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Synthesis of Functionalized 1-Trimethylsiloxy-Substituted *O*-Trimethylsilyl Alkylphosphonites and Their Derivatives

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ABSTRACT: *Nucleophilic addition of trimethylsilyl esters of tricoordinate organophosphorus acids to various functionalized aldehydes with vinyl, aryl, and heterocyclic fragments is proposed as a convenient method for the synthesis of new 1-trimethylsiloxysubstituted alkylphosphonites and their derivatives at mild conditions. Also the new functionalized derivatives of these phosphonites, including amino groups as well as certain properties of these compounds as important precursors of new functionalized 1-hydroxyalkylorganophosphorus acids, are presented.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:352–359, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20430

INTRODUCTION

Synthetically directed reaction of silyl esters of tricoordinate organophosphorus acids with organic compounds containing multiple bonds has been widely used to obtain various functionalized organophosphorus compounds [1,2]. Recently, we have synthesized new 2-substituted alkylphosphonites with aryl, heterocyclic, and organoelement fragments in high yields via the radical addition of bis(trimethylsiloxy)phosphine to functionalized alkenes [3,4]. Also the functionalized derivatives of organophosphorus acids, containing aryl, heterocyclic, or organoelement fragments, and various hydroxyl, amino, or amido groups have great interest as promising polydentate ligands in a series of catalytic systems and biologically active compounds as organophosphorus biomimetics of hydroxyl and amino acids [5,6]. In the present work, we report here the results of the nucleophilic addition of bis(trimethylsiloxy)phosphine, trimethylsilyl phosphites, and phosphonites to various functionalized aldehydes with aryl or heterocyclic fragments as well as crotonic and cinnamic aldehydes. These reactions provide a convenient synthetic route to new precursors of interesting functionalized 1-hydroxyalkyl phosphonic and phosphinic acids.

RESULTS AND DISCUSSION

In the present work, we showed that the reaction of bis(trimethylsiloxy)phosphine **A** with various functionalized unsaturated and aromatic aldehydes and development on its basis are a convenient route to functionalized *O*-trimethylsilyl trimethylsiloxymethylphosphonites **1–8**. So phosphine **A** in methylene chloride readily adds to the carbonyl group of various functionalized aldehydes to form

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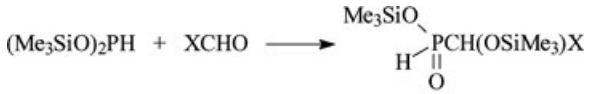
phosphonites **1–8** in high yields (Eq. (1); cf. [7, 8]).

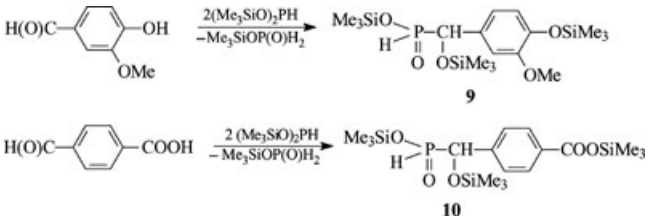


A **1–8**

X = CH=CHMe (**1**), CH=CHPh (**2**), Ph (**3**), 4-FC_6H_4 (**4**), 4-$MeOC_6H_4$ (**5**), 4-$Me_2NC_6H_4$ (**6**), 4-$MeOOCC_6H_4$ (**7**),  (**8**)

(1)

The reactions of aldehydes containing a hydroxyl or carboxy group in the aromatic ring with the excess of phosphine **A** under the similar conditions yield phosphonites **9** and **10**. Their formation is accompanied by trimethylsilylation of these groups (Eq. (2)).

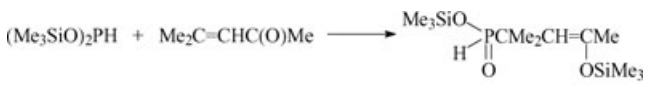


9

10

(2)

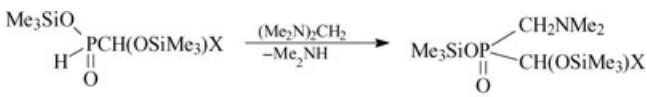
In contrast, the reaction of phosphine **A** with mesityl oxide proceeds exclusively by way of 1,4-addition involving the $POSiMe_3$ fragment to yield phosphonite **11** (Eq. (3)).



A **11**

(3)

To conclude, we proposed a convenient method to give the new trimethylsiloxy-substituted alkylphosphonites with aryl or heterocyclic fragments **1–11** (see Table 1), which are the promising synthons in organophosphorus chemistry. So readily accessible these *O*-trimethylsilyl trimethylsiloxymethylphosphonites **3–6** are smoothly aminomethylated with bis(dimethylamino)methane at 120–130°C in the presence of zinc chloride to form phosphinates **12–15** in high yields (Eq. (4); cf. [9]).

