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### SYNTHESES, STRUCTURES AND REACTIONS OF NEW AND NOVEL FOUR-, FIVE AND SIX-MEMBERED UNSATURATED N,P-HETEROCYCLE COMPLEXES

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## SYNTHESES, STRUCTURES AND REACTIONS OF NEW AND NOVEL FOUR-, FIVE- AND SIX-MEMBERED UNSATURATED N,P-HETEROCYCLE COMPLEXES

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*Metal-assisted heterocyclic ligand syntheses are reported using 2H-azaphosphirene complex 1 or 7-phosphanorbornadiene complex 7 as starting material. Thermal decomposition of complex 1 led to 1,2-dihydro-1,2,3-azadiphosphete complex 2, which was transformed into 2,6-dihydro-1,3,2,6-diazadiphosphinines 5a,b via ring expansion with carbonitriles 3a,b. Insertion of tert-butyl isonitrile into the P–P bond of 2 at ambient temperature furnished the first  $\Delta^1$ -1,3,5-azadi-phospholene complex 6; attempts to insert a phosphinidene fragment into the P–P bond of 2 using 7 failed. The 1,2,3,4-azatriphospholene complexes 9a,b were obtained by thermolysis of complex 2 in the presence of functionalized carbonitriles 8a,b.*

**Keywords:** 2H-azaphosphirenes; azadiphospholene; azatriphospholene

During the last years, we developed the synthesis of novel 3<sup>1</sup> and 5-membered<sup>2</sup> unsaturated N,P-heterocycle complexes, using new metal-assisted reactions and 2H-azaphosphirene complexes as starting material. Because of our interest to broaden the chemistry of nitrilium phosphanylide complexes [R'CNP(R)M(CO)<sub>5</sub>],<sup>3</sup> a reactive intermediate in the former reactions, we started to investigate the use of 7-phosphanorbornadiene complexes in related reactions.<sup>4</sup>

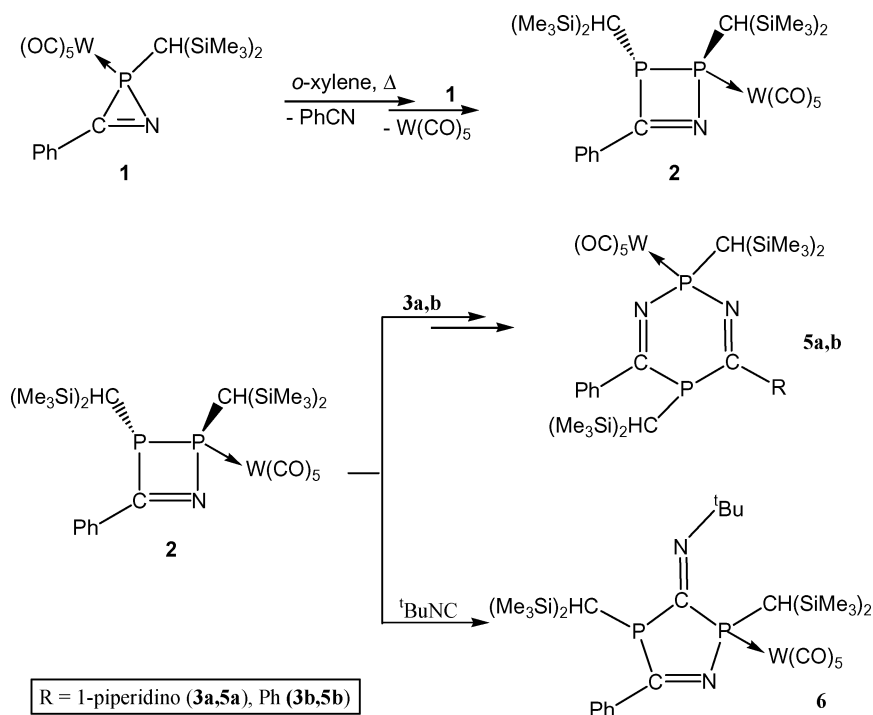
## RESULTS

Thermal decomposition of 2H-azaphosphirene complex 1 led to 1,2-dihydro-1,2,3-diphosphete complex 2—most probably via insertion of a

