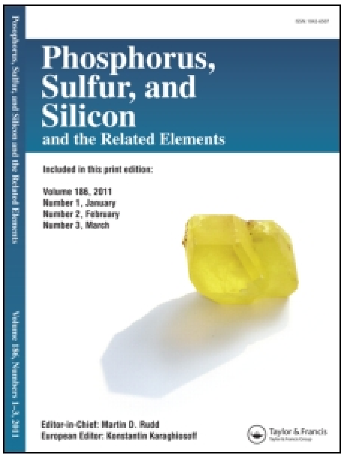

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METAL COMPLEXES OF THE TETRAETHYLESTER OF 4-(2-HYDROXY-PHENYL-AMINO)-1,3-BUTADIENE-1,3-DIPHOSPHONIC ACID AND THE LIQUID PHASE OXIDATION OF CUMENE IN THEIR PRESENCE

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METAL COMPLEXES OF THE TETRAETHYLESTER OF 4-(2-HYDROXY-PHENYL-AMINO)-1,3-BUTADIENE-1,3-DIPHOSPHONIC ACID AND THE LIQUID PHASE OXIDATION OF CUMENE IN THEIR PRESENCE

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The tetraethylester of 4-(2-hydroxy-phenylamino)-1,3-butadiene-1,3-diphosphonic acid **3** and its zinc and cobalt complexes (**3**-Zn, **3**-Co) have been synthesized and their structures were determined by IR, ^{1}H-NMR, ^{31}P {^{1}H}-NMR and ^{13}C-NMR spectral investigations. The effect of these compounds on the liquid phase oxidation of cumene is studied and compared with that of 2-aminophenol **2** and its metal complexes **2**-M. It is found that the ligand **3** shows the strongest inhibiting effect, while **3**-Co, **3**-Zn and **2**-Co accelerate the oxidation process.

INTRODUCTION

We showed earlier[1] that cobalt, nickel, copper and zinc complexes of benzylidene-2-mercaptoaniline inhibit the liquid phase oxidation of cumene. It was found that the zinc chelate has the highest stoichiometric coefficient of inhibition.

The purpose of the present work was to synthesize metal complexes, containing N, O and PO donor groups in the ligand and to study their effect on the liquid phase oxidation of cumene in comparison to that of metal complexes of 2-aminophenol, which do not contain PO groups. It is known that the inhibiting properties of 2,6-di-tert.butylphenol increase, when a PO-group is introduced in para position to the hydroxyl group.[2]

RESULTS AND DISCUSSION

1. Synthesis of the ligand and its metal complexes

One suitable ligand, containing phosphonyl, azomethine and phenol groups would be a Schiff base from phosphonacetaldehyde **1** and 2-aminophenol **2**. It was found,

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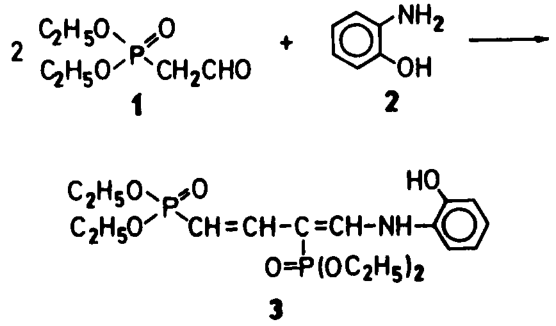
however, that by the reaction of **1** and **2** the following condensation product **3** instead of the corresponding Schiff base was formed:



SCHEME 1

The composition and the structure of the tetraethylester of 4-(2-hydroxy-phenyl-amino)-1,3-butadiene-1,3-diphosphonic acid **3** was determined by elemental analysis, IR- and NMR-spectroscopy (see below) and molecular mass. A similar product of condensation has been obtained by reaction of phosphonoacetaldehyde **1** and cyclo-hexylamine,[3] while the corresponding Schiff base has been isolated if the distillation of the reaction product is accomplished in the presence of K_2CO_3. We found, however, that the reaction of **1** and **2** leads to **3**, regardless of the working conditions.

