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LETTERS
TO THE EDITOR

New Tetradentate Ligands in the Series of Phosphorus Containing Bisazomethines

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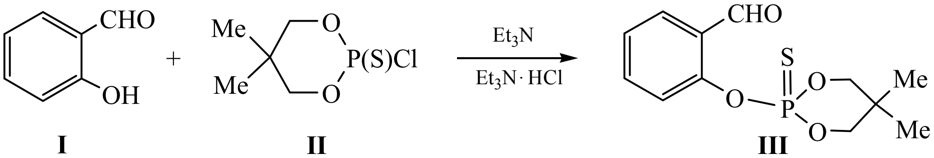
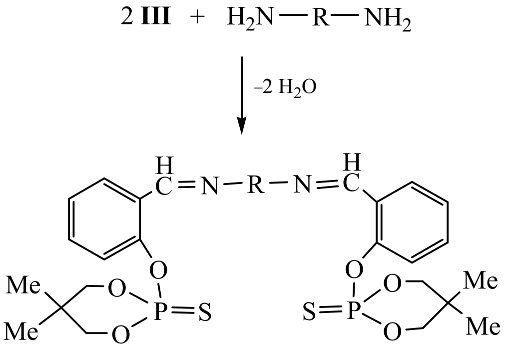
Metal complexes based on hydroxyl-containing diimines are known to exhibit catalytic properties in various chemical processes [1–6]. Some metal complexes possess high fungicidal, antibacterial, antimicrobial and antitumor activity [7–12]. We believe that *O*,*O*-di(thio)phosphorylated bisazomethines which are not found in the literature can be effective tetradentate ligands. We obtained *O*-thiophosphorylated salicylic aldehyde **III** by reaction of salicylaldehyde with 2-chloro-2-thioxo-5,5-dimethyl-1,3,2-dioxaphosphorinane **II** in the presence of triethylamine.



I **II** **III**

1,3,2-Dioxaphosphorinane **III** reacts readily with aliphatic and aromatic diamines to form the desired bisazomethines **IVa**–**IVc**.



IVa–**IVc**

R = $(CH_2)_2$ (**a**), *p*-C_6H_4 (**b**); (1*R*,2*R*)-(–)-1,2-diaminocyclohexane (**c**).

2-Thioxo-2-(2-formylphenoxy)-5,5-dimethyl-1,3,2-dioxaphosphorinane (III). To a mixture of 1.71 g of aldehyde **I** and 1.45 g of triethylamine in 30 ml of anhydrous benzene was added dropwise a solution of 2.81 g chlorothiophosphate **II** in 10 ml of benzene. The reaction mixture was refluxed for 62 h. After cooling, triethylamine hydro-chloride was separated, and the solvent was re-moved. The residue was purified by column chromatography (silica gel, methylene chloride–ethanol, 40:1). Yield 1.51 g (38%), mp 81–83°C. IR spectrum, ν, cm^{-1}: 825 (P=S), 1602 (Ph), 1694 (C=O). ^1H NMR spectrum, ($CDCl_3$), δ, ppm (*J*, Hz): 0.95 s (3H, CH_3), 1.32 s (3H, CH_3), 4.11–4.20 m (2H, OCH_2), 4.58–4.62 m (2H, OCH_2), 7.39–7.91 m (2H, CH_{Ar}), 7.61 t (1H, CH_{Ar}, $^3J_{HH}$ 7.74), 7.92 d (1H, CH_{Ar}, $^3J_{HH}$ 8.68), 10.36 s (1H, CHO). ^{31}P NMR spectrum, ($CDCl_3$): δ_P 54.27 ppm. Mass spectrum (MALDI-TOF), *m*/*z*: 287 $[M + H]^+$. Found, %: C

50.55; H 5.29; P 10.91; S 11.08. $C_{12}H_{15}O_4PS$. Calculated, %: C 50.35; H 5.24; P 10.84; S 11.19.