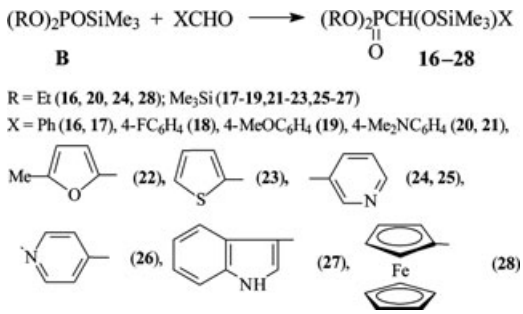


3–6 **12–15**

X = Ph (**12**), 4-FC_6H_4 (**13**), 4-$MeOC_6H_4$ (**14**),  (**15**)

(4)

Therefore, in this paper, we suggest convenient routes to trimethylsilyl derivatives of substituted dimethylaminomethyl(hydroxymethyl)phosphinic acids also containing various aromatic fragments (see Table 2), which are of great interest as potential ligands and biologically active compounds [5,6]. Also, it was found that silyl phosphites **B** smoothly add in methylene chloride to the carbonyl group of various aromatic aldehydes to form functionalized trimethylsiloxymethylphosphonates **16–28** in high yields (Eq. (5); cf. [10]).



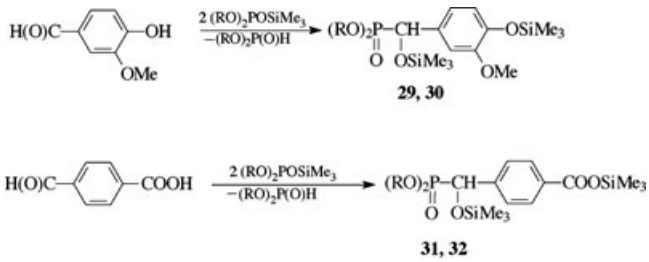
B **16–28**

R = Et (**16, 20, 24, 28**); Me_3Si (**17-19,21-23,25-27**)

X = Ph (**16, 17**), 4-FC_6H_4 (**18**), 4-$MeOC_6H_4$ (**19**), 4-$Me_2NC_6H_4$ (**20, 21**),

(5)

Arylaldehydes containing the hydroxyl or carboxy group in the aromatic ring react with the excess trimethylsilylphosphites **B** to form phosphonates **29–32**. Under these conditions, hydroxyl-containing groups are readily silylated (Eq. (6)).

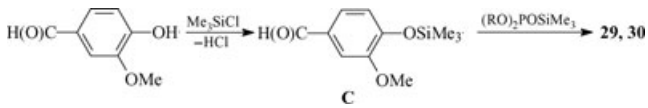


29, 30

31, 32

(6)

Phosphonates **29** and **30** are also formed by the addition of phosphites **B** to trimethylsilyl vanillin derivative **C** that was specially prepared by the reaction of vanillin with the excess of chlorotrimethylsilane (Eq. (7)).



C

(7)

We found the unique route to novel functionalized trimethylsiloxymethylphosphinates. So, 2-(triethylsilyl)ethyl- and indan-2-yl phosphonites, which were recently prepared by us [3,4], easily add to carbonyl groups of aromatic aldehydes to form corresponding phosphinates **33–36** in high yields

TABLE 1 Yields, Product Constants, and NMR Spectral Data for the HPC^1HC^2 Fragments[a] (δ, ppm; J, Hz) of Phosphonites **1–11**

No.	Yield (%)	Bp (°C) (p, mmHg), (mp, °C)	Ratio (%)	$\delta(H)$ C^1H, d	$^2J_{PH}$	$\delta(H)$ PH, d	$^1J_{PH}$	$\delta(C^1)$ d	$^1J_{PC}$	$\delta(C^2)$ d	$^2J_{PC}$	$\delta(P)$ s[c]
1	74	87 (1)	60	4.10	–	6.78	545.6	71.70	119.7	129.75	4.6	20.40
			40	4.30 m	–	6.70[b]	546.4	71.37	120.2	124.86	<1	22.36
2	81	139 (1)	60	4.45	–	6.82	555.2	72.75	116.3	123.80	5.1	19.76
			40	4.70 m	–	6.72[b]	557.2	73.03	116.3	124.86	<1	21.55
3	83	144 (2)	60	4.78	4.0	6.82	556.9	72.83	118.0	135.07	3.0	23.04
			40	4.67	11.9	6.72	556.9	73.47	117.0	135.48	<1	23.40
4	87	142 (2),	58	4.80	4.0	6.84	556.9	72.33	118.0	131.02	2.5[d]	22.39
		(49)	42	4.68	12.0	6.73	550.9	72.97	118.0	131.56	2.5[d]	23.25
5	86	172 (3)	55	4.67[b]	8.0	6.74[b]	552.9	72.44	120.2	126.90	3.0	22.74
			45	4.56[b]	10.0	6.65[b]	552.9	73.00	120.0	127.31	<1	23.44
6	83	159 (1)	53	4.69	4.0	6.80	548.9	72.75	121.9	122.19	2.5	23.09
			47	4.59	7.9	6.71	550.9	73.25	121.0	122.49	<1	23.81
7	85	116 (1),	61	4.95	8.0	6.90	560.0	72.43	116.0	129.29	<1	22.07
		(47)	39	4.84	12.0	6.78	560.0	73.07	115.0	129.48	<1	22.65
8	78	162 (2)	57	4.72	4.0	6.73	560.9	70.63	116.0	130.78	3.0	21.44
			43	4.60	13.9	6.65	562.8	71.16	117.0	131.26	<1	22.03
9	82	164 (1)	57	4.67[b]	8.0	6.77[b]	554.8	72.71	119.4	128.59	2.5	23.20
			43	4.54[b]	12.0	6.70[b]	554.9	73.33	119.4	128.83	<1	22.93
10	82	178 (1),	59	5.01[b]	7.9	6.99[b]	562.8	72.97	115.0	131.04	4.0	22.38
		(66)	41	4.89	13.8	6.85	560.8	73.66	114.0	131.24	4.0	23.15
11	86	97 (1)	[e]	4.92	8.8	6.87	533.2	36.25	94.3	107.60	4.2	28.54

