions of the proposed intermediates as well as the starting materials. The structural core of both novel compounds is reminiscent of the hexaphosphine P₆H₆, which was identified only by ³¹P NMR in a mixture of products as the 1-phosphinocyclopentaphosphine.¹³ Interestingly, these products are different from the one of the metal-induced dehydrocoupling of 1,2-diphosphinobenzene, for which Stephan et al. reported the formation of P₄- and P₁₆-containing cages and macrocycles.¹⁴



Compounds 3 and 4 are yellow crystalline solids that are almost insoluble in common organic solvents. In the EI mass spectra of 3 and 4 peaks corresponding to the molecular ion as well as to characteristic fragments are observed. Interestingly, in the mass spectrum of 4 a peak corresponding to half the molecular weight of the molecular ion corresponding to the 1H-benzo-[1,3,2]diphosphaarsole complex **[C]** is identified.

Due to its low solubility **3** cannot be characterised by NMR spectroscopy, which is possible for the somewhat more soluble **4**. In the ¹H NMR spectra of **4** two multiplets are detected at 4.77 ppm and 8.10 ppm corresponding to the AsH and aromatic protons, respectively. The resonance signal of the PH group appears as multiplets of a doublet with a coupling constant of ${}^{1}J_{P,H} = 321$ Hz. In the ${}^{31}P{}^{1}H$ NMR spectrum of

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4 four signal groups are detected. Each of them appear as doublets of doublets of doublets of an ADMX spin system (*cf.* ESI[‡]). The ¹J_{P,P} and the ²J_{P,P} coupling constants in **4** are similar to those reported for the 1-phosphino-cyclopenta-phosphine.¹³ In the recently reported 1,2,3-triphospholide anion $[C_6H_4P_3]^-$ the ¹J_{P,P} coupling constant is considerably higher (¹J_{P,P} = 514 Hz)⁶ than in **4** as a result of a delocalised aromatic system.

Compound **3** crystallises in the triclinic space group $P\overline{1}$ as a CH₂Cl₂-containing solvate.¶ The main feature of the structure of **3** is the central phosphino-cyclopentaphosphine core, which has two hydrogen atoms and two 1,2-phenylene units as substituents, leading to an exo-tricyclo-[5.2.1.0^{2,6}]-decane polycyclic system. Additionally, four of the six phosphorus atoms coordinate to four W(CO)₅ fragments (Fig. 1). Interestingly, the central cyclopentaphosphine ring presents an unusual configuration with three substituents next to each other being located on the same side whereas the other two substituents are on the opposite side of the cyclopentaphosphine ring (the position of the hydrogen atom bonded to P2 could be crystallographically located). Usually, cyclophosphines adopt the configuration with a maximum of *trans* orientation of the neighbouring substituents.¹⁵

Compound **4** is isostructural with **3**, in which the two arsenic atoms occupy the 1,3 positions in the central 1-phosphino-1,3-diarsa-cyclopentaphosphine core (Fig. 1). All phosphorus



Fig. 1 Molecular structure of 3 and 4, respectively; if different, the corresponding numbering scheme for 4 is in parentheses. Selected bond lengths (Å) and angles (°) for **3**: P(1)-P(2) 2.193(3), P(2)-P(3)2.191(4), P(3)-P(4) 2.259(3), P(4)-P(5) 2.244(3), P(5)-P(6) 2.216(3), P(1)-P(5) 2.238(3), P(1)-C(1) 1.828(8), P(3)-C(2) 1.824(9), P(4)-C(8) 1.834(10), P(6)-C(7)1.831(9); P(2)-P(1)-P(5)100.51(12), P(1)-P(2)-P(3) 91.26(12), P(2)-P(3)-P(4) 97.48(12), P(3)-P(4)-P(5)101.54(12), P(1)-P(5)-P(4) 101.12(12), P(1)-P(5)-P(6) 100.79(12),P(4)-P(5)-P(6) 95.88(12). Selected bond lengths (Å) and angles (°) for 4: P(1)-As(1) 2.315(2), As(1)-P(3) 2.312(3), P(3)-P(4) 2.266(3), P(4)-As(2) 2.337(2), As(2)-P(6) 2.335(3), P(1)-As(2) 2.347(2); As(1)-P(1)-As(2) 99.96(9), P(1)-As(1)-P(3) 87.57(9), As(1)-P(3)-P(4) 100.00(10), P(3)-P(4)-As(2) 102.96(10), P(1)-As(2)-P(4) 98.68(7), P(1)-As(2)-P(6) 101.00(9), P(4)-As(2)-P(6) 92.71(9).

atoms in 4 are coordinating to W(CO)₅ fragments. The P–P bond lengths in 3 vary from 2.191(4) Å to 2.259(3) Å and are in the expected range for single bonds. The only existing P–P bond (P(3)–P(4)) in 4 is 2.266(3) Å and is almost identical with the corresponding bond (P(3)–P(4)) in 3. The P–As bond lengths in 4 vary between 2.312(3) and 2.347(2) Å and represent single bonds. The average P–C bond lengths in 3 and 4 are 1.829(8–10) and 1.830(8–10) Å, respectively, and thus represent P–C single bonds. Shorter P–C bonds possessing multiple bond character are observed in the 1,2,3-triphospha- and 2-arsa-1,3-diphosphaindenyl anions (av. 1.778 Å and av. 1.772 Å, respectively).⁶

By analysing the structure of **3** and **4** in a retrosynthetic way, the formation of **3** and **4** can be rationalised as a hetero-Diels-Alder cycloaddition product of a 1*H*-with a 2*H*-benzo[*d*][1,2,3]triphosphole and a 1*H*- with a 2*H*-benzo[*d*][1,3,2]diphosphaarsole, respectively. In view of the recent synthesis of the 1,2,3-triphospha-, 2-arsa-1,3-diphospha-⁶ and 2-stiba-1,3-diphosphaindenyl⁷ anions the assumption of the triphosphole and diphospharsole complexes as intermediates seems to be realistic.