Bis[2-(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinyloxy)benzal]ethanediamine (IVa). To a solution of 0.56 g of aldehyde **III** in 10 ml ethanol was added 0.06 g of ethylene diamine. The reaction mixture was refluxed for 0.4 h. After 12 h the solvent was removed, and to the residue was added 5 ml of diethyl ether. The formed precipitate was separated and washed with ethanol. Yield 0.55 g (95%), mp 129–132°C. IR spectrum, ν, cm^{-1}: 1604 (C_6H_4), 1639 (C=N). ^1H NMR spectrum, $[(CD_3)_2C=O)]$, δ, ppm: 0.99 s (6H, CH_3), 1.34 s (6H, CH_3), 4.08–4.16 m (2H, CH_2N), 4.12–4.21 m (2H, CH_2N), 4.40–4.44 m (4H, CH_2O), 4.59–4.63 m (4H, CH_2O), 7.40–7.93 m (8H, C_6H_4), 8.87 s (CH=N). ^{31}P NMR spectrum, $[(CD_3)_2C=O)]$: δ_P 54.41 ppm. Found, %: P 10.44; S 10.71. $C_{26}H_{34}N_2O_6P_2S_2$. Calculated, %: P 10.38; S 10.75.

Bis[2-(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinyloxy)benzal]-1,4-diaminobenzene (IVb) was obtained similarly from 0.37 g of aldehyde **III** and 0.07 g of 1,4-diaminobenzene in 10 ml of ethanol. Yield 0.33 g (79%), mp 258–262°C. IR spectrum, ν, cm^{-1}: 1600 (C_6H_4), 1614 (C=N). ^1H NMR spectrum, ($CDCl_3$), δ, ppm: 0.96 s (6H, CH_3), 1.33 s (6H, CH_3), 4.04–4.14 m (4H, CH_2O), 4.28–4.37 m (4H, CH_2O), 7.14–7.95 m (12H, C_6H_4), 9.36 s (CH=N). ^{31}P NMR spectrum, ($CDCl_3$): δ_P 55.50 ppm. Mass spectrum (MALDI-TOF), *m/z*: 645 $[M + H]^+$. Found, %: P 9.18; S 9.88. $C_{30}H_{34}N_2O_6P_2S_2$. Calculated, %: P 9.61; S 9.95.

Bis[2-(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinyloxy)benzal]-1,2-diaminocyclohexane (IVb) was obtained similarly from 0.35 g of aldehyde **III** and 0.07 g of (1*R*,2*R*)-(–)-1,2-diaminocyclohexane in 10 ml of ethanol. Yield 0.33 g (83%), mp 80–83°C, $[\alpha]_D^{20}$ 7.0 (*c* 0.76 CH_3CN). IR spectrum, ν, cm^{-1}: 1604 (C_6H_4), 1638 (C=N). ^1H NMR spectrum, ($CDCl_3$), δ, ppm: 0.89 s (6H, CH_3), 1.28 s (6H, CH_3), 1.51–1.87 m [8H, $(CH_2)_4$], 3.48–3.50 m (CH_2N), 3.96–4.06 m (4H, CH_2O), 4.16–4.25 m (4H, CH_2O), 7.13–7.64 m (8H, C_6H_4), 8.56 s (CH=N). ^{31}P NMR spectrum, ($CDCl_3$): δ_P 54.50 ppm. Mass spectrum (MALDI-TOF), *m/z*: 651 $[M + H]^+$. Found, %: P 9.41; S 9.87. $C_{30}H_{40}N_2O_6P_2S_2$. Calculated, %: P 9.52; S 9.86.

The IR spectra were recorded on a Vector-22 Bruker spectrometer in the range of 400–3600 cm^{-1} (KBr). The ^1H NMR spectra were taken on an Avance 600 instrument operating at 600.13 MHz using the residual proton signals of the deuterated solvent ($CDCl_3$) as internal reference. The ^{31}P NMR spectra were registered on a Bruker MSL-400 Fourier spectrometer (100.62 MHz). Mass spectra (MALDI-TOF) were recorded on a Ultraflex III TOF/TOF Bruker instrument (matrix – *p*-nitroaniline).

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