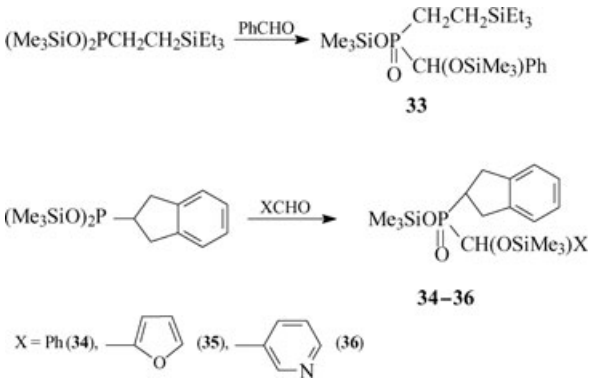
[a] In ^1H NMR spectra, the signals of these fragments for stereoisomers of **1** and **2** are multiplets and partially or completely overlap; all signals of the alkyl, aryl, trimethylsilyl, and 3-pyridyl fragments are in the standard area. In ^{13}C NMR spectra, the C^3 and C^4 signals of fragments $PC^1H_nC^2H{=}C^3H_mC^4$: **1**, 129.31 d (C^3, $^3J_{PC}$ 13.8), 18.5 s (C^4); **2**, 132.39 d (C^3, $^3J_{PC}$ 12.3), 136.72 d (C^4, $^4J_{PC}$ 7.1); **11**, 149.39 d (C^3, $^3J_{PC}$ 11.7), 23.62 d (C^4, $^4J_{PC}$ 2.7). The signals of C=O fragments, s: **7**, 165.97, and 166.07; **10**, 166.35 and 166.29. A ratio of isomers was determined from the ^1H and ^{31}P NMR spectra.
[b] dd, all $^3J_{HH}$ 4.
[c] Data of $^{31}P\{^1H\}$ spectra.
[d] In ^{13}C NMR spectra, 131.02 t (C^2, $^2J_{PC} = {}^4J_{FC}$ 2.5), 131.56 d (C^2, $^4J_{FC}$ 2.5); 162.14 d (CF, $^1J_{FC}$ 246.3), the same signals for two isomers.
[e] The compound **11** consists of one isomer.

TABLE 2 Yields, Product Constants, and NMR Spectral Data for the PC^1HC^2 and $PC^3H_2NC^4H_3$ Fragments[a] (δ, ppm; J, Hz) of Phosphinates **12–15** and Sodium Phosphinates **51–54**

No.	Yield (%)	Bp (°C) (p, mmHg), (mp, °C)	$\delta(H)$ C^1H, d	$^2J_{PH}$	$\delta(H)$ C^4H_3, s	$\delta(C^1)$ d	$^1J_{PC}$	$\delta(C^2)$ s	$\delta(C^3)$ d	$^1J_{PC}$	$\delta(C^4)$ d	$^3J_{PC}$	$\delta(P)$ s
12	91	140 (1)	4.95	8.0	2.23	71.37	113.0	136.46	54.30	112.0	47.30	10.0	36.16
			4.85	12.0	2.15	72.06	114.0	136.15	54.30	112.0	47.13	10.0	35.56
13	74	130 (1),	5.06	8.0	2.36	71.16	115.3	132.53	54.87	113.6	47.74	9.9	35.98
		(72)	4.94	11.0	2.29	72.35	117.8	133.03	54.78	110.3	47.55	9.9	35.60
14	78	152 (1)	4.96	8.0	2.29	71.30	117.8	128.49	54.75	111.9	47.54	9.9	36.25
			4.85	10.0	2.22	71.96	117.0	128.98	54.62	110.3	47.42	11.1	35.89
15	70	144 (1)	4.91	9.0	2.17	69.38	114.4	132.78	54.47	114.4	47.28	10.8	35.50
			4.82	11.8	2.09	69.95	116.9	132.95	54.65	112.8	47.15	10.0	35.07
51	95	[b]	4.81	8.0	2.30	74.32	101.0	138.01	56.20	101.0	46.49	3.0	30.69
52	96	[b]	4.81	8.0	2.31	73.05	102.0	133.76	56.25	101.0	46.50	8.0	30.47
53	96	[b]	4.76	8.0	2.33	73.20	104.0	130.53	56.17	100.0	46.47	7.0	30.56
54	94	[b]	4.84	12.0	2.89	70.78	115.0	133.48	56.46	84.0	45.35	3.0	23.17

