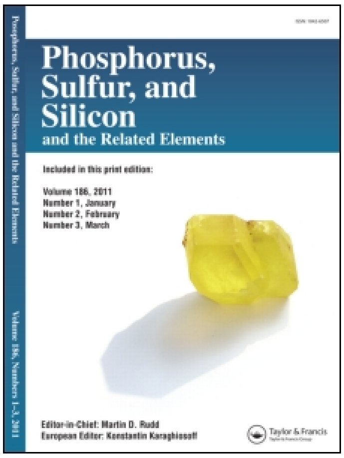

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Catalytic Reactions in Heterophosphole Complex Chemistry

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CATALYTIC REACTIONS IN HETEROPHOSPHOLE COMPLEX CHEMISTRY

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Catalytic reaction of 2H-*azaphosphirene complex* ***1*** *with* ortho-, meta-, *and* para-*benzodinitrile* (***2a–c***) *led in all cases to the* 2H-*1,4,2-diazaphosphole complexes* ***3a–c*** *if ferrocenium hexafluorophosphate was used as catalyst. In the case of the* meta- *and* para-*benzodinitriles* ***2b–c****, the bis-*2H-*1,4,2-diazaphosphole complexes* ***4b–c*** *were additionally obtained. Under the same reaction conditions, acetone, diethylketone and cyclohexanone* (***5a–c***) *reacted with complex* ***1*** *to yield* Δ^3-*1,3,2-oxazaphospholene complexes* ***6a–c*** *in good yields.*

Keywords: 2*H*-azaphosphirenes; diazaphospholes; oxazaphospholenes; radical cations; ring expansions; tungsten

We have demonstrated the widespread applicability of 2*H*-azaphosphirene complexes[1] in heterocyclic ligand synthesis using their precursor potential for electrophilic terminal phosphanediyl complexes $[RPM(CO)_5]$ and nitrilium phosphanylid complexes $[R'CNP(R)M(CO)_5]$, whereby conversion between these two reactive intermediates is easily achieved.[2] Recently, we observed that 2*H*-azaphosphirene complexes undergo P—N bond-selective ring expansion reactions, which do not proceed via the aforementioned intermediates and which have to be induced by catalytical amounts of typical one-electron oxidants such as tetracyanoethylene[3] or ferrocenium hexafluorophosphate.[4]

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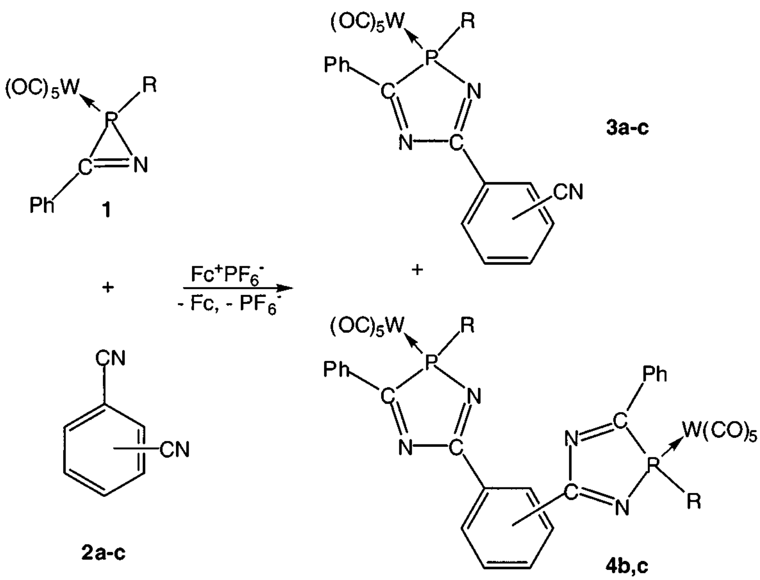
RESULTS

Reaction of $2H$-azaphosphirene complex **1** with the benzodinitriles **2a–c** in the presence of 0.2 equivalents ferrocenium hexafluorophosphate yielded both the mono- and bis-$2H$-1,4,2-diazaphosphole complexes **3a–c** and **4b–c**. The product ratio was in all cases in favor of **4b–c** (2:1) (Figure 1). The formation of complex **4a** was not observed; most probably, its formation was unfavorable for steric reasons. In all reactions, ferrocene was isolated in about 10% yield. Although the PF_6^- anion was unambigously identified by its ^{31}P data, the cation was not. Because of the need for $FcPF_6$ in these reactions, we propose that the ring expansion reaction proceeds via electron transfer catalysis, which, to the best of our knowledge, would be unprecedented in the chemistry of phosphorus heterocycles. Complexes **3a–c** and **4b–c** have ^{31}P resonances in the range of 111.5 to 114.5 ppm with ^{1}J(W,P) values of ~231 Hz for the mono- and 228 Hz for the bis-insertion products. Although the ^{13}C-NMR chemical shifts of the C^5 atom resonances of the diazaphosphole rings were observed at ~168 ppm, the C^3 atoms showed shifts at ~197 ppm, thus being significantly more deshielded [cf. 3].



R = $CH(SiMe_3)_2$; $Fc^+ = (C_5H_5)_2Fe(III)$; $Fc = (C_5H_5)_2Fe(II)$

FIGURE 1

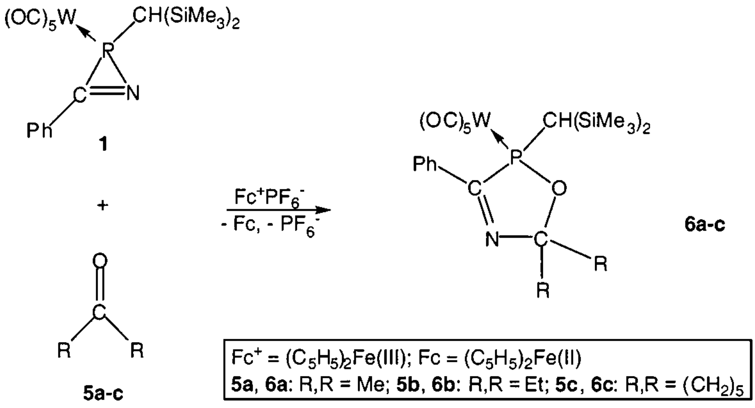


FIGURE 2

We also reacted complex **1**, under the same reaction conditions, with acetone, diethylketone, and cyclohexanone (**5a–c**) and obtained Δ^3-1,3,2-oxazaphospholene complexes **6a–c** after column chromatography in good yields (Figure 2). Remarkably, the reaction time increased with the increasing sterical demands of the substitutents at the keto function. This yields further evidence for the assumption that radical cations, formed initially, have an intact 2*H*-azaphosphirene ring system, which, initiated by a nucleophilic attack at the phosphorus, then selectively expands at the P—N bond to give five-membered rings.

Complexes **6a–c** show ^{31}P resonances in the range of 134 to 137 ppm with ^1J(W,P) values of ~277 Hz.

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