ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 6, pp. 1249–1250. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © R.Kh. Bagautdinova, A.P. Vanichkina, E.M. Pudovik, A.R. Burilov, M.A. Pudovik, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 6, pp. 1049–1050.

LETTERS
TO THE EDITOR

Phosphorus-containing Bisazomethines Based on Terephthalic Aldehyde as Tetradentate Ligand of New Type

R. Kh. Bagautdinova[a], **A. P. Vanichkina**[a], **E. M. Pudovik**[b], **A. R. Burilov**[a], **and M. A. Pudovik**[a]

[a] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center of the Russian Academy of Sciences,*
ul. Akademika Arbuzova 8, Kazan, Tatarstan, 420088 Russia
e-mail: pudovik@iopc.ru

[b] *Kazan (Volga) Federal University, Kazan, Tatarstan, Russia*

Received April 10, 2014

Keywords: terephthalic aldehydes, bisazomethines, phosphorylation

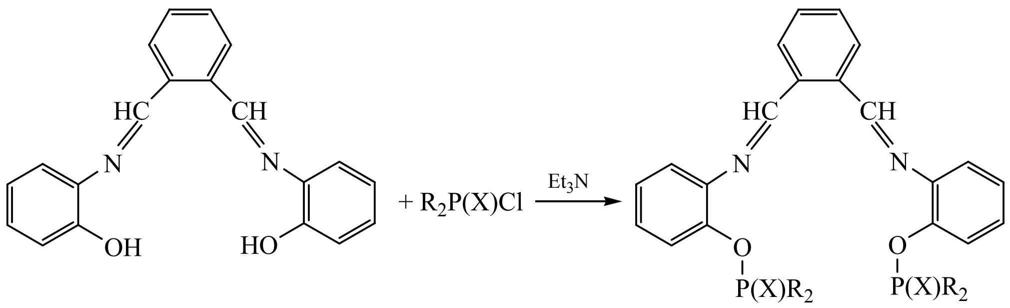
DOI: 10.1134/S1070363214060334

Recently, hydroxyl-containing bisazomethines and complexes based on them attract a great interest. A wide range of metals including biogenic Zn(II), Cu(II), Cd(II), Co(II), Ni(II), Fe(III), Pd(II), Zr(IV), U(II) was used to obtain metal complexes catalyzing enantioselective epoxidation of unsubstituted olefins [1, 2], selective *ortho*-hydroxylation of phenols [3], epoxidation of styrene [4], oxidation of styrene to carbonyl compounds under the action of hydrogen peroxide [5], oxidation of alcohols to carbonyl compounds [6], oxidation of organic sulfides to sulfoxides [7], heterogeneous hydrogenation of alkenes and alkynes [8], butadiene polymerization [9]. Some of metal complexes showed high fungicidal, antibacterial, antimicrobial, anticancer activity [10–15].

At the same time there are no data on the *O*-phosphorylated bisazomethines, which can be used as ligands for metal complexes. We performed phosphorylation of diimine **I** with P(V) acid chlorides **IIa**–**IIc** in the presence of a base to obtain diphosphorylated derivatives **IIIa**–**IIIc**. The latter are promising tetradentate ligands. Compounds **IIIa**–**IIIc** are crystalline substances. Their composition and structure were proved by elemental analysis, mass spectrometry, IR, ^{1}H and ^{31}P NMR spectroscopy methods (Scheme 1).

1,2-Phenylenebis(methanylidene)bis(azanylidene)-bis(2,1-phenylene) bis(diphenylphosphinate) (IIIa). To a suspension of 0.30 g of diimine **I** and 0.2 g of triethylamine in 10 mL of anhydrous benzene was added dropwise a solution of 0.45 g of diphenylchlorophosphine oxide in 5 mL of benzene. After 12 h, the precipitated triethylamine hydrochloride was separated, and the solvent was removed. To the residue was added 20 mL of hexane, and then the precipitate

Scheme 1.



I **IIa–IIc** **IIIa–IIIc**

R = Ph, X=O (**a**); R = Ph, X = S (**b**); R = OPh, X = O (**c**).

was separated. Yield 0.48 g (71%), mp 201–204°C. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 6.50–8.07 m (32H, Ph), 8.44 s (2H, CH=N). ^{31}P NMR spectrum (CDCl$_3$): δ_P 30.81 ppm. Mass spectrum (MALDI-TOF): *m*/*z* 716. Found P, %: 9.06. $C_{44}H_{34}N_2O_4P_2$. Calculated P, %: 8.86.

1,2-Phenylenebis(methanylidene)bis(azanylidene)-bis(2,1-phenylene) bis(diphenylthiooxophosphinate) (IIIb). To a suspension of 0.30 g of diimine **I** and 0.2 g of triethylamine in 10 mL of anhydrous benzene was added dropwise a solution of 0.48 g of diphenyl chlorothiophosphinate. The reaction mixture was refluxed for 15 h. The resulting triethylamine hydrochloride was separated, and the solvent was removed. To the residue was added 10 mL of ethanol, and the precipitate was separated. Yield 0.47 g (66%), mp 176–179°C. IR spectrum (KBr), ν, cm^{-1}: 1586 (Ph), 1616 (C=N). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 7.38–8.03 m (32H, Ph), 8.39 s (2H, CH=N). ^{31}P NMR spectrum [(CD$_3$)$_2$CO]: δ_P 80.81 ppm. Mass spectrum (MALDI-TOF): *m*/*z* 749. Found, %: P 8.66; S 8.90. $C_{44}H_{34}N_2O_2P_2S_2$. Calculated, %: P 8.27; S 8.56.