[a] All signals of alkyl, trimethylsilyl, aryl, and 3-pyridyl fragments are in the standard area. According to the NMR spectra, compounds **12–15** are mixtures of two stereoisomers. Their ratio was determined from the ^1H NMR and ^{31}P NMR spectra as 55:45 for all phosphinates **12–15**. The spectral parameters of the major isomer are given first. The signals of the diastereotopic protons of methylene groups C^3H_2 of **12–15** and **51–54** are characteristic of ABX multiplets in the range of 2–3 ppm. In the spectra of stereoisomers of phosphinates **12–15** and **51–54**, the signals of these protons partially overlap. The signals of the protons of C^4H_3 groups are doublets for two isomers of compounds: **14** ($^4J_{PH}$ 4), **15** ($^4J_{PH}$ 2.2). In ^{13}C NMR spectra, the signals of compounds: **12**: 136.15 d (C^2, $^2J_{PC}$ 3); **13**: 132.53 t (C^2, $^2J_{PC} = {}^4J_{FC}$ 3.3), 133.03 d (C^2, $^4J_{FC}$ 2.3), 162.37 d (CF, $^1J_{FC}$ 245.5), 162.50 d (CF, $^1J_{FC}$ 246.3); **15**: 132.25 d (C^2, $^2J_{PC}$ 3.3). For compounds **12**, **14**, **15**; n_D^{20}: 1.4797, 1.4875, 1.4815, respectively.
[b] The salts **51–54** are decomposed by heating; therefore, their melting points were not measured.

(Eq. (8)).



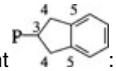
(8)

Thus we propose a convenient method for the synthesis of new functionalized trimethylsiloxymethylphosphonates **16–32** and phosphinates **33–36** including various aryl and heterocyclic fragments (see Table 3).

Trimethylsilyl esters of several functionalized organophosphorus acids were useful to obtain a series of water-soluble acids and their sodium salts (cf. [1–4]). So 1-trimethylsiloxyalkylphosphonites **1–10** smoothly react with diluted solutions of sodium methylate in methanol, giving stable crystalline sodium salts of 1-hydroxyalkylphosphonous acids **37–46** (see Table 4; Eq. (9)).

TABLE 3 Yields, Product Constants, and NMR Spectral Data for the PC^1HC^2 Fragments[a] (δ, ppm; J, Hz) of Phosphonates **16–32**[a] and Phosphinates **33–36**[a]

No.	Yield (%)	Bp (°C) (p, mmHg), (mp, °C)	$\delta(H)\ C^1H$, d	$^2J_{PH}$	$\delta(C^1)$ d	$^1J_{PC}$	$\delta(C^2)$ s	$\delta(P)$ s
16	87	145 (3)	4.60	14.0	71.12	170.6	136.58	17.45
17	85	142 (3)	4.66	14.8	72.01	178.4	137.82	1.17
18	83	133 (1), (69)	4.51	12.0	71.31	178.0	133.79	3.28
19	80	152 (2)	4.62	12.0	71.76	180.0	129.92	3.96
20	83	182 (3)	4.50	12.8	68.91	163.2	124.76	18.30
21	89	164 (1), (55)	4.64	16.0	71.76	182.0	125.16	4.44
22	81	144 (2)	4.77	12.0	66.17	188.0	151.94	0.49
23	78	142 (1)	4.74	12.5	70.85	181.4	144.02	3.24
24	78	152 (2)	4.70	14.4	69.25	172.5	132.94	16.51
25	82	146 (1), (42)	4.85	16.0	70.12	179.0	148.96[b]	2.69
26	84	172 (3)	4.66	16.0	70.98	175.0	147.57	1.81
27	90	(92)	4.72	12.4	73.49	174.2	111.67	4.64
28[c]	80	174 (1)	4.60	13.2	68.40	165.7	84.99[b]	16.72
29	81	168 (1)	4.73	12.0	71.56	172.0	130.60	20.64
30	85	170 (1), (60)	4.73	16.0	72.17	180.0	131.74	4.08
31	82	182 (1)	4.95	16.0	71.57	170.0	130.84	19.36
32	83	194 (2), (65)	4.98	16.0	72.07	177.0	130.64	2.79
33	86	157 (1)	4.99	7.2	74.11	109.9	138.16	39.87
			4.83	10.0	74.46	111.9	138.02	38.68
34	83	182 (1), (92)	4.91	9.6	74.09	114.9	137.17[b]	40.45
			5.03	7.6	74.04	115.3	137.10	39.42
35	82	169 (1)	4.79	10.0	66.86	119.8	149.77	37.38
			4.82	10.8	67.78	118.6	150.00	36.66
36	85	187 (1), (83)	4.68	9.2	70.70	114.4	132.31	38.81
			4.79	7.2	71.19	112.5	132.55	39.51

