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## 6-Methoxy-5-phosphaphenanthrene: A molecule with an unreactive P=C double bond

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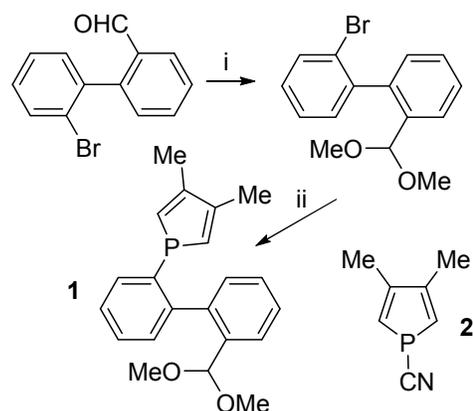
A multi-step synthesis of the title compound has been devised. In spite of its P=C double bond, the compound does not react at 100 °C with methanol and 2,3-dimethyl-1,3-butadiene. DFT calculations indicate a planar core, a long P=C double bond at 1.725 Å and a high-lying LUMO. Complexation can force the methoxy substituent to rotate out of the plane, thus restoring partly the double bond character of the P=C bond.

The 5-phosphaphenanthrenes are a highly interesting class of molecules displaying a well exposed P=C double bond and a planar core but their chemistry is almost unexplored, no doubt because of the difficulty of their synthesis. Seven steps were needed to synthesize the unstable parent species which was only characterised by UV spectroscopy and mass spectrometry<sup>1</sup>. Later, through another route, the P-W(CO)<sub>5</sub> complex was detected by <sup>31</sup>P NMR spectroscopy and some reactions of its P=C double bond were described<sup>2</sup>. Apart from this, the stable 6-phenyl derivative was obtained by two groups<sup>3,4</sup>, but no chemistry was reported. The previously published work on 2-phosphaphenol<sup>5,6</sup> showed that an alkoxy substituent on the carbon atom of the P=C double bond has a strong stabilizing effect on the phosphinine ring. On this basis, we thought that it would be interesting to synthesize and study the reactivity of a

6-alkoxy-5-phosphaphenanthrene.

This is the subject of this report.

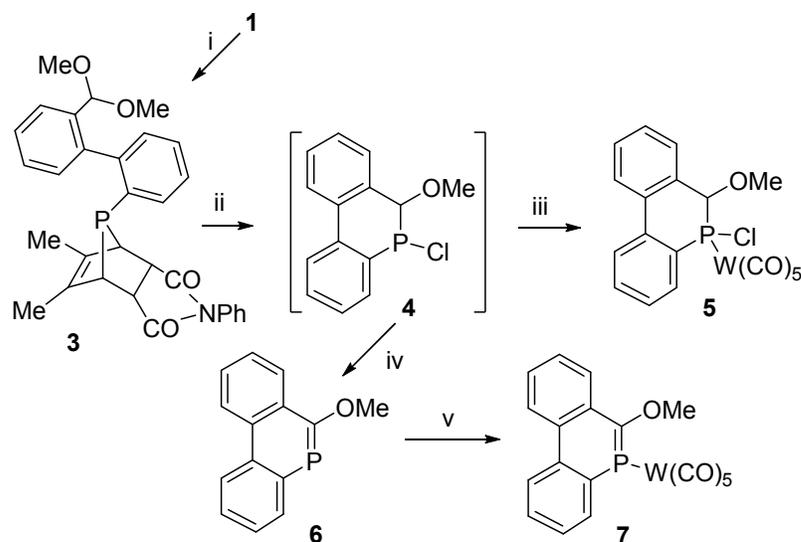
Our synthetic approach was inspired by a previous report<sup>7</sup> describing the cleavage of the RP bridge of a 7-phosphanorbornene by CBr<sub>4</sub>, leading to the dibromophosphine RPBr<sub>2</sub>. Accordingly, phosphole **1** was synthesized from 1-cyano-3,4-dimethylphosphole **2**<sup>8</sup> as shown in scheme (1).