The zinc and cobalt complexes of **3** (**3**-Zn and **3**-Co) were obtained with $Zn(OOCCH_3)_2$ and $Co(OOCCH_3)_2$ in methanol in the presence of NaOH.

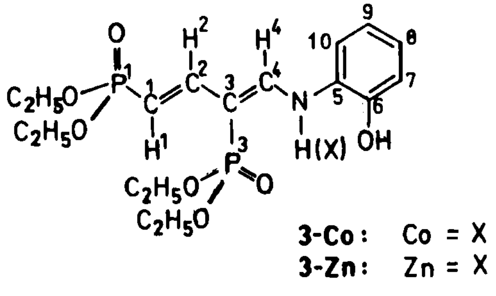
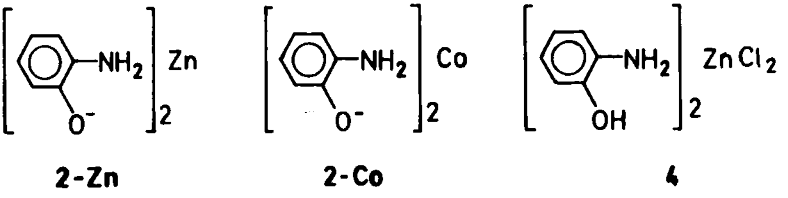


FIGURE 1



2-Zn **2-Co** **4**

FIGURE 2

With a view to obtain comparative data for the oxidation of cumene we synthetized also the zinc and cobalt salts of 2-aminophenol **2**-Zn and **2**-Co by the reaction of **2** with $Zn(OOCCH_3)_2$ and $Co(OOCCH_3)_2$ resp. according to ref.[4,5].

When $ZnCl_2$ was used instead of $Zn(OOCCH_3)_2$ the compound **4** was isolated as a main product.[4]

2. Structure of the ligand 3 and its metal complexes

The ^{1}H-NMR spectrum of **3** is analysed by 2D-NMR methods. A H,H-COSY spectrum[6] demonstrates that one of the olefinic protons is situated just between the aromatic part and the solvent resonance $CHCl_3$ (see Table I). No coupling is observed between the two olefinic parts which are separated by the quarternary carbon C_3 (see Figure 1). The differentiation between the OH— and NH— proton is given by the coupling to H_4 and H/D exchange.

Since the H,P-couplings are unambiguously extracted from a homonuclear 2D-*J*-resolved experiment,[6] the H,H-couplings can be determined easily. This allows the conclusion that protons H_1/H_2 and H_4/NH are mutually trans to each other. Together with the information that the addition of D_2O only exchanges the uncou-