[a]All signals of alkyl, trimethylsilyl, aryl, and heterocyclic fragments are in the standard area. Compounds **33–36** are the mixtures of two stereoisomers in ratio 60:40 (**33,34**) and 55:45 (**35,36**), which were measured by ^1H and ^{31}P NMR. The spectral parameters of major isomer are given first. In ^{13}C NMR spectra, the signals of compounds: **18**, 162.05 d (CF, $^1J_{CF}$ 246.1); fragment C═O, s: **31**, 166.30; **32**, 169.47; fragment $P^1C^3H_2C^4H_2Si$: **33**, 20.71 d (C^3, $^1J_{PC}$ 90.7), 1.97 d (C^4, $^2J_{PC}$ 7.5) and fragment  : 20.46 d (C^3, $^1J_{PC}$ 88.6), 2.31 d (C^4, $^2J_{PC}$ 7.8); **34**, 34.74 d (C^3, $^1J_{PC}$ 95.4), 32.94 s (C^4), 33.39 s (C^4), 141.98 d (C^5, $^3J_{PC}$ 9.3); 142.09 d (C^5, $^3J_{PC}$ 8.2) and 35.16 d (C^3, $^1J_{PC}$ 96.3), 33.74 s (C^4), 34.07 s (C^4), 141.83 d (C^5, $^3J_{PC}$ 9.2), 141.98 d (C^5, $^3J_{PC}$ 9.3); **35**, 34.97 d (C^3, $^1J_{PC}$ 96.7), 32.34 s (C^4), 32.82 s (C^4), 141.32 d (C^5, $^3J_{PC}$ 10.6); 141.42 d (C^5, $^3J_{PC}$ 11.3) and 37.44 d (C^3, $^1J_{PC}$ 97.4), 32.76 s (C^4), 33.14 s (C^4), 141.01 d (C^5, $^3J_{PC}$ 12.1), 141.10 d (C^5, $^3J_{PC}$11.9); **36**, 37.26 d (C^3, $^1J_{PC}$ 98.1), 31.11 s (C^4), 31.37 s (C^4), 140.38 d (C^5, $^3J_{PC}$ 9.0); 140.43 d (C^5, $^3J_{PC}$ 10.5) and 33.80 d (C^3, $^1J_{PC}$ 95.6), 32.12 s (C^4), 32.53 s (C^4), 140.84 d (C^5, $^3J_{PC}$ 9.1), 140.88 d (C^5, $^3J_{PC}$ 8.9). Note that the two $C^4H_2C^5$ groups in compounds **34–36** are nonequivalent and give different signals in the ^{13}C NMR spectra for each isomer (cf. [4]).

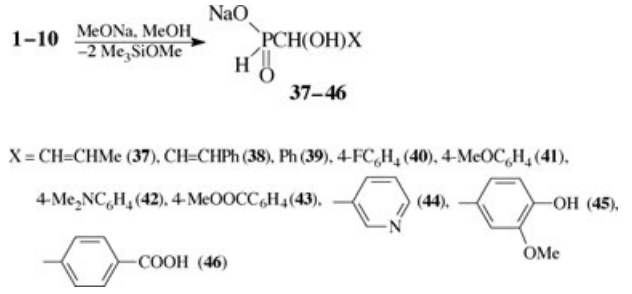
[b]d, $^2J_{PC}$: **25**, 3.0; **28**, 4.7; **34**, 4.0.

[c]Cherry-red liquid.

TABLE 4 Yields, Product Constants, and NMR Spectral Data for the $HPC^1HC^2C^3$ Fragments[a] (δ, ppm; J, Hz) of Sodium Phosphonites **37–47**[a]

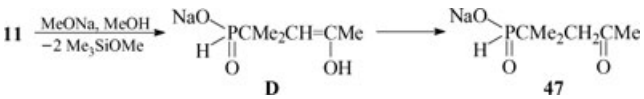
No.	Yield (%)	$\delta(H)$ C^1H, d	$^2J_{PH}$	$\delta(H)$ PH, d	$^1J_{PH}$	$\delta(C^1)$ d	$^1J_{PC}$	$\delta(C^2)$ s	$\delta(C^3)$ d	$^3J_{PC}$	$\delta(P)$ s[b]
37	95	[c]	–	6.69	514.4	72.08	106.9	130.60[c]	125.02 s	–	24.93
38	96	[c]	–	6.78	525.2	72.58	105.5	131.69[c]	124.87 s	–	23.97
39	95	4.62	8.0	6.82	522.3	72.78	104.0	130.67	127.94	6.2	26.98
40	95	4.60	8.0	6.75	520.0	73.01	105.3	133.07	128.65[d]	5.8	26.30
41	97	4.57	7.9	6.76	517.2	72.98	106.2	129.63	128.49	6.1	27.13
42	96	4.52	8.0	6.76	516.0	73.29	106.0	128.22	128.15	6.0	26.97
43[e]	97	4.78	8.0	6.84	524.0	73.52	101.0	128.38	126.70	5.2	25.91
44	97	4.66	8.1	6.77	524.2	71.34	104.1	133.73	146.99 135.87 s	5.0 –	25.16
45	96	4.51	7.8	6.76	516.4	73.09	105.2	129.54	110.96 119.80	4.2 6.0	26.71
46[e]	97	4.80	8.2	6.87	526.3	73.89	102.0	129.26	126.28	5.0	25.64
47	94	2.55[f]	11.2	6.57	506.1	33.65	92.6	48.07	214.78	12.3	37.13

