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Synthesis of Metal Complexes of Polyalkylene(arylene) Phosphorous Amides

A. T. Teleshev, Van Te, V. Yu. Mishina, I. V. Abrashina, and E. E. Nifant'ev

Moscow Pedagogical State University,
Nesvizhskii per. 3, Moscow, 119021 Russia
e-mail: chemdept@mtu-net.ru

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Abstract—Reactions of phosphorous triamides with symmetrical diols in equimolar ratio were studied. These reactions result in formation of unique poly(oligo)amidophosphorous systems. The products obtained are used as ligands for the synthesis of metal complexes of a new type.

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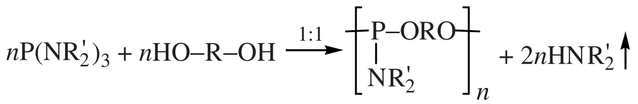
By now there has been much basic research on the chemistry of high-molecular compounds containing various P(V) functions [1–4]. At the same time, the works on analogous P(III) derivatives are few in number and often mutually contradictory [5–11]. It is significant that peculiar features inherent in compounds with phosphite, amidophosphite, and phosphonite groups have, as a rule, not been revealed.

Taking above into account, we focused on the synthesis of polyamidophosphite systems by the reaction of phosphorous triamides with glycols or diatomic phenols in an equimolar ratio. We considered this synthesis as the first part of a project devoted to the design and study of the catalytic properties of unique high-molecular systems. We expected to obtain substances combining features inherent in catalysts of different types. Actually, these compounds, being organosoluble metal complexes, could behave as known homogeneous catalysts. On the other hand, three-dimensional and cross-linked objects could prove organoinsoluble and corresponding to heterogeneous catalysts.

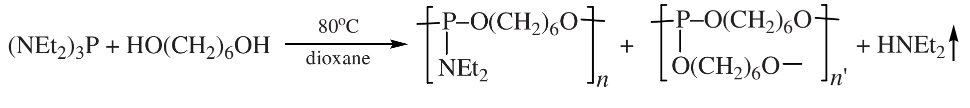
The first step of this work, which involved phosphorylation, showed that this process holds promise.



$$n\mathrm{P(NR'_2)_3} + n\mathrm{HO{-}R{-}OH} \xrightarrow{1:1} \left[\begin{array}{l}\mathrm{P{-}ORO}\\ \mid\\ \mathrm{NR'_2}\end{array}\right]_n + 2n\mathrm{HNR'_2}\uparrow$$

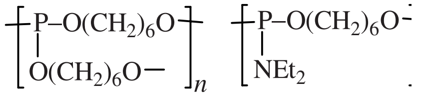
This reaction was carried out in dioxane under argon. The amine liberated in the reaction was gradually removed from the reaction medium. The process was monitored by a combination of TLC and ^{31}P NMR. After the reaction was complete, the solvent and residual amine were removed from the reaction flask. The process was performed by two alternative procedures. The first involved complete removal of volatile substances in a vacuum and afforded the target product partially modified by cross-linked molecules (form **A**). This form is represented by elastic granules no longer capable of dissolution. The second procedure involved mild distillation of the main part of volatile products in a vacuum and provides a soluble substance (form **B**). The product thus could be studied by ^{31}P NMR: Its chemical shift was 147 ppm, which corresponds to phosphorous amidodiesters.

The reaction is general in nature and can be carried out with both hexamethylphosphorous triamide and its ethyl homolog. Of aliphatic diols, hexamethylene-1,6-diol and decamethylene-1,10-diol were involved in the reaction and of aromatic diols, hydroquinone, 1,4-dihydroxydiphenyl and 2,2-bis(4-hydroxyphenyl)propane (DIAN).



$$\mathrm{(NEt_2)_3P} + \mathrm{HO(CH_2)_6OH} \xrightarrow[\text{dioxane}]{80^{\circ}\mathrm{C}} \left[\begin{array}{l}\mathrm{P{-}O(CH_2)_6O}\\ \mid\\ \mathrm{NEt_2}\end{array}\right]_n + \left[\begin{array}{l}\mathrm{P{-}O(CH_2)_6O}\\ \mid\\ \mathrm{O(CH_2)_6O{-}}\end{array}\right]_{n'} + \mathrm{HNEt_2}\uparrow$$

To characterize the resulting products, we studied their relative thermooxidative stability. The objects for study were samples **A** and **B** with the following principal structural fragments:



$$\left[\begin{array}{l} -P-O(CH_2)_6O- \\ \;\;| \\ \;O(CH_2)_6O- \end{array}\right]_n \qquad \left[\begin{array}{l} -P-O(CH_2)_6O- \\ \;\;| \\ \;NEt_2 \end{array}\right]$$

A **B**

The DTA curve of oligophosphite **B** initially shows a weak endothermic effect in the range 130–155°C with a slight weight loss due to liberation of residual volatile substances. Further heating leads to a well-defined exothermic effect in the range 280–315°C with a sharp weight loss which implies strong decomposition of the polymer.