1,2-Phenylenebis(methanylidene)bis(azanylidene)-(2,1-phenylene) bis(diphenylphosphate) (IIIc). To a suspension of 0.30 g of diimine **I** and 0.2 g of triethylamine in 10 mL of anhydrous benzene was added dropwise a solution of 0.51 g of diphenyl chlorophosphate. The next day, the precipitated triethylamine hydrochloride was separated, and the solvent was removed. To the residue was added 20 mL of hexane, and the precipitate was separated. Yield 0.7 g (95%), mp 114–115°C. ^{1}H NMR spectrum [(CD$_3$)$_2$CO], δ, ppm: 7.14–8.11 m (32H, Ph), 8.65 s (2H, CH). ^{31}P NMR spectrum [(CD$_3$)$_2$CO]: δ_P –17.70 ppm. Mass spectrum (MALDI-TOF): *m*/*z* 781. Found P, %: 7.92. $C_{44}H_{34}N_2O_8P_2$. Calculated P, %: 7.94.

The IR spectra were recorded on a Bruker Vector-22 spectrometer in the range of 400–3600 cm^{-1} from mulls in mineral oil. The ^{1}H NMR spectra were taken on an Avance 600 instrument operating at 600.13 MHz relative to the signals of residual protons of the deuterated solvent (*d*-chloroform). The ^{31}P NMR spectra were registered on a Bruker MSL-400 Fourier spectrometer (100.62 MHz). Mass spectra (MALDI-TOF) were obtained on an Ultraflex III instrument (*p*-nitroaniline matrix).

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (grant no. 12-03-00204).

REFERENCES

1. Wei Zhang, Loebach, J.L., Wilson, S.R., and Jacobsen, E.N., *J. Am. Chem. Soc.*, 1990, vol. 112, no. 7, p. 1002.
2. Geon Joong Kim, and Ji-Hoon Shin, *Tetrahedron Lett.*, 1999, vol. 40, no. 37, p. 6827.
3. Karakhanov, E.A., Maximov, A.L., Kardasheva, Yu.S., Skorkin, V.A., Kardashev, S.V., Ivanova, E.A., Lurie-Luke, E.S., Seeley, J.A., and Cron, S.L., *Industr. Eng. Chem. Res.*, 2010, vol. 49, no. 10, p. 4607.
4. Zhang Zhang Ye Zhi-Wu, Zhang Min, and Fan Chun Yan, *Synth. React. Inorg. Metal-Org. Nano-Metal Chem.*, 2008, vol. 38, no. 4, p. 352.
5. Velusamy, S. and Punniyamurthy, T., *Eur. J. Org. Chem.*, 2003, no. 20, p. 3913.
6. Adam, W., Gelalcha, F.G., Saha-Moeller, C.R., and Stegmann, V.R., *J. Org. Chem.*, 2000, vol. 65, no. 7, p. 1915.
7. Sevel, R., Rajagopal, S., Srinivasan, C., Alhaji, N.I., and Chellamani, A., *J. Org. Chem.*, 2000, vol. 65, no. 11, p. 3334.
8. Kerr, J.M. and Suckling, C.J., *Tetrahedron Lett.*, 1998, vol. 29, no. 43, p. 5545.
9. Endo Kiyoshi, and Nakatani Kenji, *Nippon Gomu Kyokaishi,* 2007, vol. 80, no. 1, p. 13.
10. Mashaly Mahmoud, M., Abd-Elwahab, Z.H., and Faheim, A.A., *Synth. React. Inorg. Metal-Org. Nano-Metal Chem.*, 2004, vol. 34, no. 2, p. 233.
11. El-Wahab, Z.H., Mashaly, M.M., Salman, A.A., El-Shetary, B.A., and Faheim, A.A., *Spectrochim. Acta (A)*, 2004, no. 12, p. 2861.
12. Yildiz, M, Duelger, B, Koyuncu, S.Y., and Yapici, B.M., *J. Indian Chem. Soc.*, 2004, vol. 81, no. 1, p. 7.
13. Ahmed, A.K.S., Salam, M.A., Sattar Anowara, Alam, S.B., and Mridha, A.U., *J. Bangladesh Chem. Soc.*, 2003, vol. 5, no. 1, p. 73.
14. Abdallah, S.M., Mohamed, G.G., Zayed, M.A., and El-Ela, M.S., *Spectrochim. Acta (A)*, 2009, vol. 73, no. 5, p. 833.
15. Ansari, K.I., Grant, J.D., Kasiri, S., Woldemariam, G., Shrestha, B., and Mandal, S.S., *J. Inorg. Biochem.*, 2009, vol. 103, no. 5, p. 818.