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5-Phosphorylated 1,2-Disubstituted Imidazoles

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ABSTRACT: *1,2-Disubstituted imidazoles react with phosphorus(III) halides in pyridine regioselectively at position 5. The reaction proceeds the more readily, the higher the electron-donating ability of the 2-substituent in the starting imidazole. Hitherto unknown dihalo(imidazol-5-yl)phosphines have been obtained, and their properties have been studied. Also synthetic methods for the preparation of various monohalo(organyl)(imidazolyl)phosphines have been developed.* © 2009 Wiley Periodicals, Inc. Heteroatom Chem 20:289–308, 2009; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20550

INTRODUCTION

C-Phosphorylated imidazoles have attracted considerable pharmaceutical and synthetic interest because a number of them are remarkable for their high biological activity and also represent promising ligands for metal complex catalysis [1,2]. Moreover, 4(5)-phosphorylated imidazole derivatives can serve as reactants for the synthesis of phosphorus-containing purine analogues [3,4] and function as ligands in metalloenzymes [5], selective inhibitors of nucleoside deaminases, glycosyl- and acetyltransferases [6,7], and neuromediator antagonists [8] in metabolic regulation.

The compounds concerned are studied for about two decades, and a series of synthetic approaches are currently available to obtain imidazolylphosphonates and tertiary phosphines as, for instance, the Pd-catalyzed reaction of 4(5)-imidazolyl bromides or iodides with phosphites [3,6], cyclization of functionalized phosphonates [8–10], condensation of diethyl(2,2-dichloro-1-isocyanoethenyl)phosphonate [11] or diethyl α-aminocyanomethylphosphonate [4] with primary amines, and the reaction of Li and Mg derivatives of disubstituted imidazoles with phosphorus acid chlorides [5,7,12]. However, some key functional compounds such as imidazol-4(5)-yl-halo- or dihalophosphines remained unknown until our research.

As previously reported, 1,3-azoles can be directly C-phosphorylated with phosphorus(III) halides in pyridine in the presence of Et_3N [13]. Under such conditions, 1-alkylimidazoles readily react with $PHal_3$ to give 2-phosphorylated products [14], whereas 1-aryl-2-methylimidazoles undergo phosphorylation at the methyl group [15]. The latter work also included reaction of 1-methyl-2-methylthioimidazole with PCl_3 at position 5, though only the ^{31}P NMR characterization data for the final product is present.

Here we address phosphorylation of 1,2-disubstituted imidazoles with phosphorus(III) halides focusing on the features that influence the readiness of the reaction. The objective of the study is 1-methyl-2-R-substituted imidazoles **1a–c** with the 2-substituent sterically and electronically varied (R = NMe_2 (a), SMe (b), Ph (c)). As phosphorylating agents, we used phosphorus trihalides

Phosphorylated Azoles. Part IV.

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TABLE 1 Reaction Conditions for the Synthesis Of Phosphines **7a–c** by Phosphorylation with Ph_2PHal

	NMe_2 (a)	SMe (b)	Ph (c)	
	Ph_2PCl	Ph_2PBr	Ph_2PBr	
	20°C	30°C	100°C	20°C
Reaction time	22 h	8 days	54 h	–
Yield (%)	84	70	54	–

$PHal_3$ (Hal=Cl; Br; see Table 1), easily available functionalized dihalophosphines $RPHal_2$ (R=Ph; CCl_3; CCl_2=CCl, Me_2N), and diphenylhalo+ Ph_2PHal (Hal=Cl; Br).

