



Communication

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

Vasily V. Bashilov, Allan G. Ginzburg*, Alexander F. Smol'yakov, Fedor M. Dolguschin, Pavel V. Petrovskii, Viatcheslav I. Sokolov

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28, Vavilov St., 119991 Moscow, Russian Federation

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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 $[(CO)_3Mn-\eta^4-2,5-Ph_2H_2C_4P(=O)H]^- [K-Crown]^+$, where Crown = 18-crown-6 (**2**) or dicyclohexyl-18-crown-6 (**3**). Complexes **2** and **3** are characterized by 1H , ^{31}P , ^{13}C NMR and IR-spectra. The structure of **2** is established by X-ray crystal structure data.

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1. Introduction

(η^5 -Cyclopentadienyl)manganesetricarbonyl(cymantrene) is one of the most studied π -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 π -complexes phosphacymantrenes have been investigated mostly by group of Mathey [2–4]. According to quantum chemical calculations, the LUMO-orbital 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 η^5 -3,4-dimethylphosphacymantrene (THF, $-78^\circ C$) when reacting with PhLi or t-BuLi could add Ph or t-Bu groups on phosphorus. From the ^{31}P NMR data it was proposed that unstable intermediates with η^4 -type coordination of phosphoryl 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 to form anionic salt-like complexes $[(CO)_3Mn-\eta^4-2,5-Ph_2H_2C_4P(=O)H]^- [K-Crown]^+$, 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 ^{31}P NMR-spectra, however, single crystals were not obtained. The reaction has been monitored by ^{31}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^+ 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 $R_2P(=O)H$ are well-known in organophosphorus chemistry [6,7].

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

The crystal structure of **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

* Corresponding author. Fax: +7 499 135 5058.

E-mail address: allan@ineos.ac.ru (A.G. Ginzburg).

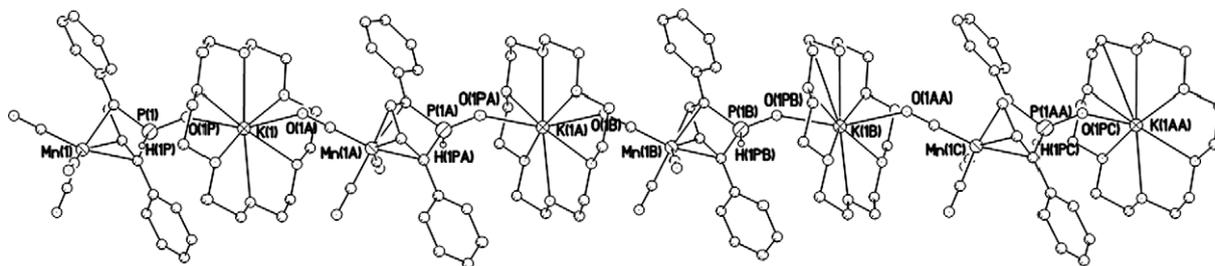


Fig. 2. Infinite chain in the crystal **2** formed due to the cation–anion K–O coordination bonds.

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 $\nu(\text{CO})$ frequencies, 60 and 45 cm^{-1} in **2** and **3** is also in accordance with a strong delocalization of negative charge (usually in anionic Mn complexes $\Delta\nu(\text{CO})$ is 80–100 cm^{-1} or more).

3. Experimental

2,5-Diphenylphosphacymantrene (**1**) was prepared according to the procedure [13]. ^1H , ^{31}P and ^{13}C NMR-spectra were registered using spectrometer Bruker–Avance 400 at 400.16 MHz for ^1H , 161.9 MHz for ^{31}P and 100.6 MHz for ^{13}C . Chemical shifts were measured relative TMS (^1H , ^{13}C) or H_3PO_4 (^{31}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_2Cl_2 , one granule of solid KOH (56–60 mg, ~10-fold excess) was added and the mixture was shaken from time to time at room temperature in the dark. After ~24 h on monitoring ^{31}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 $\text{C}_{31}\text{H}_{37}\text{O}_{10}\text{PKMn}$: C, 53.60; H, 5.37; P, 4.46. Found: C, 52.91; H, 5.33; P, 4.46%. Spectral data for **2**. ^1H NMR (CD_2Cl_2), δ , ppm: 7.92 (dt, 1H, $^1J(\text{H}_p\text{--P}) = 516.0$, $^4J(\text{H}_p\text{--H}_{3,4}) = 2.3$ Hz, P(O)H); 7.40 (d, 4H), 7.18 (t, 4H), 6.99 (t, 2H), 10H, *o*, *m*, *p* C_6H_5 ; 5.37 [dd, 2H, $^3J(\text{H}_{3,4}\text{--P}) = 13.7$, $^4J(\text{H}_{3,4}\text{--H}_p) = 2.3$ Hz, H(3,4)]; 3.47 (s, 24H, CH_2 in crown ether). ^{31}P NMR (CD_2Cl_2): δ 0.95 ppm, dt, $^1J(\text{P--H}_p) = 516.0$, $^3J(\text{P--H}_{3,4})$ 13.7 Hz.

^{13}C NMR (CD_2Cl_2), δ , ppm: 228.8, Mn(CO) $_3$; 140.9, key-C-atoms of C_6H_5 ; 128.2, 125.3, 124.0, C-atoms of *o,m,p*-positions of C_6H_5 ; 79.3, d, $J(^{13}\text{C}\text{--}^{31}\text{P}) = 17$ Hz, two C-atoms in β -positions to P; 70.2, C-atoms of crown ether; 66.7, d, $J(^{13}\text{C}\text{--}^{31}\text{P}) = 91$ Hz, two C-atoms in α -positions to P.

IR-spectra (CH_2Cl_2): $\nu(\text{CO})$ 1890 cm^{-1} (broad, E-mode), 1980 cm^{-1} (A_1 -mode). IR-spectra in the solid state (nujol): $\nu(\text{CO})$ 1872 (E-mode), 1964 cm^{-1} (A_1 -mode). For **1** (CH_2Cl_2): $\nu(\text{CO})$ 1950 cm^{-1} (broad, E-mode), 2025 cm^{-1} (A_1 -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_2Cl_2 , yield ~30 mg.

Spectral data for **3**: ^1H NMR (CDCl_3) δ , ppm: 8.10 (dt, 1H, $^1J(\text{H}_p\text{--P}) = 521.0$, $^4J(\text{H}_p\text{--H}_{3,4}) = 2.2$ Hz, PH); 7.39 (d, 4H), 7.13 (t, 4H), 6.94 (t, 2H), 10H, *o*, *m*, *p* C_6H_5 ; 5.32 (dd, $^3J(\text{H}_{3,4}\text{--P}) = 13.6$, $^4J(\text{H}_{3,4}\text{--H}_p) = 2.2$ Hz (2H, protons H(3,4)). The protons of crown ether appear as two multiplets at 3.41 and 1.24. ^{31}P NMR-spectra:

0.20, dt, $^1J(\text{P--H}_p) 521.0$, $^3J(\text{P--H}_{3,4}) = 13.6$ Hz. IR-spectra (CH_2Cl_2): $\nu(\text{CO})$ 1890 and 1980 cm^{-1} .

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. $\text{C}_{31}\text{H}_{37}\text{KO}_{10}\text{PMn}$, $M = 694.62$, 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 3 , $D_{\text{calc}} = 1.401$ g/cm 3 , $Z = 4$, $\mu = 0.630$ mm $^{-1}$. 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, ω -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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