TABLE I

^{1}H, ^{13}C and ^{31}P-NMR data of **3** and **3**-Zn

^{13}C ($CDCl_3$)	C1	C2	C3	C4	others
δ[ppm] CH-multiplicity	104.8(d)	148.6(d)	91.0(s)	150.8(d)	C5 = 128.3(s), C6 = 146.5(s), C7 = 115.6 (d), C8 = 120.3(d), C9 = 123.7(d), C10 = 113.3(d)
J_{CP} [Hz]	C_1P_1 = 195 C_1P_3 = 3.3	C_2P_1 = 9.2 C_2P_3 = 9.2	C_3P_3 = 183 C_3P_1 = 26.5	C_4P_3 = 10.6	$-OCH_2CH_3$: 61.4/62.1(t) (J = 5 Hz), 16.2/16.4(q) (J = 6.5 Hz)
^{31}P($CDCl_3$A)	P1		P3		
δ [ppm]	23.5 $^4J_{PP}$ = 4 Hz		21.4		
^{1}H ($CDCl_3$)	H1	H2	H3	H4	others
δ [ppm]/mult.	5.52(dd)	7.14(ddd)	—	7.85(dd)	NH = 10.41 (d; H_4NH = 13.9 Hz); OH = 9.39 (s)
J [Hz]	H_1H_2 = 17.8 H_1P_1 = 17.8	H_1H_2 = 17.8 H_2P_1 = 23.7 H_2P_3 = 30		H_4NH = 13.9 H_4P_3 = 37.8	aromatic: 7.0–6.8 (m) OCH_2 = 4.2–3.9 (m), OCH_2CH_3 = 1.32 (t,d; J_{HH} = 7.06 Hz)
^{1}H (DMSO)	H1	H2	H3	H4	others
δ [ppm]/mult.	5.47(dd)	7.28(ddd)	—	8.49(dd)	NH = 10.46 (d; H_4NH = 13.8 Hz); OH = 10.09 (s)
J [Hz]	H_1H_2 = 17.5 H_1P_1 = 18.9	H_1H_2 = 17.3 H_2P_1 = 23.0 H_2P_3 = 29.3		H_4NH = 13.8 H_4P_3 = 38.1	aromatic: H7 = 7.54 (d; 7.9 Hz), H10 = 7.01 (d; 7.4 Hz), 6.9–6.8 (2xt) OCH_2 = 4.2–3.9 (m), OCH_2CH_3 = 1.33 (t,d; J_{HH} = 7.08 Hz)
Zn-complex ^{1}H (DMSO)	H1	H2	H3	H4	others
δ [ppm]/mult.	5.06 (dd)	7.26 (ddd)	—	8.60	H7 = 7.37 (d; 7.3 Hz), H8 = 6.63 (t; 2 × 7.3 Hz), H9 = 6.83 (t, 2 × 7.3 Hz), H10 = 7.07 (d; 7.3 Hz)
J [Hz]	H_1H_2 = 18.3 H_1P_1 = 18.3	H_1H_2 = 17.0 H_2P_1 = 23.1 H_2P_3 = 31.1		H_4P_3 = 40.6	

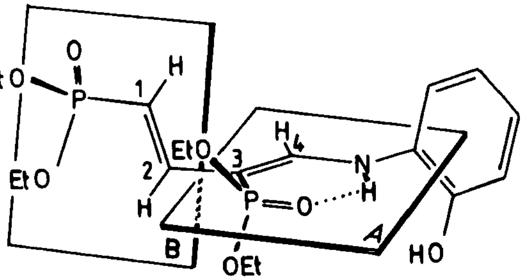


FIGURE 3 Conformational drawing of the free ligand 3 as revealed by NMR-data

pled OH-proton at 9.4 ppm but doesn't affect the NH-proton, we can propose the partial structure A for **3** in Figure 3 (the NH signal is only exchanged by traces of D_2SO_4).

The ^{31}P $\{^1H\}$-NMR spectrum shows two doublets with a coupling $^4J_{PP}$ ~ 4 Hz. In the proton-coupled spectrum the upfield resonance is mainly a broadened triplet, while we observe only one broad downfield signal (neglecting the enormous fine structure by the OR-groups). This is even confirmed by a 2D-^{31}P-^1H shift correlated spectrum,[6] where the upfield ^{31}P-signal shows correlations only to the downfield olefinic protons, while the downfield ^{31}P-signal only corresponds to the upfield proton. Because of the complex fine structure of the coupled ^{31}P-spectrum, it was not possible to discriminate between $^3J_{H_2P_1}$ and $^3J_{H_2P_3}$ in a selective proton decoupling experiment. The more interesting remark is the observation that the downfield signal is unstable during the accumulation, while the upfield resonance doesn't show this behaviour. We think, that this observation strengthens the argumentation for the structure of the molecule, since P_1 is conformationally labile and may exhibit e.g. some temperature sensitivity while P_3 is incorporated into a rigid ring system via hydrogen bonding (Figure 3). The ^{13}C-NMR-spectrum can be analysed by the CH-multiplicities via APT-spectrum,[7] ^{13}C-^{31}P-coupling patterns as well as incremental calculations for the aromatic portion of the spectrum.[8] The most interesting information is the $^3J_{C_1P_3}$ ~ 3 Hz value which leads, via a Karplus-type dependence for vicinal C—P-coupling,[8] to the result that the dihedral angle C_1—C_2/C_3—P_3 is either ~ 50° or ~ 115°, while the trans planar system P_1—C_1—C_2—C_3 shows a large $^3J_{C_3P_1}$-value of 26.5 Hz. Thus there seems to be no conjugation in the diene system, as it is expected from the absence of an allylic coupling between H_2/H_4, and the inspection of molecular models demonstrates that the angle must be around 115°.