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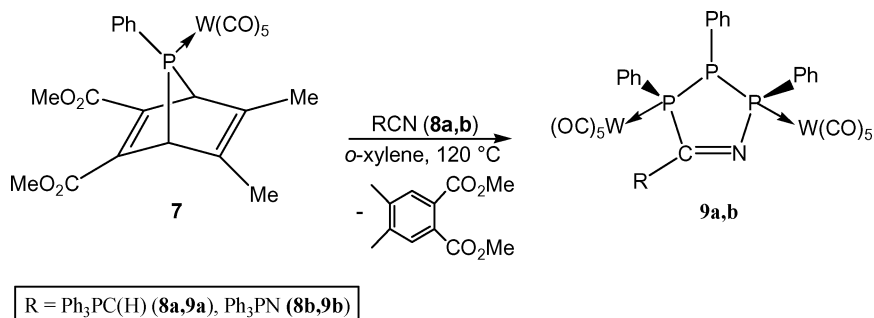
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phosphinidene complex into the P–N bond of **1**<sup>5</sup>—which could be transformed into 2,6-dihydro-1,3,2,6-diazadiphosphinines **5a,b** at 120°C in *o*-xylene via ring expansion using 1-piperidino nitrile and benzo-nitrile (**3a,b**) in 30% (**5a**) and 90% (**5b**) yield.<sup>6</sup> <sup>31</sup>P NMR reaction monitoring revealed that these reactions proceed via the intermediate formation of the dinuclear 2-aza-1,4-diphosphabutadiene complex **4**, which reacted in regioselective [4+2]-cycloaddition reactions with carbonitriles **3a,b** to afford **5a**<sup>7</sup> and **5b**<sup>6</sup> (Scheme 1). Surprisingly facile insertion of *tert*-butyl isonitrile into the P–P bond of **2** occurred at ambient temperature, thus furnishing the first  $\Delta^1$ -1,3,5-azadiphos-pholene complex **6** ( $\delta^{31}\text{P} = 99.0$  and  $-9.0$  (broad)) (Scheme 1).<sup>6</sup>



SCHEME 1

Attempts to insert a phosphinidene fragment into the P–P bond of **2** using the thermal decomposition of 7-phosphanorbornadiene complex **7** in toluene at 120°C failed; we also tried to use the Cu(I)Cl-catalyzed decomposition of complex **7** at 65°C in the presence of complex **2** but this also did not work. This is somehow surprising because we easily obtained the 1,2,3,4-azatriphosholene complexes



## SCHEME 2

**9a**<sup>8</sup> and **9b**<sup>9</sup> via thermolysis of complex **7** in the presence of the functionalized carbo-nitriles  $\text{Ph}_3\text{P}=\text{C(H)CN}$  (**8a**) and  $\text{Ph}_3\text{P}=\text{NCN}$  (**8b**) (Scheme 2). Whereas in the case of **8a** diastereomeric atropisomeric C–H insertion products were formed additionally,<sup>8</sup> reaction with **8b** proceeded very selective to **9b**. Complexes **9a,b** show both first-order <sup>31</sup>P NMR spectra—for example **9a**:  $-38.9$  ( $^1J(\text{P,P}) = 285.2$  and  $241.8$  Hz,  $\text{PP(Ph)P}$ ),  $13.9$  ( $^4J(\text{P,P}) = 50.5$  Hz,  $\text{Ph}_3\text{P}$ ),  $59.2$  ( $^1J(\text{P,P}) = 285.2$ ,  $^4J(\text{P,P}) = 50.5$ ,  $^3J(\text{P,P}) = 10.9$ ,  $^1J(\text{W,P}) = 284.1$  Hz,  $\text{NP(Ph)W}$ ) and  $107.1$  ( $^1J(\text{P,P}) = 241.8$ ,  $^3J(\text{P,P}) = 10.9$ ,  $^1J(\text{W,P}) = 279.2$  Hz,  $\text{CP(Ph)W}$ ).

We currently are investigating the scope of the ring expansion reactions of complex **2**.

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