Russian Journal of General Chemistry, Vol. 73, No. 2, 2003, pp. 315–316. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 2, 2003, pp. 339–340.

LETTERS TO THE EDITOR

Addition of Bis(trimethylsiloxy)phosphine to Diphenyl(vinyl)- and Phenyldivinylphosphines

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Received April 30, 2002

Addition of diphenylphosphine to substituted vinylphosphines is a convenient method for preparing a series of ligands widely used as components of catalytic systems [1]. In the present work we have prepared new derivatives of functionally substituted organophosphorus acids containing P(III) fragments. Hence, bis(trimethylsiloxy)phosphine easily adds to diphenyl(vinyl)- and phenyldivinylphosphines in the presence of azobis(isobutyronitrile) at 120°C to give phosphonites **I** and **II** in high yields (cf. [2]).

$$n(Me_3SiO)_2PH + (CH_2{=}CH)_nPPh_{3-n} \xrightarrow{R^{\cdot}} [(Me_3SiO)_2PCH_2CH_2]_nPPh_{3-n},$$

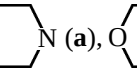
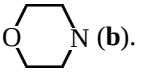
I, II

$R^{\cdot} = Me_2(NC)C^{\cdot}$; n = 1 (**I**), 2 (**II**).

Phosphonite **I** is smoothly aminomethylated with bis(dialkylamino)methanes at 130°C in the presence of catalyst (zinc chloride) to form phosphinates **IIIa, IIIb** in high yields.

$$\mathbf{I} \xrightarrow[-Me_3SiNR_2]{(R_2N)_2CH_2,\ ZnCl_2} Me_3SiOP(O)(CH_2CH_2PPh_2)(CH_2NR_2)$$

IIIa, IIIb

R_2N =  N (**a**),  N (**b**).

Treatment of phosphonites **I, II** and phosphinates **III** with dilute solutions of sodium methylate in methanol gives sodium phosphonites **IV, V** and phosphinates **VI** which show promise as water-soluble ligands.

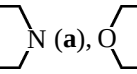
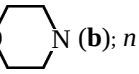
Salts **IV**–**VI** are white hygroscopic crystals. The ^{1}H NMR spectra of compounds **I**–**IV** contain characteristic signals of the $P^1C^1H_2P^2Ph$ and $PC^3H_2NC^4H_2$ fragments. Their parameters are listed below. Signals in

$$\mathbf{I, II} \xrightarrow[-2nMe_3SiOMe]{n\text{MeONa},\ n\text{MeOH}} \left[NaO(H)P(O)CH_2CH_2 \right]_n PPh_{3-n}$$

IV, V

$$\mathbf{IIIa, IIIb} \xrightarrow[-Me_3SiOMe]{MeONa,\ MeOH} NaOP(O)(CH_2CH_2PPh_2)(CH_2NR_2)$$

VIa, VIb

R_2N =  N (**a**), O  N (**b**); n = 1 (**IV**), 2 (**V**).

the ^{1}H NMR spectra of these fragments partially or completely overlap.

Bis(trimethylsilyl) [2-(diphenylphosphino)ethyl]-phosphonite (I). A mixture of 17 g of bis(trimethylsiloxy)phosphine, 10.7 g of diphenyl(vinyl)phosphine, and 0.2 g of azobis(isobutyronitrile) was heated to 100°C and then, within 1 h, to 120°C. Distillation of the reaction mixture gave 17.7 g (83%) of phosphonite **I**, bp 164°C (1 mm). ^{13}C NMR spectrum, δ_C, ppm: 36.44 d.d (C^1, $^1J_{PC}$ 27.2, $^2J_{PC}$ 10.7 Hz), 18.54 t (C^2, $^1J_{PC}$ 13.3 Hz). ^{31}P NMR spectrum, δ_P, ppm: 157.23 d (P^1), –15.17 d (P^2), $^3J_{PP}$ 22.5 Hz.

Phosphine **II** was obtained analogously.

Bis[2-bis(trimethylsiloxy)phosphinoethyl]-phenylphosphine (II). Yield 87%, bp 192°C (1 mm). ^{13}C NMR spectrum, δ_C, ppm: 35.75 d.d (C^1, $^1J_{PC}$ 26.4, $^2J_{PC}$ 8.4 Hz), 17.63 d.d (C^2, $^1J_{PC}$ 15.1, $^2J_{PC}$ 12.2 Hz). ^{31}P NMR spectrum, δ_P, ppm: 156.96 d ($2P^1$), –20.67 t (P^2), $^3J_{PP}$ 20.0 Hz.

Trimethylsilyl [2-(diphenylphosphino)ethyl]-(*N*-piperidinomethyl)phosphinate (IIIa). A mixture of 4.2 g of phosphinite **I**, 3.6 g of bis(*N*-piperidino)-methane, and 0.1 g of zinc chloride was heated at

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110–130°C for 1.5 h. Distillation of the reaction mixture gave 2.9 g of phosphinate **IIIa**, yield 65%, bp 208°C (1 mm), n_D^{20} 1.5495. ^{13}C NMR spectrum, δ_C, ppm: 24.91 d.d (C^1, $^1J_{PC}$ 91.2, $^2J_{PC}$ 15.0 Hz), 19.87 d.d (C^2, $^1J_{PC}$ 14.9, $^2J_{PC}$ 4.6 Hz), 57.84 d (C^3, $^1J_{PC}$ 113.5 Hz), 16.31 d (C^4, $^3J_{PC}$ 9.2 Hz). ^{31}P NMR spectrum, δ_P, ppm: 41.32 d (P^1), –14.69 d (P^2), $^3J_{PP}$ 50.5 Hz.

