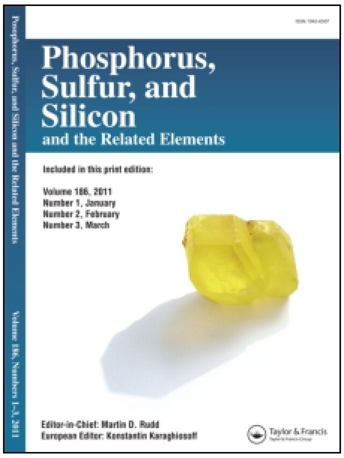

**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
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# SYNTHESES, STRUCTURES AND REACTIONS OF NEW AND NOVEL FOUR-, FIVEAND SIX-MEMBERED UNSATURATED N,P-HETEROCYCLE COMPLEXES

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**To cite this Article** Streubel, Rainer , Ionescu, Emanuel and Hoffmann, Nils(2004) 'SYNTHESES, STRUCTURES AND REACTIONS OF NEW AND NOVEL FOUR-, FIVEAND SIX-MEMBERED UNSATURATED N,P-HETEROCYCLE COMPLEXES', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 4, 809 — 811

**To link to this Article: DOI:** 10.1080/10426500490427196

**URL:** http://dx.doi.org/10.1080/10426500490427196

*Phosphorus, Sulfur, and Silicon*, 179:809–811, 2004
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490427196

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

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(Received August 21, 2003; accepted October 3, 2003)

*Metal-assisted heterocyclic ligand syntheses are reported using 2*H-*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-azadiphospholene 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:* 2*H*-azaphosphirenes; azadiphospholene; azatriphospholene

During the last years, we developed the synthesis of novel 3-[1] and 5-membered[2] unsaturated N,P-heterocycle complexes, using new metal-assisted reactions and 2*H*-azaphosphirene complexes as starting material. Because of our interest to broaden the chemistry of nitrilium phosphanylide complexes [$R'CNP(R)M(CO)_5$],[3] a reactive intermediate in the former reactions, we started to investigate the use of 7-phosphanorbornadiene complexes in related reactions.[4]

## RESULTS

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

We are grateful to the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for financial support.

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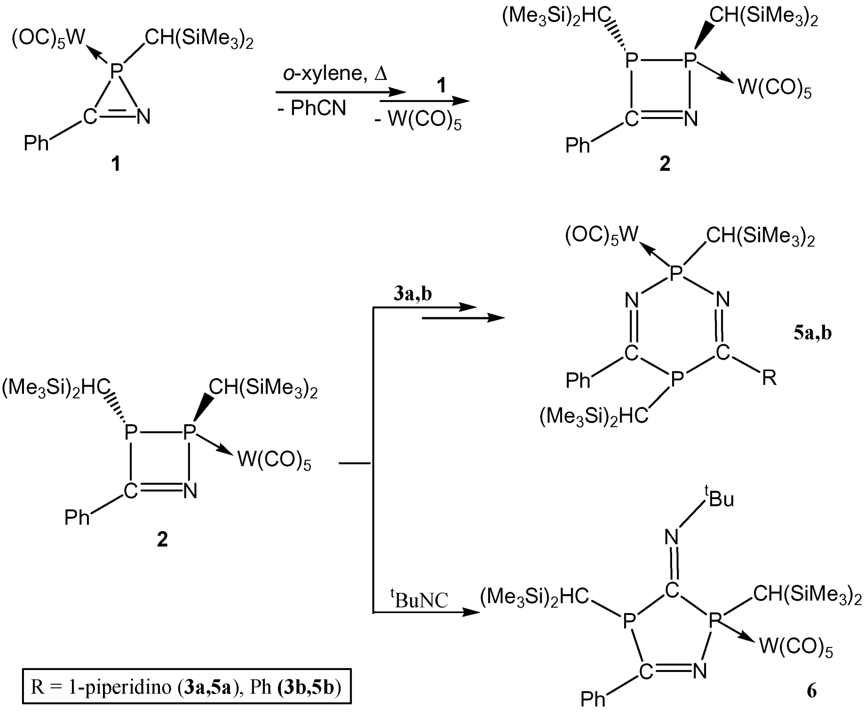
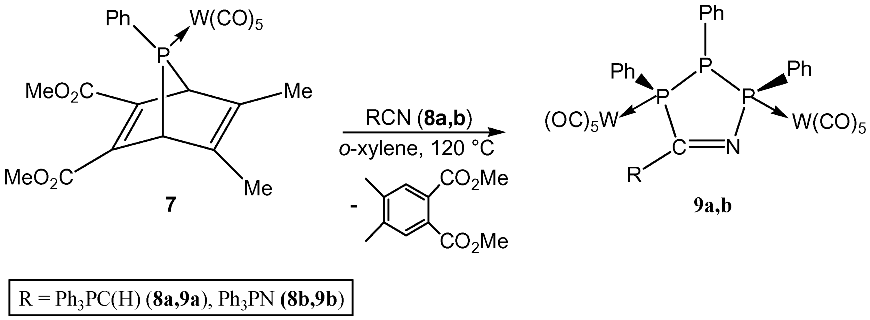
phosphinidene complex into the P—N bond of **1**[5]—which could be transformed into 2,6-dihydro-1,3,2,6-diazadiphosphinines **5a**,**b** at 120°C in *o*-xylene via ring expansion using 1-piperidino nitrile and benzo-nitrile (**3a**,**b**) in 30% (**5a**) and 90% (**5b**) yield.[6] $^{31}$P NMR reaction 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**[7] and **5b**[6] (Scheme 1). Surprisingly facile insertion of *tert*-butyl isonitrile into the P—P bond of **2** occured at ambient temperature, thus furnishing the first $\Delta^1$-1,3,5-azadiphos-pholene complex **6** ($\delta^{31}$P = 99.0 and −9.0 (broad)) (Scheme 1).[6]



**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-azatriphospholene complexes



**SCHEME 2**

**9a**[8] and **9b**[9] via thermolysis of complex **7** in the presence of the functionalized carbo-nitriles $Ph_3P{=}C(H)CN$ (**8a**) and $Ph_3P{=}NCN$ (**8b**) (Scheme 2). Whereas in the case of **8a** diastereomeric atropisomeric C—H insertion products were formed additionally,[8] reaction with **8b** proceeded very selective to **9b**. Complexes **9a**,**b** show both first-order $^{31}$P NMR spectra—for example **9a**: −38.9 ($^{1}J(P,P) = 285.2$ and 241.8 Hz, $PP(Ph)P$), 13.9 ($^{4}J(P,P) = 50.5$ Hz, $Ph_3P$), 59.2 ($^{1}J(P,P) = 285.2$, $^{4}J(P,P) = 50.5$, $^{3}J(P,P) = 10.9$, $^{1}J(W,P) = 284.1$ Hz, $NP(Ph)W$) and 107.1 ($^{1}J(P,P) = 241.8$, $^{3}J(P,P) = 10.9$, $^{1}J(W,P) = 279.2$ Hz, $CP(Ph)W$).

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

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