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A New Route to a 2-Phosphanaphthalene

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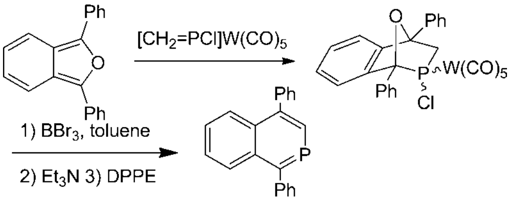
ABSTRACT

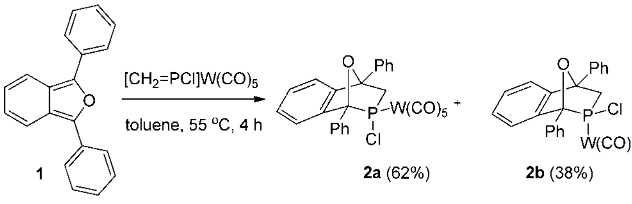


The reaction between methylenechlorophosphine-pentacarbonyltungsten and an isobenzofuran affords a [4 + 2] adduct whose oxygen bridge is broken by BBr_3, leading to a 2-phosphanaphthalene.

Despite their simplicity, only a very limited amount of data are available in the literature on 2-phosphanaphthalenes (isophosphinolines). The first synthesis of these species was reported in 1973 by Bickelhaupt[1] and relied on a lengthy series of steps starting from acyclic precursors. The second, shorter route relied on the ring expansion of phosphindoles by acid chlorides.[2] More recently, Regitz unveiled a third route starting from phosphaalkynes and giving bifunctional derivatives.[3] The complexity of these various approaches explains why the known chemistry of these derivatives is essentially limited to a few cycloaddition reactions.[3,4]

Recently, we reported the conversion of furan into 2-hydroxyphosphinine[5] by [4 + 2] cycloaddition with $[CH_2{=}PCl]W(CO)_5$.[6] We were curious to see whether this transformation could be applied to isobenzofurans and give a simple access to 2-phosphanaphthalenes. Accordingly, we allowed the methylenechlorophosphine tungsten complex to react with isobenzofuran (**1**)[7] and observed the quantitative formation of the [4 + 2] cycloadducts (**2a**) and (**2b**) (Scheme 1). Both structures were checked by X-ray analysis. As expected, the cycloadduct (**2a**) with the bulky tungsten complexing group in the *exo* position is the major isomer.

Scheme 1. Cycloaddition of Methylenechlorophosphine-Pentacarbonyltungsten and Benzofuran



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(8) **3**: ^{31}P NMR: ($CDCl_3$): δ 183.8; ^{1}H NMR ($CDCl_3$): δ 7.46–7.56 (m, 12H, C*H*), 7.87–7.89 (m, 1H, C*H*), 7.96–7.98 (m, 1H, C*H*), 8.32 (d, $^{2}J_{HP}$ = 39.6 Hz, 1H, P=C*H*); ^{13}C NMR ($CDCl_3$): δ 125.55 (d, J_{CP} = 9.6 Hz, =CH), 126.80 (d, J_{CP} = 5.7 Hz, =CH), 127.01 (d, J_{CP} = 3.9 Hz, =CH), 127.55 (2s, =CH), 128.22 (s, =CH), 128.33 (s, =CH), 129.16 (d, J_{CP} = 4.5 Hz, =CH), 129.66 (s, =CH), 130.37 (d, J_{CP} = 10.9 Hz, =CH), 133.19 (d, J_{CP} = 10.1 Hz, =C), 135.97 (d, J_{CP} = 11.0 Hz, =C), 142.64 (d, J_{CP} = 24.8 Hz, =C), 142.93 (d, J_{CP} = 3.6 Hz, =C), 143.41 (d, $^{1}J_{CP}$ = 53.8 Hz, P=CH), 147.44 (d, HRMS *m*/*z* 299.0986 (calcd for $C_{21}H_{16}P$: 299.0990). **5**: ^{31}P NMR: ($CDCl_3$): δ 22.5; ^{1}H NMR ($CDCl_3$): δ 1.64 (s, 3H, C*H₃*), 1.76 (s, 3H, C*H₃*), 2.25–2.41 (m, 2H, C*H₂*), 2.76–2.83 (m, 1H, C*H₂*), 3.21 (pseudo t, $^{2}J_{PH}$ = $^{2}J_{HH}$ = 18.3 Hz, 1H, C*H₂*), 6.32 (d, $^{2}J_{PH}$ = 15.6 Hz, 1H, =C*H*), 7.12–7.47 (m, 14H, Ph); ^{13}C NMR ($CDCl_3$): δ 19.87 (s, CH_3), 21.74 (d, J_{CP} = 12.4 Hz, CH_3), 30.60 (d, $^{1}J_{CP}$ = 69.6 Hz, P—CH_2), 46.12 (s, CH_2), 47.13 (d, $^{1}J_{CP}$ = 63.0 Hz, P—C), 118.20 (d, $^{1}J_{CP}$ = 90.6 Hz, P—CH=), 121.30 (d, $^{2}J_{CP}$ = 5.7 Hz, =C), 127.14 (s, =CH), 127.41 (s, =CH), 127.86 (d, J_{CP} = 9.5 Hz, =C), 128.19 (s, =CH), 128.32 (d, J_{CP} = 5.7 Hz, =CH), 128.54 (s, =CH), 128.62 (s, =CH), 128.79 (s, =CH), 129.67 (s, =CH), 129.82 (d, J_{CP} = 3.8 Hz, =CH), 131.06 (s, =CH), 133.80 (d, J_{CP} = 14.3 Hz, =C), 137.10 (d, J_{CP} = 5.7 Hz, =C), 141.19 (d, J_{CP} = 14.3 Hz, =C), 141.88 (d, J_{CP} = 5.7 Hz, =C), 155.34 (s, =C). HRMS *m*/*z* 395.1549 (calcd for $C_{27}H_{24}OP$: 395.1565).