Phosphinate **IIIb** was obtained analogously.

Trimethylsilyl (*N*-morpholinomethyl)[2-(diphenylphosphino)ethyl]phosphinate (IIIb). Yield 68%, bp 202°C (1 mm), n_D^{20} 1.5505. ^{13}C NMR spectrum, δ_P, ppm: 24.43 d.d (C^1, $^1J_{PC}$ 91.5, $^2J_{PC}$ 15.2 Hz), 19.52 d.d (C^2, $^1J_{PC}$ 14.8, $^2J_{PC}$ 2.6 Hz), 56.86 d (C^3, $^1J_{PC}$ 112.6 Hz), 54.83 d (C^4, $^3J_{PC}$ 9.1 Hz). ^{31}P NMR spectrum, δ_P, ppm: 39.95 d (P^1), –15.18 d (P^2), $^3J_{PP}$ 49.7 Hz.

Sodium 2-(diphenylphosphino)ethylphosphonite (IV). To a solution of 0.54 g of sodium methylate in 30 ml of methanol, a solution of 4.2 g of phosphonite **I** in 5 ml of diethyl ether was added with stirring at 10°C. The resulting mixture was heated to boil, the solvent was distilled off, and the residue was kept in a vacuum (1 mm) for 1 h. Salt **IV**, 2.9 g (96%), was obtained. ^1H NMR spectrum, , ppm: 6.88 d (PH, $^1J_{PH}$ 508.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.99 d (C^1, $^1J_{PC}$ 87.5 Hz, $^2J_{PC}$ 13.8 Hz), 19.32 d (C^2, $^1J_{PC}$ 10.1 Hz). ^{31}P NMR spectrum, δ_P, ppm: 27.29 d (P^1), –15.61 d (P^4), $^3J_{PP}$ 53.7 Hz. Found, %: C 55.87; H 5.12. $C_{14}H_{15}NaO_2P_2$. Calculated, %: C 56.01; H 5.04.

Salts **V, VI** were obtained analogously.

(3-Phenyl-3-phosphapentane-1,5-diyl)bis(sodium hydrogen phosphonite) (V). Yield 93%. ^1H NMR spectrum, δ, ppm: 6.90 d (PH, $^1J_{PH}$ 506.4 Hz). ^{13}C NMR spectrum, δ_P, ppm: 27.70 d.d (C^1, $^1J_{PC}$ 86.8, $^2J_{PC}$ 10.3 Hz), 18.47 d (C^2, $^1J_{PC}$ 7.9 Hz). ^{31}P NMR spectrum, δ_P, ppm: 27.43 d ($2P^1$), –19.29 t (P^2), $^3J_{PP}$ 46.4 Hz. Found, %: C 35.30, H 4.59. $C_{10}H_{15}Na_2O_4P_3$. Calculated, %: C 35.52; H 4.47.

Sodium [2-(diphenylphosphino)ethyl](*N*-piperidinomethyl)phosphinate (VIa). Yield 95%. ^{13}C NMR spectrum, δ_C, ppm: 28.08 d.d (C^1, $^1J_{PC}$ 92.6, $^2J_{PC}$ 12.1 Hz), 21.57 d.d (C^2, $^1J_{PC}$ 11.8, $^2J_{PC}$ 4.5 Hz), 59.27 d (C^3, $^1J_{PC}$ 105.2 Hz), 56.80 d (C^4, $^3J_{PC}$ 4.9 Hz). ^{31}P NMR spectrum, δ_P, ppm: 34.09 d (P^1), –14.43 d (P^2), $^3J_{PP}$ 47.1 Hz. Found, %: C 60.26; H 6.69. $C_{20}H_{26}NNaO_2P_2$. Calculated, %: C 60.45; H 6.60.

Sodium (*N*-morpholinomethyl)[2-(diphenylphosphino)ethyl]phosphinate (VIb). Yield 95%. ^{13}C NMR spectrum, δ_C, ppm: 27.81 d.d (C^1, $^1J_{PC}$ 89.7, $^2J_{PC}$ 12.5 Hz), 21.79 d (C^2, $^1J_{PC}$ 12.1 Hz), 58.78 d (C^3, $^1J_{PC}$ 103.3 Hz), 55.60 d (C^4, $^3J_{PC}$ 7.5 Hz). ^{31}P NMR spectrum, δ_P, ppm: 34.16 d (P^1), –14.97 d (P^2), $^3J_{PP}$ 48.4 Hz). Found, %: C 56.83; H 6.16. $C_{19}H_{24}\cdot NNaO_3P_2$. Calculated, %: C 57.15; H 6.06.

The NMR spectra were obtained on a Varian VXR-400 spectrometer in $CDCl_3$ or D_2O (salts **IV**–**VI**) against TMS (^1H, ^{13}C) and 85% H_3PO_4 in D_2O (^{31}P).

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