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Communication

# The reaction of 2,5-diphenylphosphacymantrene with solid KOH in the presence of crown ethers: Synthesis of the anionic $\eta^4$ -phosphoryl manganese complexes

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#### ABSTRACT

2,5-Diphenylphosphacymantrene (1) reacts with solid KOH in the presence of crown ethers in  $C_6H_6$  or  $CH_2Cl_2$  at room temperature adding OH nucleophile to the phosphorus atom to afford anionic complexes  $[(CO)_3Mn-\eta^4-2,5-Ph_2H_2C_4P(=O)H]^-$  [K–Crown]<sup>+</sup>, where Crown = 18-crown-6 (2) or dicyclohexyl-18-crown-6 (3). Complexes 2 and 3 are characterized by <sup>1</sup>H, <sup>31</sup>P, <sup>13</sup>C NMR and IR-spectra. The structure of 2 is established by X-ray crystal structure data.

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## 1. Introduction

 $(n^{5}-Cyclopentadienyl)$ manganesetricarbonyl(cymantrene) is one of the most studied  $\pi$ -complexes of transition metals with carbonyl ligands (for the recent review see Ref. [1]). Replacement of one CH group in the ligand for a heteroatom changes the property of a compound greatly. Among this group of  $\pi$ -complexes phosphacymantrenes have been investigated mostly by group of Mathey [2-4]. According to quantum chemical calculations, the LUMOorbital in phosphacymantrenes is largely localized on the P atom and by this reason the nucleophilic attack could be expected to proceed on phosphorus atom [2,3]. Previously, it was established that  $\eta^5$ -3,4-dimethylphosphacymantrene (THF, -78 °C) when reacting with PhLi or t-BuLi could add Ph or t-Bu groups on phosphorus. From the <sup>31</sup>P NMR data it was proposed that unstable intermediates with  $\eta^4$ -type coordination of phospholyl ligand with Mn were formed [3,4]. Later we found that 2,5-diphenylphosphacymantrene (1) reacts with  $Na_2PdCl_4$  and NaOAc in ROH (R = Me, Et) to form P-alkoxyderivatives [5]. We were interested to investigate the addition of other nucleophilic reagents to that substrate. In this communication we report on the reaction of 1 with solid KOH in the presence of crown ethers.

## 2. Results and discussion

We found that in dichloromethane at room temperature 1 can react with solid KOH in the presence of 1 equiv. of a crown ether anionic salt-like complexes  $[(CO)_3Mn-\eta^4-2,5$ to form  $Ph_2H_2C_4P(=0)H]^-$  [K-Crown]<sup>+</sup>, where Crown = 18-crown-6 (2) or dicyclohexyl-18-crown-6 (3) (Scheme 1). In the absence of crown ether the reaction 1 with KOH proceeds as well according to <sup>31</sup>P NMR-spectra, however, single crystals were not obtained. The reaction has been monitored by <sup>31</sup>P NMR-spectra but we have not been able to detect any intermediate and registered only the transitions  $1 \rightarrow 2$  or 3. Probably the primary anionic intermediate is very unstable and quickly rearranges into the final anions  $2^-$  or  $3^-$  with the migration of H from oxygen to phosphorus, counter ion being K<sup>+</sup> complexed to crown ether. Similar rearrangements of the unstable compounds of the type  $R_2P(OH)$  (R = alkyl, aryl) into the stable four-coordinated compounds R<sub>2</sub>P(=O)H are well-known in organophosphorus chemistry [6,7].

Complexes **2** and **3** are solids stable in inert atmosphere and characterized by IR, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR-spectra. Formation of them is accompanied by the sharp changes in <sup>31</sup>P NMR-spectra: instead of a singlet, at -30.6 ppm (**1**), a doublet centered between 0 and 1 ppm arises with a great <sup>1</sup>*J*(H–P) = 516 or 521 Hz for **2** or **3** which evidences the direct P–H bond.

The crystal structure of  ${\bf 2}$  is established by X-ray data. It is the salt composed of the  $[(CO)_3Mn-\eta^4-2,5-Ph_2H_2C_4P]^-$  anion and

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Scheme 1.

cation  $K^+$  coordinated by six oxygen atoms of the crown ether (Fig. 1).

