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Synthesis of the first 2,3-dihydro-1,2,3-azadiphosphete complex†

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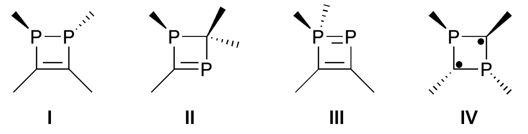
Synthesis of the first 2,3-dihydro-1,2,3-azadiphosphete complex was achieved *via* thermal reaction of a 2*H*-azaphosphirene complex in *o*-xylene, whereby a 2,5-dihydro-1,3-diaza-2,5-diphosphinine complex and a further unidentified byproduct were formed; the structure of the title compound was established through an X-ray single-crystal diffraction study.

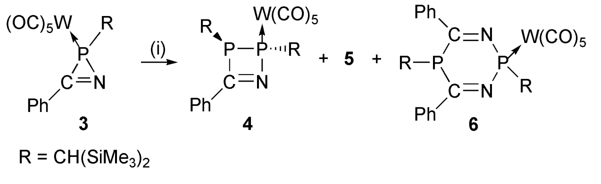
The short communication of W. Mahler on the first synthesis of 1,2-dihydro-1,2-diphosphete and 1,2,3-triphospholene derivatives[1] is one of the landmarks in the chemistry of phosphorus carbon heterocyclic chemistry.[2] For example, the isomeric $C_2P_2R_4$ heterocycles **I**,[1] **II**,[3] **III**[4] or **IV**[5] (Scheme 1) have fascinated phosphororganic and coordination chemists and spurred experimental and theoretical studies, especially with regard to rearrangements of **I–IV**. Surprisingly, none of the related CNP_2R_3 heterocycles in which one CR moiety in **I–IV** is replaced by a nitrogen atom has been experimentally or theoretically investigated.



Scheme 1 Monocyclic isomers of $C_2P_2R_4$ **I–IV** (lines denote organic or elementorganic substituents).

In previous studies, we showed that 2*H*-azaphosphirene complexes are new versatile building blocks[6] for unsaturated phosphorus heterocycles. We also provided proof that two highly reactive species were involved in such thermal reactions in solution: electrophilic terminal phosphinidene complexes[7] and nitrilium phosphane-ylide complexes.[8] Very recently, we reported the synthesis of the first 1,2,3,4-azatriphospholene complex, having a heterocyclic ligand that is related to compound **2**.[9]

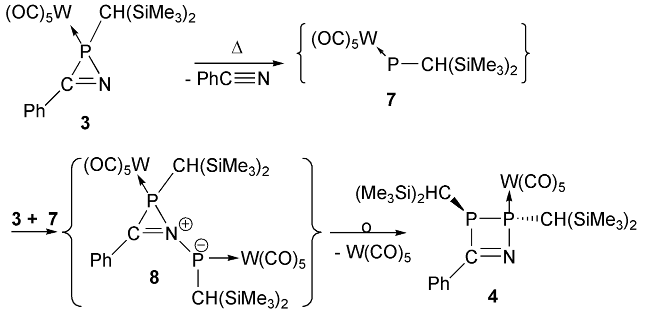
Here, we report the synthesis of complex **4**, having the novel 2,3-dihydro-1,2,3-azadiphosphete as ligand, *via* thermal reaction of the 2*H*-azaphosphirene complex **3**[10] in *o*-xylene. Complex **4** was obtained as the main product (*ca.* 45–50% as determined by ^{31}P NMR spectroscopy) together with complex **5** (*ca.* 20–25%) and the 2,5-dihydro-1,3-diaza-2,5-diphosphinine complex **6**[11] (*ca.* 20–25%) (Scheme 2). The NMR data of complex **5** (295.5 ($|^1J(^{183}W,^{31}P)|$ = 217.0 Hz) point to a compound having a low-coordinated phosphorus centre;[12] unfortunately, this product decomposed during chromatography.



Scheme 2 Reagents and conditions (i) 570 mg (0.92 mmol) of complex **3** in 2 mL of *o*-xylene, 90 °C, 20 min; column chromatography (SiO_2, −50 °C, *n*-pentane); **4**: yellow solid, yield: 30%, mp 130 °C (decomp.).

It seems plausible that the primarily formed terminal phosphinidene complex **7** reacts with complex **3** to yield the betaine-type intermediate **8** in the first reaction step, which then rearranges with loss of pentacarbonyltungsten to the final product **4** (Scheme 3).*cf.*[13–15]

The composition of complex **4** in solution was unambiguously deduced from NMR data.‡ The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR data of complex **4** are characteristic of four-membered phosphorus heterocycles such as 1,2-dihydro-1,2-diphosphetes.[2] For example, the carbon atom of the imine moiety



Scheme 3 Proposed reaction course for the formation of the 2,3-dihydro-1,2,3-azadiphosphete complex **4**.