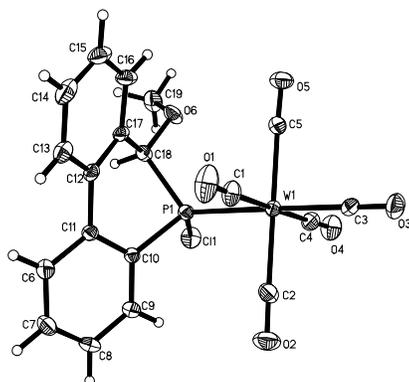
**Scheme 1** Reagents and conditions:

i, MeOH, NH<sub>4</sub>Cl, 80°C, 4 d; ii *n*-BuLi, THF, -78°C, then **2** from -78°C to r.t.

Phosphole **1** was then allowed to react with *N*-phenylmaleimide to give the 7-phosphanorbornene **3**, following a preceding work<sup>9</sup>. The reaction of **3** with oxalyl chloride then gave the cyclic chlorophosphine **4** (scheme 2) whose structure was established by X-ray crystal analysis of its P-W(CO)<sub>5</sub> complex **5** (fig. 1).



**Scheme 2** Reagents and conditions: i, *N*-phenylmaleimide, toluene, 100°C, 2 h; ii, (COCl)<sub>2</sub>, 2 eq., MeCN, r. t., 10 min.; iii, W(CO)<sub>5</sub>(MeCN), THF, 35 °C., 10 h.; iv, DABCO, 2 eq., MeCN, r. t., 30 min. 51% yield; v, W(CO)<sub>5</sub>(MeCN), THF, r. t., 15 h.

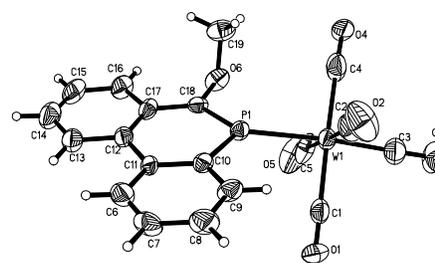


**Figure 1** X-ray crystal structure of complex **5**. Selected bond lengths (Å) and angles (°): P(1)-W(1) 2.451(1); P(1)-Cl(1) 2.068(2); P(1)-C(10) 1.809(5); P(1)-C(18) 1.845(5); C(11)-C(12) 1.485(7); C(10)-P(1)-C(18) 96.0(2).

The heterocyclic structure is highly distorted. The planes of the two arene rings make an angle of 25.17 deg. The synthesis of the title compound **6** was finally achieved by dehydrochlorination of **4** with 1,4-

diazabicyclo [2.2.2] octane (scheme 2).

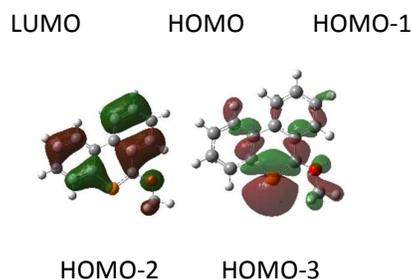
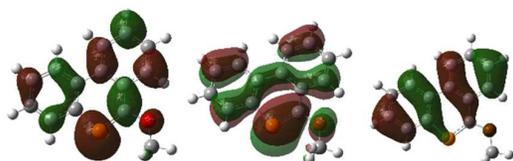
Phosphaphenanthrene **6** is characterized by a <sup>31</sup>P resonance at relatively high field ( $\delta^{31}\text{P}$  96.5 in CDCl<sub>3</sub>) and a <sup>13</sup>C resonance at very low field ( $\delta^{13}\text{C}$  197.56 in CDCl<sub>3</sub>, <sup>1</sup>J<sub>C=P</sub> = 38.5 Hz), in line with what is observed for phosphalkenes with inverse electron density<sup>10</sup>. The structure was confirmed by X-ray crystal analysis of the P-W(CO)<sub>5</sub> complex **7** (fig. 2).