[a]The salts **37–47** are very hydroscopic crystals; therefore, their melting points were not measured. In ^1H NMR spectra, all signals of the alkyl, vinyl, phenyl, and ferrocenyl fragments are in the standard area.
[b]Data of $^{31}P\{^1H\}$ spectra.
[c]The C^1H proton signals are multiplets in the range 4–4.4 ppm and the $C^2H{=}C^3H$ proton signals, in the range of 5.4–6.3 ppm; in ^{13}C NMR spectrum, (C^2H, d): **37**, $^2J_{PC}$ 11.7; **38**, $^2J_{PC}$ 10.8.
[d]dd, $^2J_{FC}$ 8.3.
[e]In ^{13}C NMR spectrum, δ(C═O), s: **43**, 169.01; **46**, 169.33.
[f]Fragment $C^1Me_2C^2H_2C^3(O)Me$, ^1H NMR spectrum: 1.04 d (Me_2, $^3J_{PH}$ 16.8), 2.20 s (Me); ^{13}C NMR spectrum: 19.82 s (Me_2), 32.10 s (Me).



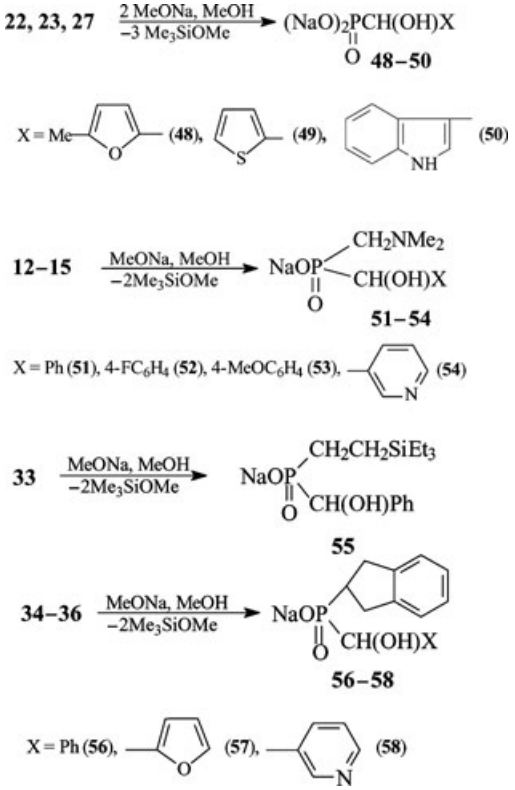
(9)

Note that the methanolysis of phosphonite **11** is accompanied by the rearrangement of the intermediate unstable enol **D**, forming salt **47** (Eq. (10)).



(10)

Also the treatment of phosphonates **22, 23, 27** and phosphinates **12–15** and **33–36** with the diluted solution of sodium methylate in methanol results in water-soluble disodium phosphonates **48–50** and sodium phosphinates **51–58** as white hygroscopic crystals (Eq. (11)).



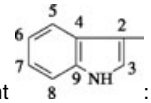
(11)

Also phosphonates **17–19, 21, 25, 26, 30, 32** were easily transformed to corresponding

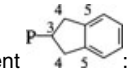
TABLE 5 Yields, Product Constants, and NMR Spectral Data for the PC^1HC^2 Fragments[a] (δ, ppm; J, Hz) of Disodium Phosphonates **48–50**, Sodium Phosphinates **55–58**, and Phosphonic Acids **59–66**[a]

No.	*Yield (%)*	*$\delta(H)$ C^1H, d*	*$^2J_{PH}$*	*$\delta(C^1)$ d*	*$^1J_{PC}$*	*$\delta(C^2)$ s*	*$\delta(P)$ s*
48	95	4.51	12.1	66.45	148.1	152.07	13.32
49	94	4.81	12.0	69.35	146.2	144.55	14.02
50[b]	95	4.67	12.2	77.56	154.3	114.69	16.92
55[c]	97	4.78	7.5	75.26	104.5	136.52	33.65
56[d]	98	4.80	9.8	72.48	105.7	137.26	34.65
57[d]	97	4.65	10.2	69.57	106.4	151.49	33.14
58[d]	96	4.75	12.0	71.72	104.8	133.06	34.53
59	97	4.69	16.1	70.80	159.2	140.46	18.83
60	96	4.70	12.1	70.05	160.0	136.67	18.51
61	98	4.63	12.0	70.23	160.0	132.28	20.76
62	96	4.54	12.2	70.51	161.0	128.09	19.44
63	97	5.02	16.0	65.10	183.1	152.30	13.54
64	96	5.04	16.1	69.94	178.2	150.22	12.70
65[e]	95	4.20	16.0	80.85	164.0	127.41	16.16
66[f]	97	4.78	16.2	70.69	157.5	129.66	17.68

[a]The melting point of compounds (in °C): **59**, 168; **60**, 69; **61**, 78; **62**, 152; **65**, 144. The other acids and salts are very hygroscopic crystals; therefore, their melting points were not measured. In ^1H and ^{13}C NMR spectra, all signals of the alkyl, aryl, and heterocyclic fragments are in the standard area. In ^{13}C NMR spectra.