The bond length P(1)=O(1P) 1.492(2) Å in **2** is almost equal to the bond length P=O in the triphenylphosphinoxide (1.482 Å). In crystal, both cation and anion are situated in general position. In anion  $2^{-}$  five-membered cycle C<sub>4</sub>P is in the "envelope" conformation, P atom is going out from the plane C(1)-C(2)-C(3)-C(4) by 0.675 Å to the site opposite to the manganese atom. Distance Mn(1)-P(1) 2.8081(7) Å exceeds considerably the sum of covalent radii Mn (1.35 Å) and P (1.13 Å) [8]. The distance Mn(1)–P(1) in 2 is greatly elongated as compared to the bond lengths (Mn)-(P) (2.368–2.422 Å) in the complexes with  $\eta^5$ -phosphoryl ligand such as the ketone  $\eta^5$ -2-benzoyl-3,4-dimethylphosphacymantrene [9]  $(2.387(2) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5 [10] (2.376(3) \text{ Å}); \text{ complex } (1) \rightarrow W(CO)_5$  $(CO)_{2}(L)Mn-\eta^{5}-3,4-Me_{2}-2-CHO-C_{4}HP,$ where  $L = PPh_3$ [11] (2.420(1) Å). In these complexes P atom is going out from the plane C(1)-C(4) no more than 0.048–0.050 Å, but in anion  $2^-$  this distance is 0.675 Å. From these data it may be concluded that bond Mn–P in **2** is absent or very weak, and phosphoryl ligand is  $\eta^4$ coordinated with Mn. Besides that, a small change in the C-C bond length in the five-membered ring is observed alternating as "longshort-long" that evidences the violation of the  $\eta^5$ -srtucture of that fragment. To our knowledge, complex 2 is the first anionic complex with  $\eta^4$ -coordinated to manganese phosphoryl ligand characterized by X-ray data. Earlier the highly relevant zwitterionic complex  $(CO)_3Mn^--\eta-3,4-Me_2H_2P^+(Ph)(CH_2CH_2CO_2Et)$  was described by Mathey and coworkers [3]. The noteworthy feature of this complex was "a relatively weak P-Mn interaction at 2.7651(8) Å". Crystal structure of the related zwitterion complex (CO)<sub>3</sub>Mn<sup>-</sup>-η<sup>4</sup>- $(CRCRCRCP^+Me_2)$  where R = CO<sub>2</sub>Me had been described by Lindner et al. [12], but this complex did not contain P-Mn bond.

It is important to emphasize that cation K<sup>+</sup> in crystal takes part in two more coordinative interactions, with O atom of a phosphoryl group [K(1)–O(1P) 2.618(2) Å] and with oxygen atom of a carbonyl group in a neighbor molecule [K(1)–O(1)<sub>x,0.5-y,-0.5+z</sub>



**Fig. 1.** Molecular structure and numbering scheme for compound **2**. Selected bond lengths (Å) and angles (°): Mn(1)–C(1) 2.172(3), Mn(1)–C(2) 2.084(3), Mn(1)–C(3) 2.078(3), Mn(1)–C(4) 2.155(3), Mn(1)–P(1) 2.8081(7), P(1)–O(1P) 1.492(2), P(1)–H(1P) 1.30(3), P(1)–C(1) 1.778(3), P(1)–C(4) 1.777(3), C(1)–C(2) 1.441(4), C(2)–C(3) 1.418(4), C(3)–C(4) 1.438(3), K(1)–O(1P) 2.618(2), K(1)–O(1)\_{x,0.5-y.-0.5+z} 2.772(2), K(1)–O(crown) 2.766(2)–2.859(2), C(1)–P(1)–C(4) 89.4(1), O(1P)–P(1)–H(1P) 110(1).



Fig. 2. Infinite chain in the crystal 2 formed due to the cation-anion K-O coordination bonds.

2.772(2) Å] to form the supramolecular structure as an infinite chain along the crystallographic axes *c* (Fig. 2). This probably points out to the strong delocalization of a negative charge in anion over all oxygen atoms in phosphinoxide and carbonyl groups. A relatively slight shift of v(CO) frequencies, 60 and 45 cm<sup>-1</sup> in **2** and **3** is also in accordance with a strong delocalization of negative charge (usually in anionic Mn complexes  $\Delta v(CO)$  is 80–100 cm<sup>-1</sup> or more).

# 3. Experimental

2,5-Diphenylphosphacymantrene (**1**) was prepared according to the procedure [13]. <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C NMR-spectra were registered using spectrometer Bruker–Avance 400 at 400.16 MHz for <sup>1</sup>H, 161.9 MHz for <sup>31</sup>P and 100.6 MHz for <sup>13</sup>C. Chemical shifts were measured relative TMS (<sup>1</sup>H, <sup>13</sup>C) or H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). Complexes **2** and **3** were obtained and handled under argon atmosphere.