Because of its low solubility in $CDCl_3$, the Zn-complex of **3** had to be analysed in DMSO. Therefore, the data of the free ligand in DMSO are included in table 1 for a better comparison.

The ^1H-NMR spectrum of the Zn complex is well understood on the basis of the conformation of the free ligand (Figure 4).

The elemental analysis indicates that the ligand should be dianionic. Substitution of the NH-proton and the OH proton by the zinc ion offers the possibility of a rigid double chelate configuration of the complexed ligand. Thus, we expect bonding between zinc, the phenolic oxygen, the nitrogen and, as a third ligand, similar to the

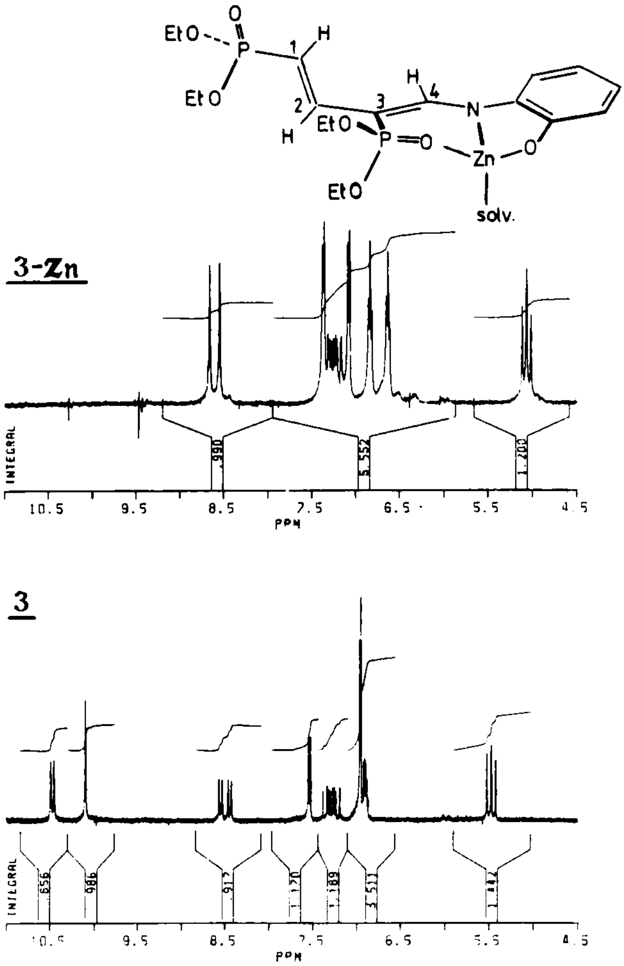


FIGURE 4 Downfield part of the ^{1}H-NMR-spectra of 3 and 3-Zn in DMSO

hydrogen bonding situation, the oxygen from the phosphonyl group. In DMSO there is probably one solvent molecule associated with the metal atom to give a coordination number four, but there is no indication for this in the NMR spectrum.

The rigid double chelate (see Figure 4) shows up in a much better differentiation of the four aromatic protons as compared to **3**, where rotation about the N—aryl bond is possible.

The conformation of the C=C—PO(OEt)$_2$ substituent relative to the chelate system seems to be rather unchanged. Because of line broadening by paramagnetism the cobalt complex **3**-Co could not be analysed by NMR.