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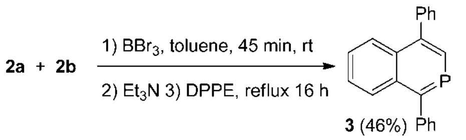
Scheme 2. Conversion of the [4 + 2] Cycloadducts into Phosphanaphthalene



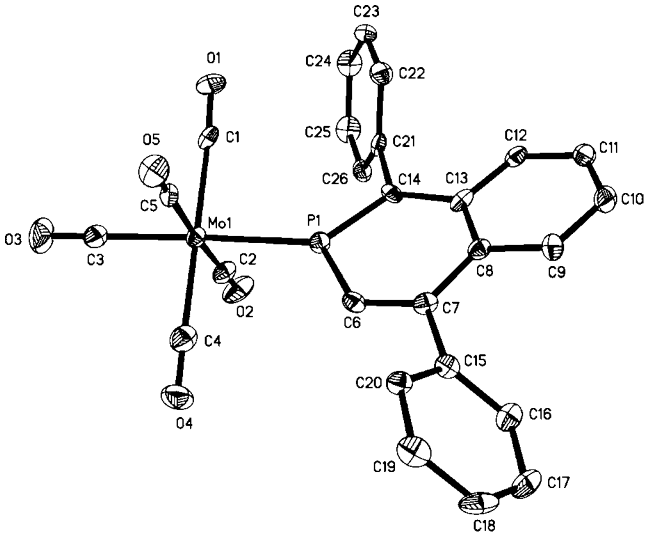
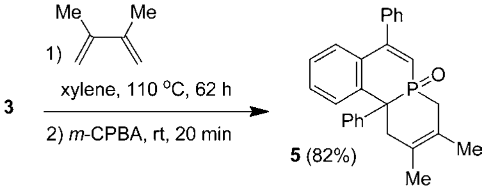


Figure 1. X-ray structure of **4**.

Upon reaction with boron tribromide in the cold, the oxygen bridge of **2a,b** is cleaved, and upon further treatment in situ with triethylamine and 1,2-bis(diphenylphosphino)-ethane in boiling toluene overnight, the phosphanaphthalene (**3**) is directly obtained (Scheme 2). It was purified by chromatography on silica gel at −6 °C (to avoid P-oxidation) with hexane/CH_2Cl_2 5:1 as the eluent and obtained as a yellow solid in 46% yield. The loss of oxygen and tungsten probably occurs during the second part of the reaction. Phosphanaphthalene (**3**) was characterized by NMR and HRMS.[8] The ^{31}P resonance is close to that observed for other phosphanaphthalenes.[1−3] In order to further confirm its structure, it was converted into its $Mo(CO)_5$ complex ($Mo(CO)_6$, toluene, 90 °C, 5 h) and the resulting P−$Mo(CO)_5$ complex (**4**) was characterized by X-ray crystal structure analysis (Figure 1).

Scheme 3. Reaction of **3** with Dimethylbutadiene



As expected the phosphanaphthalene nucleus is planar. The planes of the two phenyl substituents make angles of 65.5° (C14) and 50.0° (C7) with this central plane. The two P−C bonds are almost equal at 1.710(7) (P1−C14) and 1.734(8) Å. This observation contrasts with the computed data for the parent phosphanaphthalene (1.721 and 1.771 Å).[9] The P1−C14 is more reactive than the P1−C6 bond as a dienophile in [2 + 4] cycloaddition reactions as shown by the reaction of **3** with 2,3-dimethylbutadiene (Scheme 3).

The same regioselectivity was already observed by Regitz.[3] With this relatively simple access to phosphanaphthalenes, we can consider that their chemistry is now open for deeper investigation.

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Supporting Information Available. Experimental section and X-ray data for **2a**, **2b**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.