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

We have demonstrated the widespread applicability of 2*H*-azaphosphirene complexes¹ 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 tetracyanoethylene³ or ferrocenium hexafluorophosphate.⁴

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RESULTS

Reaction of 2*H*-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 PF₆⁻ anion was unambigously identified by its ³¹P data, the cation was not. Because of the need for FcPF₆ 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 ³¹P resonances in the range of 111.5 to 114.5 ppm with ${}^{1}J(W,P)$ values of \sim 231 Hz for the mono- and 228 Hz for the bis-insertion products. Although the ¹³C-NMR chemical shifts of the C⁵ 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

$$(OC)_{5}W CH(SiMe_{3})_{2}$$

$$PH 1 (OC)_{5}W CH(SiMe_{3})_{2}$$

$$+ \frac{Fc^{+}PF_{6}^{-}}{-Fc, -PF_{6}^{-}} R$$

$$Fc^{+} = (C_{5}H_{5})_{2}Fe(III); Fc = (C_{5}H_{5})_{2}Fe(II)$$

$$5a, 6a: R, R = Me; 5b, 6b: R, R = Et; 5c, 6c: R, R = (CH_{2})_{5}$$

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 2H-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 $^{1}J(W,P)$ values of \sim 277 Hz.

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