**Figure 2** X-ray crystal structure of complex **7**. Selected bond lengths (Å) and angles (°): P(1)-W(1) 2.472(3); P(1)-C(10) 1.760(11); P(1)-C(18) 1.700(11); C(18)-O(6) 1.405(13); C(18)-C(17) 1.402(16); C(17)-C(12)

1.423(17); C(12)-C(11) 1.452(17);  
C(11)-C(10) 1.435(15); C(10)-P(1)-  
C(18) 103.2(6).

There are two identical molecules in the cell, whose parameters are given in the caption of fig. (2). The core of the molecule (excluding the methoxy substituent) is strictly planar. The two molecules in the cell are in a head to tail disposition and the distance between their planes is 3.61 Å. The P=C bond is normal at 1.700(11) Å. We immediately noticed that **6** is highly unreactive. No reaction was observed with methanol or 2,3-dimethyl-1,3-butadiene at 100°C in toluene, whereas the P-W(CO)<sub>5</sub> complex of the parent phosphaphenanthrene readily reacts with these reagents at room temperature<sup>2</sup>. In order to understand this lack of reactivity, we decided to compare the electronic structures of **6** and the parent 5-phosphaphenanthrene using DFT computations at the RB3LYP/6-311+G(d,p) level. The computed structure of **6** displays a P=C bond that is significantly longer (1.725 Å) than in the parent molecule (1.694 Å). The C-P-C intracyclic angle is 100.7 °. The OMe substituent is coplanar with the ring and directed toward phosphorus, in sharp contrast with **7** where the P-C-O-Me dihedral angle is 95.6 °. This situation allows a perfect overlap between the  $\pi$  lone pair at oxygen and the P=C  $\pi$  bond, thus increasing the polarization of the double bond. The most significant orbitals (Kohn Sham) of **6** are shown in figure (3).



**Figure 3** Main orbitals of **6**

As can be seen, the LUMO includes the  $\pi^*$  and the HOMO the  $\pi$  orbital of the P=C double bond and the phosphorus lone pair corresponds to HOMO-3. When compared to the orbitals of the parent compound, no drastic difference is observed, but all of the orbitals of **6** are shifted to higher energies. The most affected is the HOMO whose energy rises by 0.33 eV. In this respect, **6** resembles the phosphinines described by Müller<sup>11</sup> with significant  $\pi$ -donor properties. The LUMO also rises by 0.27 eV, thus explaining the low reactivity of **6** toward 2,3-dimethyl-1,3-butadiene and MeOH.

In order to check if the coplanarity of the methoxy substituent is the key factor in the low reactivity of the P=C bond, we also computed the structure of **6** with a fixed P-C-O-Me torsion angle of 90 °. The distorted structure lies 5.3 kcal mol<sup>-1</sup> higher in energy than the ground state. The P=C bond becomes shorter at 1.709 Å. The LUMO is shifted to lower energies by 0.27 eV and lies at the same level as that of the parent molecule. The HOMO is shifted by 0.19 eV. In other words, the rotation of the methoxy substituent out of the plane restores the normal characteristics of the P=C double bond.

This low reactivity and the planar structure of **6** are interesting

characteristics which suggest that **6** could be used to incorporate  $sp^2$  phosphorus into conjugated materials for optoelectronic applications. The use of **6** as a ligand in homogeneous catalysis can also be envisaged, although the complexation of phosphorus could induce the rotation of the methoxy substituent out of the plane and restore some reactivity of the P=C bond.

Electronic supplementary information (ESI) available: Full experimental details, X-ray data for **5** (CCDC 1026163) and **7** (CCDC 1025472) and XYZ files for **6** and 5-phosphaphenanthrene.

#### Acknowledgements

This work was supported by the National Natural Science Foundation (21272218), Specialized Research Fund for the Doctoral Program of Higher Education (20134101110004), Zhengzhou Science and Technology Department (131PYSGZ204), and Henan Science and Technology Department (No. 144300510011) of China.

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