The DTA curve of oligophosphite **A** shows initiation of a strong thermal decomposition in the temperature range 260–320°C; the observed effect is associated with the heat release attendant in the decomposition of a linear oligomer admixture. However, the observation of a peak in this temperature range can also attest continuation of chemical reactions in the solid bulk of the oligomer, such as, first, further disproportionation to form triester fragments (cross-linking of the polymer) is possible and, second, reactions involving the amido groups, specifically P–N bond cleavage with P–OH bond formation.

The most vigorous exothermic destruction of oligophosphite **A** with a sharp weight loss takes place in the temperature range 320–350°C.

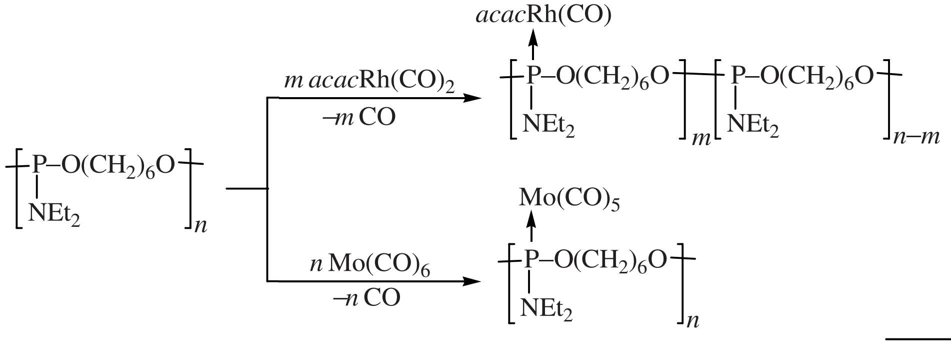
To verify the assignment the *exo* effects on the thermal decomposition of linear (**B**) and cross-linked (**A**) oligomers, we prepared their calibration mixture obtained from hexane-1,6-diol and hexamethylphosphorous triamiide in a 1.2:1.0 molar ratio. The ^{31}P NMR spectrum of the calibration mixture contained expected signals at 147 and 139 ppm with an intensity ratio of 1.2:1. The DTA curve of this sample showed exo effects in the corresponding ranges: 250–300°C and 300–340°C.

Thus, cross-linked oligomers proved to be thermally more stable than linear.

Analyzing the DTA results as a whole we can note that the polyamidophosphites and polyphosphites in hand decompose at relatively high temperatures. This characteristic makes these compounds useful candidates for various technologies demanding highly thermally stable polymers.

The second part of this investigation involved reactivity assessment of the obtained compounds in the **B** form**.** We found that these compounds are can be easily oxidized with di-*tert*-butyl peroxide and can take up sulfur.

We also studied the possibility of application of the obtained compounds as ligands for immobilized metal complexes. Rhodium and molybdenum complexes were synthesized.



The ligand exchange in acetylacetonatodicarbonylrhodium(I) was performed in dioxane at room temperature using the **B** form (P:Ph molar ratio 3:1). The excess of the organophosphorus oligomer does not affect the degree of ligand exchange in acacRh(CO)$_2$ and gives rise to a mono-substituted complex like *acac*Rh(CO)L. The formation of the complex is confirmed by the observation of a ν(CO) band at 1989 cm^{-1} in the IR spectrum and a doublet at 138.4 ppm ($^1J_{PRh}$ 248.5 Hz), characteristic of amidophosphite rhodium complexes, in the ^{31}P NMR.

It should be noted that upon complex formation oligomer **B** almost loses its ability to dissolve in

Catalytic activity of complexes *acac*Rh(CO)L in the hydrogenation and isomerization of hept-1-ene (toluene, 70°C, P_{H_2} 1 atm, [Rh]=5×10^{-3} g-at l^{-1}, [1-heptene] = 1 mol l^{-1}, reaction time 100 min)

L in *acac*Rh(CO)L	Catalytic properties			
	α, mol H_2 (g-at Rh^{-1}) min^{-1}	yield, %		
		heptane	*trans*-hept-2-ene	*cis*-hept-2-ene
Oligo(hexamethylene diethylphosphoamidite)	0.41	20	35	14
Triethyl phosphite	0.42	21	19	10
Triphenylphosphine	0.57	29	21	11

organic solvents. Due to this property, the metal polymer containing excess free P(III) atoms holds promise for application in catalytic reactions of carbon(II) oxide. Such reactions, e.g., hydroformylation, require the acacRh(CO)L–*n*L reaction system to contain a buffer organic P(III) ligand *n*L for maintaining existence of active centers in the catalytic system [12].