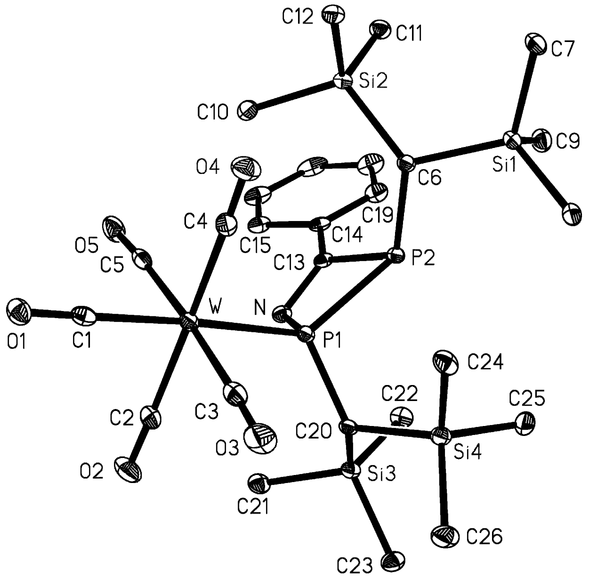


Fig. 1 Molecular structure of **4** in the crystal (thermal ellipsoids at 30% probability level; H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P(1)–P(2) 2.2577(8), P(2)–C(13) 1.846(2), C(13)–N 1.304(3), N–P(1) 1.7473(18), P(1)–W 2.5257(6); N–P(1)–P(2) 78.51(6), C(13)–P(2)–P(1) 69.92(7), N–C(13)–P(2) 107.80(15), C(13)–N–P(1) 101.26(14).

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† This work is dedicated to Dr Hans-Martin Schiebel on the occasion of his 70th birthday.

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shows a resonance (195.9 (dd, $|^{1}J(^{31}P,^{13}C)|$ = 33.6 Hz, $|^{1}J(^{31}P,^{13}C)|$ = 12.6 Hz). These data are also similar to those of PC(Ph)=N subunits in five-membered heterocycles, such as 2*H*-1,4,2-diazaphosphole in complexes.[16] The solid state structure of complex **4** was determined by single-crystal X-ray diffraction analysis (Fig. 1).§ The bis(trimethylsilyl)methyl groups adopt *trans* positions at the slightly folded four-membered ring (N–P(1)–P(2)–C(13) 8.9°), whereby the torsion angle for C(6)–P(2)–P(1)–C(20) was determined to be −136.9°.

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Notes and references

‡ Elemental analysis for complex **4**: calc: C 38.66, H 5.37, N 1.73; found: C 38.48, H 5.44, N 1.71. NMR data were recorded in $CDCl_3$ solutions (295 K) at 50.3 MHz (^{13}C) and 81.0 MHz (^{31}P), using TMS and 85% H_3PO_4 as standard references; *J*/Hz. Selected spectroscopic data for **4**: $^{13}C\{^{1}H\}$ NMR: δ 2.0 (s br, 2 × $SiMe_3$), 2.5 (s br, $SiMe_3$), 3.3 (d, $^{3}J(P,C)$ = 2.1 Hz, $SiMe_3$), 14.7 (dd, $J(P,C)$ = 64.0 Hz, $J(P,C)$ = 17.8 Hz, $CH(SiMe_3)_2$), 32.6 (dd, $J(P,C)$ = 11.5 Hz, $J(P,C)$ = 6.6 Hz, $CH(SiMe_3)_2$), 127.2 (d, $J(P,C)$ = 2.8 Hz, C_{arom}), 128.2 (d, $J(P,C)$ = 3.5 Hz, C_{arom}), 128.5 (s, C_{arom}), 128.7 (s, C_{arom}), 132.2 (m, C_{arom}), 138.1 (dd, $J(P,C)$ = 20.9 Hz, $J(P,C)$ = 24.9 Hz, C_{arom}), 195.9 (dd, $J(P,C)$ = 33.6 Hz, $J(P,C)$ = 12.6 Hz, P*C*NP), 197.8 (dd, $J(P,C)$ = 8.6 Hz, $J(P,C)$ = 2.2 Hz, *cis*-*C*O), 199.6 (d, $J(P,C)$ = 24.6 Hz, *trans*-*C*O). $^{31}P\{^{1}H\}$ NM: δ 78.7 (d, $^{1+3}J(P,P)$ = 91.3 Hz, $^{3}J(W,P)$ = 3.0 Hz), 79.8 (d, $^{1}J(W,P)$ = 251.7 Hz).

§ Crystal structure determination of **4**, $C_{26}H_{43}NO_5P_2Si_4W$. *Crystal data*: Monoclinic, space group $P2_1/n$, a = 14.7253(8), b = 13.0428(8), c = 18.8621(12) Å, β = 97.072(4)°, U = 3595.1 Å^3, Z = 4, T = −140 °C. *Data collection*: a crystal *ca*. 0.14 × 0.13 × 0.08 mm was used to register 73721 intensities (Mo-Kα radiation, $2\theta_{max}$ 60°) on a 'Bruker SMART 1000 CCD' diffractometer. An absorption correction was performed with SADABS. *Structure refinement*: the structure was refined anisotropically against F^2 (program SHELXL-97[17]) to *wR*2 0.045, *R*1 0.022 for 364 parameters, 59 restraints (to displacement parameters of the light atoms) and 10522 independent reflections. Hydrogen atoms were included using a riding model or rigid methyl groups. CCDC 188876. See http://www.rsc.org/suppdata/cc/b2/b206233j/ for crystallographic files in CIF or other electronic format.

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