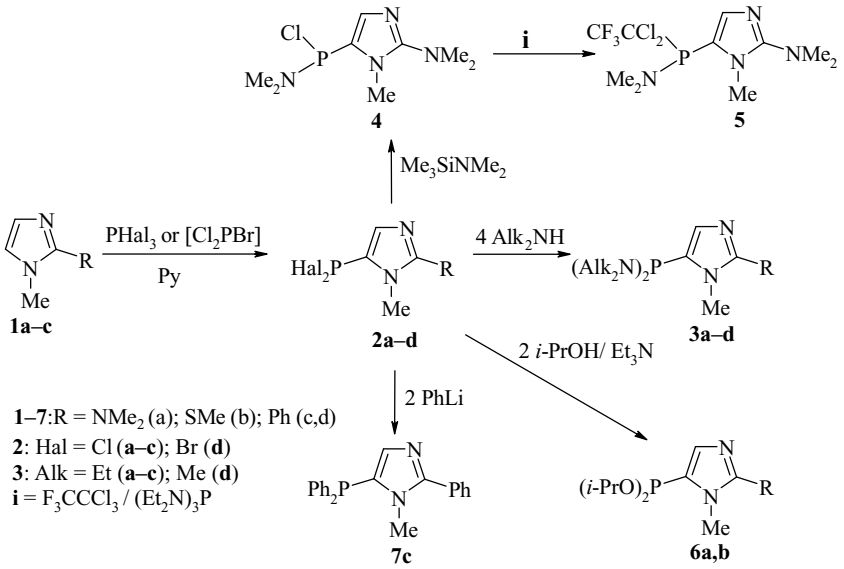
RESULTS AND DISCUSSION

Phosphorylation with Phosphorus(III) Halides: Synthesis of Imidazol-5-yl-phosphonous Dihalides

As it was found that imidazoles **1a–c** reacted with $PHal_3$ in pyridine in a 2:1 ratio to give imidazol-5-yl-phosphonous dihalides **2a–d** (Scheme 1). Among the peculiarities of this reaction, we note that the presence of triethylamine leads to tar formation and an increased amount of by-products, unlike the analogous phosphorylation of 1,3-azoles [13,14]. With a stronger base, diisopropylethylamine, the reaction proceeds likewise so that the target phosphorylated products cannot be detected even spectroscopically. Using the starting imidazole as a hydrogen chloride acceptor, it is possible to suppress tar formation and to increase target product yields (e.g., from 49% to 92% for dichloride **2a**). Although the reaction is generally performed with 2 equiv of imidazoles **1a–c**, a two- to three-fold $PHal_3$ excess is needed for only monohalo substitution to occur. It is noteworthy that on longer heating at 120°C, imidazole **1c** reacts with PCl_3 in a 1:1 ratio, with HCl finally captured by pyridine.

The most reactive is imidazole **1a** bearing a strong electron-donating NMe_2 group at position 2; its reaction with PCl_3 is complete at 20°C within 2 h. Compounds **1b**,**c** containing less electron-donating 2-substituents, the SMe and Ph groups, respectively, are phosphorylated with PCl_3 very slowly at 20°C but, if heated to 100°C, the reaction is completed within 3 h for **1b** and 48 h for **1c**. The heating of **1b** at 100°C for more than 3 h is useless because under these conditions imidazole hydrochloride can be dealkylated [16], thus leading to SH-phosphorylation and hence to a mixture of products. It has been found that it is conveniently to prepare phosphonous dichlorides using Cl_2PBr (a mixture of PCl_3 and PBr_3 in $2n$:1 ratio, where $n \geq 1$); in this case (method B), the reaction with **1c** is completed at 120°C within 2 h. A stronger phosphorylating agent, PBr_3, reacts with **1c** at 20°C within 8 days to afford phosphonous dibromide **2d**. Compounds **2a–d** appear as pale yellow viscous liquids most readily hydrolyzed by atmospheric moisture and can be distilled in vacuo without decomposition (Table 2).