## 3.1. Synthesis of complexes 2 (or 3)

Complex 2: 37.4 mg 1 (0.1 mmol) and 28 mg of 18-crown-6 (0.106 mmol) were dissolved in 3-4 ml CH<sub>2</sub>Cl<sub>2</sub>, one granule of solid KOH (56–60 mg,  $\sim$ 10-fold excess) was added and the mixture was shaken from time to time at room temperature in the dark. After  $\sim$ 24 h on monitoring <sup>31</sup>P NMR-spectra the starting compound **1** reacted to give 2 in quantitative yield. Excess of KOH was removed. To yellow solution 10 ml of pentane were added, the light-yellow crystals being formed. The crystals were washed twice with pentane and dried in vacuum. Yield 44 mg. Anal. Calc. for C<sub>31</sub>H<sub>37</sub>O<sub>10</sub>PKMn: C, 53.60; H, 5.37; P, 4.46. Found: C, 52.91; H, 5.33; P, 4.46%. Spectral data for **2**. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$ , ppm: 7.92  $(dt, 1H, {}^{1}J(H_{P}-P) = 516.0, {}^{4}J(H_{P}-H_{3.4}) = 2.3 \text{ Hz}, P(O)H); 7.40 (d,$ 4H), 7.18 (t, 4H), 6.99 (t, 2H), 10H, o, m, p C<sub>6</sub>H<sub>5</sub>; 5.37 [dd, 2H,  ${}^{3}J(H_{3,4}-P) = 13.7, {}^{4}J(H_{3,4}-H_{P}) = 2.3 \text{ Hz}, H(3,4)]; 3.47 (s, 24H, CH_{2} in)$ crown ether). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  0.95 ppm, dt, <sup>1</sup>J(P–H<sub>P</sub>) = 516.0, <sup>3</sup>*J*(P–H<sub>3,4</sub>) 13.7 Hz.

<sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>), *δ*, ppm: 228.8, Mn(CO)<sub>3</sub>; 140.9, key-C-atoms of C<sub>6</sub>H<sub>5</sub>; 128.2, 125.3, 124.0, C-atoms of *o*,*m*,*p*-positions of C<sub>6</sub>H<sub>5</sub>; 79.3, d,  $J({}^{13}C-{}^{31}P) = 17$  Hz, two C-atoms in β-positions to P; 70.2, C-atoms of crown ether; 66.7, d,  $J({}^{13}C-{}^{31}P) = 91$  Hz, two C-atoms in α-positions to P.

IR-spectra (CH<sub>2</sub>Cl<sub>2</sub>): v(CO) 1890 cm<sup>-1</sup> (broad, E-mode), 1980 cm<sup>-1</sup> (A<sub>1</sub>-mode). IR-spectra in the solid state (nujol): v(CO)1872 (E-mode), 1964 cm<sup>-1</sup> (A<sub>1</sub>-mode). For **1** (CH<sub>2</sub>Cl<sub>2</sub>): v(CO)1950 cm<sup>-1</sup> (broad, E-mode), 2025 cm<sup>-1</sup> (A<sub>1</sub>-mode).

Complex **3** prepared as described above from 25 mg **1** (0.067 mmol) and 25 mg of dicyclohexyl-18-crown-6 (0.067 mmol) in 2.5–3 ml CH<sub>2</sub>Cl<sub>2</sub>, yield  $\sim$ 30 mg.

Spectral data for **3**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ , ppm: 8.10 (dt, 1H, <sup>1</sup>*J*(H<sub>P</sub>-P) = 521.0, <sup>4</sup>*J*(H<sub>P</sub>-H<sub>3,4</sub>) = 2.2 Hz, PH); 7.39 (d, 4H), 7.13 (t, 4H), 6.94 (t, 2H), 10H, *o*, *m*, *p* C<sub>6</sub>H<sub>5</sub>; 5.32 (dd, <sup>3</sup>*J*(H<sub>3,4</sub>-P) = 13.6, <sup>4</sup>*J*(H<sub>3,4</sub>-H<sub>P</sub>) = 2.2 Hz (2H, protons H(3,4)). The protons of crown ether appear as two multiplets at 3.41 and 1.24. <sup>31</sup>P NMR-spectra:

0.20, dt,  ${}^{1}J(P-H_P)$  521.0,  ${}^{3}J(P-H_{3,4})$  = 13.6 Hz. IR-spectra (CH<sub>2</sub>Cl<sub>2</sub>): v(CO) 1890 and 1980 cm<sup>-1</sup>.

#### 3.2. X-ray crystal data for 2

The single crystals for X-ray study were obtained by slow diffusion of pentane into the benzene solution of **2** in NMR-tube.  $C_{31}H_{37}KO_{10}PMn$ , M = 694.62, monoclinic, space group  $P2_1/c$ , a = 20.372(1), b = 7.4744(5), c = 22.817(1)Å,  $\beta = 108.551(1)^\circ$ , V = 3293.8(4)Å<sup>3</sup>,  $D_{calc} = 1.401$  g/cm<sup>3</sup>, Z = 4,  $\mu = 0.630$  mm<sup>-1</sup>. Single-crystal X-ray diffraction experiment was carried out with a Bruker SMART 1000 CCD diffractometer [14] (graphite monochromated Mo K $\alpha$  radiation,  $\lambda = 0.71073$ Å,  $\omega$ -scan technique, T = 120 K). The H(1P) atom was localized from different Fourier synthesis and involved in refining in isotropic approximation. The refinement converged to  $wR_2 = 0.1247$  and GOF = 0.990 for all 7148 independent reflections [ $R_1 = 0.0520$  was calculated against *F* for 5710 observed reflections with  $I > 2\sigma(I)$ ], 401 refined parameters. The SHELXTL-97 program package [15] was used throughout the calculations; CCDC reference number 735789.

#### Supplementary material

CCDC 735789 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif.

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