To prove the proposed retrosynthesis attempts were performed to trap the intermediates. Indeed, the reaction of the pentelidene complexes **1** and **2**, respectively, with 1,2-C₆H₄(PH₂)₂ in the presence of 2,3-dimethylbuta-1,3-diene leads to the formation of the cycloaddition products **5** and **6** (Scheme 1), which could be identified in the reaction mixture by NMR spectroscopy and mass spectrometry.¹⁶ Additionally, **6** could be isolated. Moreover, the formation of Cp*H was proven by NMR spectroscopy in this reaction and in reaction (1). A proposed reaction pathway for the formation of **3** and **4** is shown in Scheme 2.

The pentelidene complexes react with 1,2-diphosphinobenzene by elimination of Cp*H and subsequent rearrangement reactions to give the pentelidene–phosphene complexes E. By intramolecular hydrophosphination reaction, the dihydrodiphosphapentelole derivatives F are formed, which eliminate hydrogen to give the corresponding diphosphapenteloles C'. Subsequently, in a [2 + 4]-cycloaddition reaction they dimerise to 3 and 4, respectively.

In summary, we have shown that the phosphinidene and arsinidene complexes 1 and 2 can be used in a reaction with



Scheme 1 Trapping reaction of the intermediately formed triphosphole and diphosphaarsole complexes by butadiene.



Scheme 2 Proposed reaction mechanism for the formation of 3 and 4.

primary diphosphines to generate the 1,2,3-triphosphole and 2-arsa-1,3-diphosphole derivatives as intermediates that subsequently react to give novel polycyclic phosphorus and arsenic containing cage compounds. The found pentelideneinduced aggregation process is different from the previously reported metal-mediated dehydrocoupling leading both to group 15 element-rich cage compounds.¹⁴

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Notes and references

§ 3: A solution of 1,2-diphosphinobenzene (62 mg, 0.44 mmol) was added to a solution of $[Cp*P{W(CO)_5}_2]$ (1) (175 mg, 0.22 mmol) in toluene (20 cm³) at room temperature. The blue colour of 1 turns to orange after 16 hours stirring at room temperature. The reaction mixture was concentrated to approximately 2 cm³ and layered with 5 cm³ hexane to give pale yellow crystals of 3.1.5CH₂Cl₂ (27 mg, 8%). MS (EI, 70 eV) m/z 1636 (M⁺, 2%), 1312 (M⁺-W(CO)₅, 2). IR (KBr) $\nu_{\rm max}/{\rm cm}^{-1}$ 2068m, 1998vs, 1946s (CO). 4: A solution of 1,2-diphosphinobenzene (58 mg, 0.41 mmol) was added to a solution of $[Cp*As{W(CO)_5}_2]$ (2) (172 mg, 0.20 mmol) in toluene (20 cm³) at -78 °C. After the reaction mixture was allowed to slowly warm up to room temperature and stirred for two days, the colour of the reaction mixture turned to brown. The reaction mixture was concentrated to approximately 5 cm³ and layered with 5 cm³ hexane to give pale yellow crystals of $4 \cdot C_6 H_5 CH_3$ (38 mg, 11%). ¹H NMR δ_H (400 MHz; CD₂Cl₂; Me₄Si) 4.77 (1 H, m, As–H), 6.94 (1 H, dm, J_{HP} 321 Hz, P–H), 8.10 (8 H, m, C₆H₄). ³¹P{¹H} NMR δ_P (161 MHz; CD₂Cl₂; Me₄Si) –31.5 (1 P, ddd, J_{PP} 4, J_{PP} 13, J_{PP} 17, P⁴), 13.4 (1 P, ddd, J_{PP} 3, J_{PP} 12, J_{PP} 17, P⁴), 13.4 (1 P, ddd, J_{PP} 3, J_{PP} 12, J_{PP} 17, J_{PP (1), add, σ_{PP}^{-1} , $\sigma_{PP}^{ (1/2 \cdot M^+, 42).$

¶ Crystal data for 3·CH₂Cl₂: $C_{33}H_{12}O_{20}Cl_2P_6W_4$, M = 1720.51, triclinic, space group $P\overline{1} \ a = 11.547(3)$, b = 14.237(3),

c = 17.070(7) Å, α = 111.295(6), β = 104.846(7), γ = 99.201(18)°, V = 2425.6(13) Å³, T = 123(1) K, Z = 2, μ(Cu_{Kα}) = 20.615 mm⁻¹, 10 270 reflections measured, 6061 unique (R_{int} = 0.027) which were used in all calculations. The final R_1 [I > 2σ(I]] was 0.0301. The low completeness and relatively low resolution of the data set affect adversely the geometric parameters (see ESI‡). Crystal data for 4-C₇H₈: C₃₉H₁₈As₂O₂₀P₄W₄, M = 1815.61, triclinic, space group PI, a = 12.2685(5), b = 12.4386(5), c = 18.7689(7) Å, α = 96.500(3), β = 102.035(4), γ = 115.791(4)°, V = 2453.6(2) Å³, T = 123(1) K, Z = 2, μ(Cu_{Kα}) = 20.288 mm⁻¹, 13743 reflections measured, 7523 unique (R_{int} = 0.0401) which were used in all calculations. The final R_1 [I > 2σ(I]] was 0.0390.

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