Like arylphosphonous dihalides, dihalides **2a–d** actively react with N-, O-, and C-nucleophiles



SCHEME 1

TABLE 2 Physical and Analytical Data of 5-Phosphorylated 1,2-Disubstituted Imidazoles

Compound	Yield (%)	Mp (°C) (Cryst. solvent) Bp/pressure, (°C)/Torr	Molecular Formula	Found (Calcd) (%)	
				N	P
2a	92	83–85/0.02	$C_6H_{10}Cl_2N_3P$	18.77 (18.59)	13.62 (13.70)
2b	90	67–69; 104–106/0.02	$C_5H_7Cl_2N_2PS$	12.04 (12.23)	13.48 (13.52)
2c	62	145–150/0.05	$C_{10}H_9Cl_2N_2P$	10.55 (10.81)	10.87 (11.96)
2d	64	186–190/0.05	$C_{10}H_9Br_2N_2P$	8.01 (8.06)	8.94 (8.90)
3a	53	154–156/0.03	$C_{14}H_{30}N_5P$	23.15 (23.39)	10.25 (10.35)
3b	48	136–139/0.02	$C_{13}H_{27}N_4PS$	18.68 (18.53)	10.27 (10.24)
3c	54	135–140/0.02	$C_{18}H_{29}N_4P$	16.67 (16.85)	9.24 (9.32)
3d	75	140–141/0.02	$C_{14}H_{21}N_4P$	20.20 (20.28)	11.10 (11.21)
4	83	110–120/0.05	$C_8H_{16}ClN_4P$	23.84 (23.88)	13.07 (13.20)
5	73	64–66 (pentane)	$C_{10}H_{16}Cl_2F_3N_4P$	15.90 (15.96)	8.80 (8.82)
6a	76	106–107/0.02	$C_{12}H_{24}N_3O_2P$	15.30 (15.37)	11.27 (11.33)
6b	82	94–95/0.02	$C_{11}H_{21}N_2O_2PS$	10.05 (10.14)	11.16 (11.21)
7a	84	162–165/0.02	$C_{18}H_{20}N_3P$	13.70 (13.58)	10.15 (10.01)
7b	42	165–175/0.02	$C_{17}H_{17}N_2PS$	8.86 (8.97)	9.86 (9.92)
7c	54	100–103/0.05	$C_{22}H_{19}N_2P$	8.05 (8.18)	9.04 (9.05)
8a	56	Oil	$C_{14}H_{30}N_5PS$	21.15 (21.13)	9.31 (9.34)
8b	91	64–66 (pentane)	$C_{13}H_{27}N_4PS_2$	16.60 (16.75)	9.22 (9.26)
8c	95	98–100 (hexane)	$C_{18}H_{29}N_4PS$	15.33 (15.37)	8.42 (8.50)
8d	83	101–102 (cyclohexane)	$C_{14}H_{21}N_4PS$	18.04 (18.17)	10.08 (10.04)
8e	73	65–67 (heptane)	$C_{12}H_{24}N_3O_2PS$	13.68 (13.76)	10.12 (10.14)
8f	66	Oil	$C_{11}H_{21}N_2O_2PS_2$	9.10 (9.08)	9.96 (10.04)
10a	44	Oil	$C_{14}H_{30}N_5OP$	22.17 (22.21)	9.77 (9.82)
10b	48	47–49 (pentane)	$C_{13}H_{27}N_4OPS$	17.52 (17.60)	9.70 (9.73)
10c	66	79–81 (hexane)	$C_{18}H_{29}N_4OP$	16.06 (16.08)	8.83 (8.89)
10e	71	Oil	$C_{12}H_{24}N_3O_3P$	14.47 (14.52)	10.65 (10.71)
10f	48	122–124/0.02	$C_{11}H_{21}N_2O_3PS$	9.47 (9.58)	10.57 (10.60)
11	91	112–114 (Et_2O)	$C_{10}H_{16}Cl_2F_3N_4OP$	15.23 (15.26)	8.46 (8.44)