The immobilized metal complex of the acacRh(CO)L type, where L is oligo(hexamethylene diethylphosphoramidite) was studies as a catalyst for hydrogenation of hept-1-ene. The hydrogenation was carried out at 70°C in toluene.

According to the resulting data, oligo[acetylacetonatocarbonyl(hexamethylene diethylphosphoramidite)] as a catalyst precursor offers no advantages over rhodium complexes with trethyl phosphite or triphenylphosphine ligands (see table). Note that the reaction with the catalyst based on oligo(hexamethylene diethylphosphoramidite) occurs in preference for isomerization to *trans*-hept-2-ene, probably due to stereo-chemical features of the carrier ligand (see table).

Attempted additional activation of the rhodium oligo(hexamethylene diethylphosphoramidite) complex by treatment with molecular oxygen led to a sharp fall of the hydrogenating activity of the system, which is probably connected with oxidation of the oligomeric phosphorus-containing ligand.

EXPERIMENTAL

The ^{31}P NMR spectra were registered on a Bruker WP-80 instrument at 32.4 MHz, external reference 85% H_3PO_4. Thermal analysis was carried out on a Shimadzu DTG-50 instrument, accuracy 1%, sensitivity 0.005 mg, heating rate 20.0°C min^{-1}, reference an empty aluminum cell. The IR spectra were registered on a Specord 75IR instrument from KBr pellets.

Synthesis of preparing oligo(phosphoramidites) (form B) *(general procedure)*. To 0.01 mol of diol in 10 ml of dioxane, 0.01 mol of phosphorous triamide was added, and the mixture was stirred at 20–45°C (200–250 mm Hg) for 12–15 h. The solvent was then removed by vacuum distillation (1 mm Hg) at 45°C. Yield 85%. ^{31}P NMR spectrum (dioxane), δ_P, ppm: 147; 139.

Oligo[acetylacetonatocarbonyl(hexamethylene diethylphosphoramidite)rhodium(I)]. To 2.19 g (0.01 mol) of oligo(hexamethylene diethylphosphoramidite) (form **B**) in 10 ml of dioxane, 0.86 g (0.0033 mol) of acetylacetonatodicarbonylrhodium(I) was added. The mixture was stirred at 20°C for 30 min under argon. Precipitate formation was observed. The solvent was removed by vacuum distillation, and the residue was dried at 70–80°C (1 mm Hg). The product is a solid friable light-yellow substance insoluble in organic solvents. Decom. point 135–150°C. IR spectrum (KBr): ν(CO) 1989 cm^{-1}. ^{31}P NMR spectrum (dioxane): δ_P 138.4 ppm. Found, %: C 45.81, 45.93; H 6.37, 6.61; P 7.67, 7.94. $C_{16}H_{28}NO_3PRh$. Calculated, %: C 46.16; H 6.78; P 7.44.

Oligo[pentacarbonyl(hexamethylene diethylphosphoramidite)molybdenum(0)]. To 2.19 g (0.01 mol) of oligo(hexamethylene diethylphosphoramidite) (form **B**) in 10 ml of dioxane, 2.64 g (0.0033 mol) of hexacarbonylmolybdenum(0) was added. The mixture was stirred under argon at 95°C for 2 h. The solvent was then removed by distillation, and the residue was dried in a vacuum at 70–80°C. The product is a solid friable substance. ^{31}P NMR spectrum (dioxane): δ_P 164.3 ppm. Found, %: C 47.19, 46.88; H 6.98, 6.79; P 8.57, 8.39. $C_{15}H_{27}MoNO_2P$. Calculated, %: C 47.37; H 7.16; P 8.14.

Hydrogenation. The complex *acac*Rh(CO)L, 5×10^{-5} mol, was placed under argon to a reactor maintained at 70°C and containing 10 ml of toluene.

Hept-1-ene, 10^{-2} mol, was injected to the reactor through a membrane, and the system was purged with a dry oxygen-free hydrogen. The reaction time was counted from the moment when the stirrer was turned on. The specific activity α was calculated from the volume of consumed hydrogen. The yields of heptanes and isomerization products was calculated from GLC data (column 15% β,β-oxydipropionitrile on Chromosorb P).

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