3. Cumene oxidation in the presence of metal complexes or their ligands

The kinetic curves of the oxidation of cumene, initiated by azo-bis-isobutyronitrile (AIBN) in the presence of metal complexes **2**-M and **3**-M or their ligands **2** and **3**

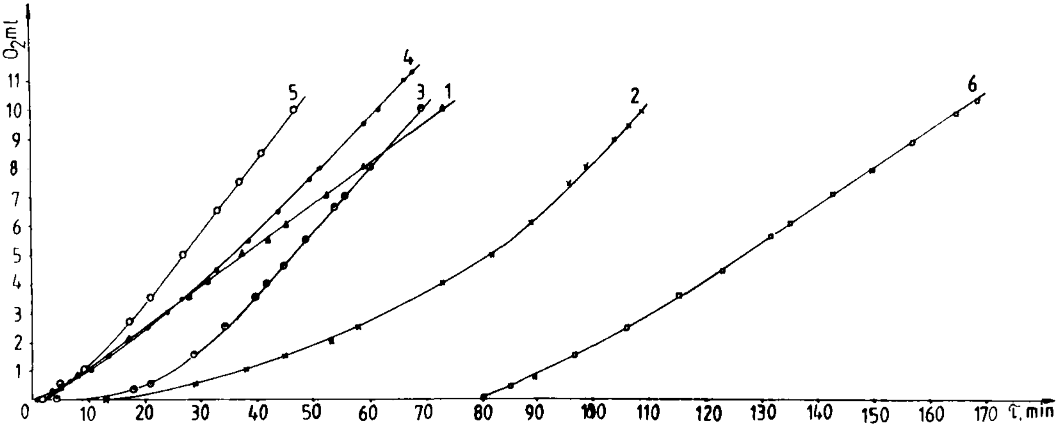


FIGURE 5 The oxygen absorption by the cumene oxidation at 60° in the presence of AIBN. 1. Cumene oxidation + AIBN(5.10^{-2}M): 2. the same as 1 + **2**(10^{-3} M); 3. as 1 + **2**-Co (10^3M); 4. as 1 + **3**(10^{-3}M); 5. as 1 + **3**-Zn (10^{-3}M); 6. as 1 + **4** (10^{-3} M).

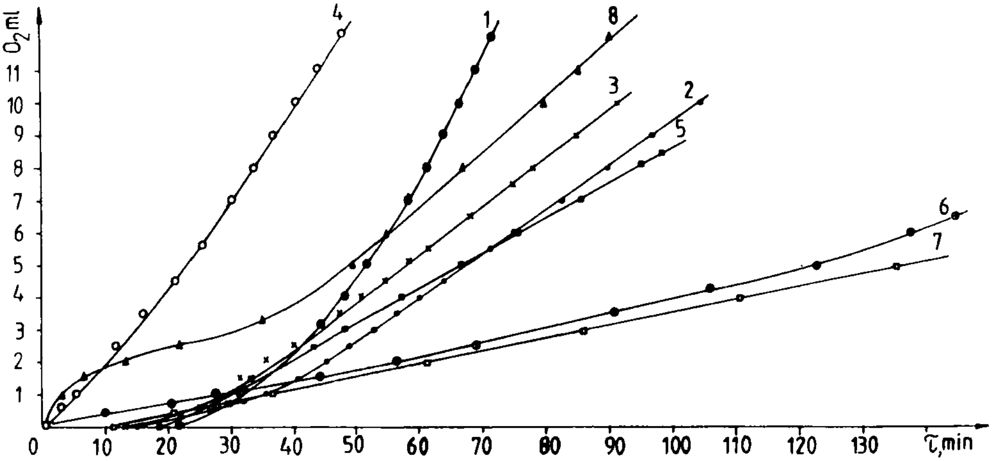


FIGURE 6 The oxygen absorption by the cumene oxidation at 110°C. 1. only cumene; 2. as 1 + **2**(10^{-3} M); 3. as 1 + **3**-Co (10^{-3} M); 4. as 1 + **2**-Zn (10^{-3}M); 5. as 1 + **3**-Zn (10^{-3} M); 6. as 1 + **4** (10^{-3} M); 7. as 1 + **3** (10^{-3} M); 8. as 1 + **2**-Co (10^{-3} M).