[b]Fragment  : 127.55 d (C^3, $^3J_{PC}$ 5.1); 130.47 d (C^4, $^3J_{PC}$ 8.0) 121.28 s, 121.64 s, 123.52 s (C^5, C^6, C^7), 113.83 s (C^8), 137.82 s (C^9).

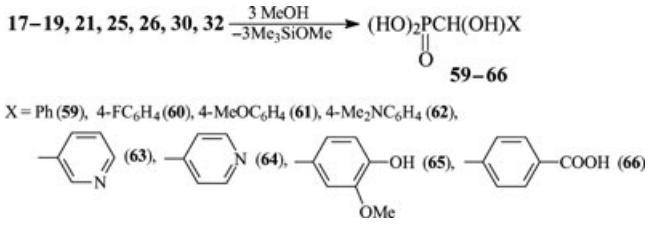
[c]Fragment $PC^3H_2C^4H_2Si$: 20.04 d (C^3, $^1J_{PC}$ 87.5), 1.89 d (C^4, $^2J_{PC}$ 7.2).

[d]Fragment  : **56**, 36.59 d (C^3, $^1J_{PC}$ 96.7), 33.45 s (C^4), 33.78 s (C^4), 142.95 d (C^5, $^3J_{PC}$ 10.3); 143.39 d (C^5, $^3J_{PC}$ 10.1); **57**, 36.79 d (C^3, $^1J_{PC}$ 97.3), 33.38 s (C^4), 33.48 s (C^4), 143.30 d (C^5, $^3J_{PC}$ 10.1); 143.40 d (C^5, $^3J_{PC}$ 10.1); **58**, 35.72 d (C^3, $^1J_{PC}$ 95.8), 33.51 s (C^4), 33.85 s (C^4), 142.97 d (C^5, $^3J_{PC}$ 10.0); 143.21 d (C^5, $^3J_{PC}$ 9.8).

[e]C_{Ar}–O: 146.64 s, 147.59 s.

[f] C═O: 167.8.

phosphonic acids **59–66** in high yields (Eq. (12)).



(12)

Synthesized salts **48–58** and acids **59–66** are white hygroscopic crystals (see Tables 2 and 5) and may be used as water-soluble ligands in promising catalytic complexes as well as biologically active compounds (cf. [5, 6]). The elemental analysis data of some synthesized compounds are summarized in Table 6.

EXPERIMENTAL

The ^1H, ^{13}C, and ^{31}P NMR spectra were registered on the Varian VXR-400 and Bruker Avance-400 spectrometers (400, 100, and 162 MHz, respectively) in $CDCl_3$ (**1–36**) or D_2O and $(CD_3)_2SO$ (**37–66**) against TMS (^1H, ^{13}C) and 85% H_3PO_4 in D_2O (^{31}P). All reactions were carried out under dry argon in anhydrous solvents.

*O-Trimethylsilyl-1-(trimethylsiloxy)but-2-enylphosphonite (**1**)*

To a solution of 35 g of phosphine **A** in 60 mL of methylene chloride, a solution of 8.5 g of crotonic aldehyde in 30 mL of methylene chloride was added dropwise with stirring and cooling to 10°C. The reaction mixture was kept for 1 h at 20°C, the solvent was then removed, and the residue was distilled in a vacuum to obtain 25.2 g of phosphonite **1**.

Phosphonites **2–11** were prepared similarly.

*O-Trimethylsilyl(dimethylaminomethyl)[phenyl-(trimethylsiloxy)methyl]phosphinate (**12**)*

A mixture of 7.6 g of *O*-trimethylsilyl[phenyl-(trimethylsiloxy)methyl]phosphonite **3**, 4.9 g bis-(dimethylamino)methane, and 0.1 g zinc chloride

TABLE 6 Elemental Analyses Data of Synthesized Compounds[a]