12a	31	91–92 (EtOAc)	$C_{15}H_{33}IN_5P$	15.60 (15.87)	6.94 (7.02)
12b	25	119–120 (EtOAc)	$C_{14}H_{30}IN_4PS$	12.56 (12.61)	6.95 (6.97)
13	26	36–38 (Et_2O)	$C_{10}H_{20}N_3O_2P$	17.11(17.13)	12.58 (12.63)
14	77	62–64 (hexane)	$C_{14}H_{26}N_7P$	30.26 (30.32)	9.55 (9.58)
15	44	170/0.05	$C_{12}H_{20}ClN_6P$	26.61 (26.70)	9.83 (9.84)
16	76	95–96 (Et_2O)	$C_{14}H_{26}N_7OP$	28.85 (28.89)	9.07 (9.13)
17a	66	168–170 (Et_2O)	$C_{18}H_{30}N_9P$	31.20 (31.24)	7.65 (7.68)
17b	36	94–95 (Et_2O)	$C_{15}H_{21}N_6PS_3$	20.27 (20.37)	7.55 (7.51)
17c	46	210–212 (Et_2O)	$C_{30}H_{27}N_6P$	16.66 (16.72)	6.10 (6.16)
18b	11	Oil	$C_{15}H_{21}N_6PS_3$	20.33 (20.37)	7.46 (7.51)
19b	90	192–193 (Et_2O)	$C_{15}H_{21}N_6OPS_3$	19.60 (19.61)	7.17 (7.23)
19c	67	218–219 (Et_2O)	$C_{30}H_{27}N_6OP$	16.14 (16.21)	5.93 (5.97)
20b	60	Oil	$C_{15}H_{21}N_6OPS_3$	19.45 (19.61)	7.25 (7.23)
20c	7	135–140 ($CHCl_3$)	$C_{30}H_{27}N_6OP$	16.33 (16.21)	5.92 (5.97)
21a	70	231–232 (CH_3CN)	$C_{18}H_{30}N_9PS$	28.90 (28.94)	7.03 (7.11)
21b	85	194–195 (Et_2O)	$C_{15}H_{21}N_6PS_4$	18.92 (18.90)	7.00 (6.97)
21c	97	272–273 (Et_2O)	$C_{30}H_{27}N_6PS$	15.67(15.72)	5.72 (5.79)
22b	65	207–208 (Et_2O)	$C_{22}H_{28}N_7OPS_3$	18.35 (18.37)	5.76 (5.80)
22c	33	233–234 (Et_2O)	$C_{37}H_{34}N_7OP$	15.70 (15.72)	4.91 (4.97)
23a	44	140–145/0.05	$C_{12}H_{15}ClN_3P$	15.65 (15.70)	11.56 (11.57)
23b	45	143–146/0.05	$C_{11}H_{12}ClN_2PS$	10.33 (10.35)	11.38 (11.44)
23c	55	205–210/0.05	$C_{16}H_{14}ClN_2P$	9.50 (9.32)	10.36 (10.30)
25	35	140–141 (Et_2O)	$C_{18}H_{25}N_6PS$	21.64 (21.63)	7.95 (7.97)
26	61	Oil	$C_7H_{10}Cl_4N_3P$	13.54 (13.60)	10.66 (10.03)
27	76	130/0.05	$C_8H_{10}Cl_4N_3P$	13.06 (13.09)	9.61 (9.65)
28	86	210/0.05	$C_{14}H_{20}Cl_3N_6P$	20.48 (20.51)	7.52 (7.56)
29	50	140–150/0.05	$C_{10}H_{16}Cl_3N_4P$	16.97 (17.00)	9.34 (9.40)
30	40	122–123 (pentane)	$C_{10}H_{16}Cl_3N_4PS$	15.47 (15.49)	8.50 (8.56)
31	87	118–119 (pentane)	$C_{14}H_{28}ClN_6PS$	22.10 (22.18)	8.12 (8.17)
32a	80	Oil	$C_{14}H_{20}Cl_3N_6OP$	19.71 (19.74)	7.15 (7.28)
32b	55	Oil	$C_{14}H_{20}Cl_3N_6PS$	19.05 (19.02)	7.23 (7.01)