(concentration 10^{-3} molar) at 60°C and 110°C are given in Figures 5 and 6. The parameters obtained by treatment of the kinetic curves from Figures 5 and 6 are shown in Table II.

The longest induction period at 60°C appears in the presence of ligand **3** and, with the same compound, the rates of both the AIBN and the thermally initiated oxidation of cumene are the smallest ones. The cobalt complex **3**-Co, on the other hand, accelerates the thermally initiated oxidation (at 110°C) of cumene and the zinc complex **3**-Zn accelerates both processes of initiated cumene oxidation. These results show that the exchange of hydrogen atoms from the OH and NH groups by metal atoms leads to a loss of the inhibiting behaviour.

TABLE II

Oxidation of cumene in the presence of metal complexes **2**-M, **3**-M or in the presence of the ligands **2**,**3** (concentration 10^{-3} M, initiator [AIBN] = 5.10^{-2}M)

Compound	Induction period τ 60°C	110°C	$W_{max} \times 10^5$ mol/l.s 60°C	110°C	Stoichiometric coefficient of inhibition, f
Cumene	—	41	—	6.6	—
Cumene + AIBN	0	—	2.2	—	—
2	24	24	3.1	2.2	0.2
2-Zn	—	11.5	—	0.6	—
2-Co	0	0	3.3	4.3	0
3	90	0	2.0	0.65	2.3
3-Zn	0	19	3.7	1.6	0
3-Co	—	0	—	2.6	0
4	61	31	3.1	2.0	2.0

2-Aminophenol **2** causes the appearance of an induction period of oxidation (Table II), but after consumption of the inhibitor the rate of oxidation increases. Consequently the products of the reaction of 2-aminophenol **2** with cumeneperoxy radicals are initiating additions. The low stoichiometric coefficient of inhibition, determined experimentally (0.2, Table II) confirms this assumption. The cobalt complex of 2-aminophenol (**2**-Co) proves to be a catalyst of cumene oxidation by both types of initiation. On the other hand the zinc complex of **2** (**2**-Zn) at 110°C inhibits the oxidation process, so that in this case the maximal rate of oxidation is > 10 times lower than that of the pure cumene. An interesting behaviour shows the adduct of **2** with $ZnCl_2$ (**4**), which at 60°C inhibits the oxidation process, while at 110°C does not effect it.

The strong inhibiting effect of the ligand **3** obviously is due to its possibility to react with cumeneperoxide radicals. The disappearance of inhibiting properties in the complexes **3**-Zn and **3**-Co shows that the electrophilic attack of cumeneperoxide radicals is directed to OH or NH groups of **3**. Most probably, the OH group is affected, because a similar absence of inhibiting properties is inherent to the **2**-Co.

The presence of inhibiting properties of the **2**-Zn as opposed to **2**-Co could mean that this complex (**2**-Zn) has a more complicated, still unknown structure, possibly a polymeric one.

The particular S-form of the kinetic curve of oxygen absorption in the presence of **3**-Co probably is connected with its small solubility in cumene. The existence of a prooxidizing effect in the beginning of the process (Figure 6, curve 3) seems to be due to the ability of **3**-Co to react with the arising hydroperoxides giving free radical products.

Earlier we established[1] that the oxidation of cumene is weakly influenced by *N*,*N*′-bis(salicylidene)hydrazine and *N*,*N*′-bis(salicylidene)ethylenediamine as well as by their metal complexes. The considerably higher inhibiting properties of the now studied ligand **3**, containing PO groups in addition to O and N donor atoms can be ascribed to the further possibility for hydroperoxide decomposition by PO groups and in this way influencing the degenerating chain branching. Complexes **3**-M are not only less efficient oxidation inhibitors because of loss of OH and NH hydrogen atoms, but by coordinating PO groups.