No.	Empirical Formula	Formula Weight	Calcd. (%)		Found (%)	
			C	H	C	H
16	$C_{14}H_{25}O_4PSi$	316.41	53.14	7.96	52.93	7.88
20	$C_{16}H_{30}NO_4PSi$	359.49	53.46	8.41	53.28	8.30
24	$C_{13}H_{24}NO_4PSi$	317.40	49.19	7.62	48.87	7.54
28	$C_{18}H_{29}FeO_4PSi$	424.34	50.95	6.89	50.83	6.81
29	$C_{18}H_{35}O_6PSi_2$	434.62	49.74	8.12	49.57	8.03
31	$C_{18}H_{33}O_6PSi_2$	432.60	49.98	7.69	49.71	7.60
37	$C_4H_8NaO_3P$	158.07	30.39	5.10	30.02	5.14
38	$C_9H_{10}NaO_3P$	220.13	49.10	4.58	48.83	4.69
39	$C_7H_8NaO_3P$	194.10	43.32	4.15	43.08	4.09
40	$C_7H_7FNaO_3P$	212.10	39.64	3.33	39.49	3.38
41	$C_8H_{10}NaO_4P$	224.13	42.87	4.50	42.69	4.57
42	$C_9H_{13}NNaO_3P$	237.17	45.58	5.52	45.40	5.57
43	$C_9H_{10}NaO_5P$	252.14	42.87	4.00	42.65	4.08
44	$C_6H_7NNaO_3P$	195.10	36.94	3.62	36.81	3.70
45	$C_8H_{10}NaO_5P$	240.13	40.02	4.20	39.86	4.22
46	$C_8H_8NaO_5P$	238.11	40.36	3.38	40.28	3.43
47	$C_6H_{12}NaO_3P$	186.12	38.72	6.50	38.49	6.64
48	$C_6H_7Na_2O_5P$	236.08	30.53	2.99	30.35	3.03
49	$C_5H_5Na_2O_4PS$	238.12	25.22	2.12	25.07	2.05
50	$C_9H_8NNa_2O_4P$	271.12	39.87	2.97	39.68	2.92
51	$C_{10}H_{15}NNaO_3P$	251.20	47.81	6.02	47.65	6.09
52	$C_{10}H_{14}FNNaO_3P$	269.19	44.62	5.24	44.49	5.28
53	$C_{11}H_{17}NNaO_4P$	281.22	46.98	6.09	46.81	6.16
54	$C_9H_{14}N_2NaO_3P$	252.18	42.87	5.60	42.68	5.66
55	$C_{15}H_{26}NaO_3PSi$	336.43	53.55	7.79	53.41	7.72
56	$C_{16}H_{16}NaO_3P$	310.27	61.94	5.20	61.72	5.22
57	$C_{14}H_{14}NaO_4P$	300.22	56.01	4.70	55.66	4.65
58	$C_{15}H_{15}NNaO_3P$	311.26	57.88	4.86	57.61	4.78
59	$C_7H_9O_4P$	188.12	44.69	4.82	44.52	4.74
60	$C_7H_8F\ O_5P$	206.11	40.79	3.91	40.65	4.05
61	$C_8H_{11}O_5P$	218.15	44.05	5.08	43.90	5.12
62	$C_9H_{14}NO_4P$	231.19	46.76	6.10	46.64	6.16
63	$C_6H_8NO_4P$	189.11	38.11	4.26	37.94	4.12
64	$C_6H_8NO_4P$	189.11	38.11	4.26	37.89	4.15
65	$C_8H_{11}O_6P$	234.15	41.04	4.74	40.92	4.81
66	$C_8H_9O_6P$	232.13	41.39	3.91	41.23	3.86

[a]The other compounds are unstable in the air atmosphere; therefore, these substances were analyzed as their sodium salts.

was heated at 110–140°C for 1.5 h and then was distilled to give 8.2 g of phosphinate **12**.

Phosphinates **13–15** were prepared similarly.

*O,O-Diethyl-phenyl(trimethylsiloxy)methylphosphonate (**16**)*

To a solution of 12.6 g of diethyl trimethylsilyl phosphite in 30 mL of methylene chloride, a solution of 5.3 g of benzaldehyde in 10 mL of methylene chloride was added dropwise with stirring at 10°C. The reaction mixture was stirred for 0.5 h and heated to boil. The solvent was removed, and the residue was distilled in a vacuum to give 13.8 g of phosphonate **16** (cf. [10]).

Phosphonates **17–32** and phosphinates **33–36** were prepared similarly. Phosphonate **27** was crystallized from hexane.

*3-Methoxy-4-(trimethylsiloxy)benzaldehyde (**C**)*

A mixture of 7.6 vanillin and 30 g of chlorotrimethylsilane was refluxed under argon until hydrogen chloride no longer evolved. The solvent was removed, and the residue was distilled in vacuum to give 8.7 g (87%) of compound **C**, bp 133°C (1 mmHg). The ^{1}H NMR spectrum, δ (ppm): 0.24 s (CH_3Si), 3.83 s (CH_3O), 6.9–7.4 m (C_6H_3), 9.80 s (CHO). ^{13}C NMR spectrum, δ_C (ppm): 0.45 s (CH_3Si), 55.40 s (CH_3O), 150.81 s, and 151.44 s (OC=), 190.87 s (CHO).

*Sodium(1-hydroxybut-2-enyl)phosphonite (**37**)*

To 60 mL of methanol, a solution of 18 g of phosphonite **1** in 20 mL of diethyl ether was added at 10°C with stirring and cooling, followed by a solution of 3.7 g of sodium in 75 mL of methanol. The resulting

mixture was heated to the boil, the solvent was removed in a vacuum, and the residue was kept in a vacuum (1 mm) for 1 h to obtain 9.6 g of salt **37** as colorless hygroscopic crystals.

The salts **38–58** were obtained similarly.

*Phenyl(hydroxy)methylphosphonic acid (**59**)*

A solution of 10.5 g of phosphonate **17** in 10 mL of diethyl ether was added dropwise with stirring at 10°C to 30 mL of methanol. The resulting mixture was heated to boil, the solvent was distilled in a vacuum, and the residue was kept in vacuum (1 mmHg) for 1 h to give 4.7 g of acid **59** as colorless hygroscopic crystals (cf. [11]).

The acids **60–66** were obtained similarly.

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