EXPERIMENTAL

The diethylphosphonacetaldehyde **1** was obtained from triethylphosphite and the diethylacetal of chloroacetaldehyde according to the method described by B. C. Sounders and P. Simpson.[9] All the NMR-spectra are recorded at room temperature on a Bruker AM-360-spectrometer (360 MHz for protons). $^{31}P/^{13}C$-spectra are measured using broadband equipment. The data are always referenced to the solvent signal (7.25/77.0 ppm for $CHCl_3/CDCl_3$ and 2.6 ppm for DMSO) despite ^{31}P data which are referred to external 85% H_3PO_4/H_2O. The 2D-spectra are recorded using standard manufacturer software. To avoid artefacts, all the pulse lengths are determined on the actual samples using the fast method described earlier.[10]

The oxidation of cumene was carried out in the manometric apparatus described in our previous paper.[11] For every run of oxidation samples of 5 ml were taken. Azo-bis-isobutyronitrile (AIBN) was used as initiating agent.

The experiments were carried out in the presence of the complexes or ligands, each of them in concentrations of 10^{-3}M at temperatures of 60°C and 110°C.

1. *Tetraethylester of 4-(2-hydroxy-phenylamino)-1,3-butadiene-1,3-diphosphonic acid* **3**. A mixture of 8.50 g (0.047 mol) of diethylphosphonacetaldehyde **1** and 2.55 g (0.023 mol) of 2-aminophenol[2] in 100 ml anhydrous benzene is refluxed with azeotropic distillation of the water. After cooling the pale yellow precipitation of **3** (7.70 g, m.p. 196°–198°C) is filtered, washed with ether and recrystallized from ethanol. m.p. of the pure **3** 198–199°C.

$C_{18}H_{29}O_7P_2N$ (433.4) Calc. %: C, 49.88; H, 6.74; P, 14.29; N, 3.23. Found %: C, 49.62; H, 7.00; P, 14.60; N, 3.19. Mol. mass (THF) 428. IR ($CHCl_3$); 1020 and 1050 cm^{-1} (ν_{P-O-C}), 1630 cm^{-1} ($\nu_{C=C}$), 3200 cm^{-1} ($\nu_{NH(OH)}$). NMR: See Table I.

2. *Zinc complex of* **3** (**3**-*Zn*). A mixture of 1.70 g (0.004 mol) of **3** and 0.37 g (0.009 mol) of NaOH is dissolved in anhydrous methanol under an argon atmosphere, then 0.740 g (0.004 mol) of $Zn(OOCCH_3)_2$ is added. The solution is stirred and refluxed for 3 hrs. After cooling yellow crystals of **3**-Zn precipitate (yield 1.50 g, 76%), which do not melt until 300°C. **3**-Zn is recrystallized from DMSO.

$C_{18}H_{27}O_7P_2NZn$(496.7) Calc. %: C, 43.52; H, 5.48; N, 2.82. Found %: C, 43.55; H, 5.61; N, 2.80. Mol. mass (DMSO) 440. IR (nujol): 1020 and 1050 cm^{-1} (ν_{P-O-C}), 1180 cm^{-1} ($\nu_{P=O}$), 1545 and 1600 cm^{-1} ($\nu_{C=C}$). NMR: See Table I.

3. *Cobalt complex of* **3** (**3**-*Co*). Similar to the procedure for preparing **3**-Zn, **3**-Co is obtained from 1.50 g (0.0035 mol) of **3** and 0.14 g (0.0035 mol) of NaOH in 35 ml methanol and 0.62 g (0.0035 mol) of Co $(OOCCH_3)_2$ in 30 ml of methanol after heating for 3 hrs, followed by cooling, as a dark green precipitate (0.80 g, 98%). The crystals do not melt until 300°C.

$C_{18}H_{27}NO_7P_2Co$ (490.2) Calc. %: C, 44.10; H, 5.50; N, 2.85. Found %: C, 43.61; H, 5.71; N, 2.48. IR (nujol): 1020 and 1050 cm^{-1} (ν_{P-O-C}), 1160 cm^{-1} ($\nu_{P=O}$), 1545 and 1590 cm^{-1} ($\nu_{C=C}$). ^1H-NMR spectra could not successfully be recorded because of the paramagnetism of the product.

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