(Continued)

TABLE 2 Continued

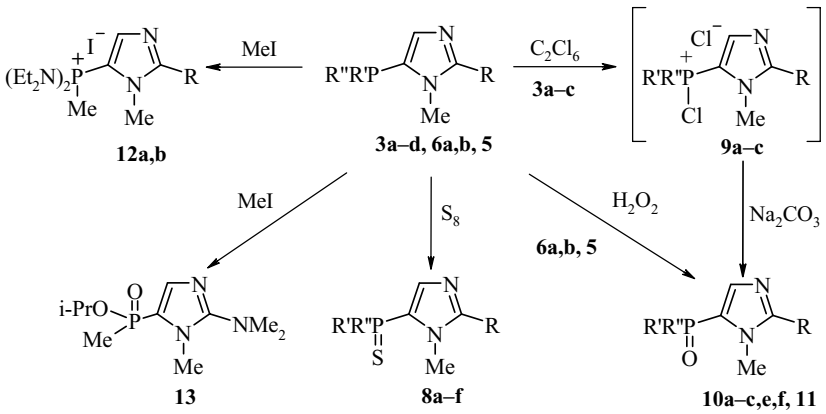
Compound	Yield (%)	Mp (°C) (Cryst. solvent) Bp/pressure, (°C)/Torr	Molecular Formula	Found (Calcd) (%) N	Found (Calcd) (%) P
32c	78	Oil	$C_{20}H_{25}Cl_3N_7P$	19.60 (19.58)	6.15 (6.18)
33a	97	Oil	$C_{18}H_{32}ClN_8OP$	25.28 (25.30)	6.94 (6.99)
33b	86	174–175 (Et_2O)	$C_{18}H_{32}ClN_8PS$	24.36 (24.41)	6.68 (6.75)
34a	81	161–164	$C_{19}H_{23}IN_3P$	9.22 (9.31)	6.83 (6.86)
35a	77	109–110 (hexane)	$C_{18}H_{20}N_3OP$	12.80 (12.92)	9.43 (9.52)
35b	79	145–146 (cyclohexane)	$C_{17}H_{17}N_2OPS$	8.75 (8.53)	9.45 (9.43)
35c	35	120–121 (pentane)	$C_{22}H_{19}N_2OP$	7.55 (7.82)	8.57 (8.64)
36a	75	78–80 (hexane)	$C_{18}H_{20}N_3PS$	12.20 (12.31)	9.02 (9.07)
36b	74	137–135 (MeOH)	$C_{17}H_{17}N_2PS_2$	8.25 (8.13)	9.02 (8.99)
36c	80	184–185 (Et_2O)	$C_{22}H_{19}N_2PS$	7.62 (7.48)	8.25 (8.27)
37a	65	145–147 (hexane)	$C_{25}H_{27}N_4OP$	12.92 (13.01)	7.10 (7.20)
37b	50	93–94 (pentane)	$C_{24}H_{24}N_3OPS$	9.67 (9.69)	7.08 (7.14)

thus providing synthetic routes to diverse types of phosphorus(III) compounds such as **3a–d, 4, 6a,b**, and **7c** (Scheme 1). Phosphonamidous chloride **4** reacts with the trifluoromethyl(dichloro)methanide ion $CF_3CCl_2^-$ [17] to produce functional phosphinous amide **5**.

Compounds **3a–d, 5**, and **6a,b** can be converted to a diversity of phosphorus(V) derivatives **8–10** and **11** by classical methods (Scheme 2). The alkylation of diamides **3a–c** with CH_3I affords phosphonium salts **12a–c** in about 30% yield. Phosphonate **6a** reacts with CH_3I producing phosphinate **13** by the Arbuzov-type rearrangement. The reaction was conducted without heating (at 20°C) to minimize the competing alkylation at the imine nitrogen atom in the imidazole ring (Scheme 2).

The structure of diamide **8b** was determined by X-ray diffraction analysis. According to their data (Fig. 1), the phosphorus atom is located near the heterocyclic C-5 atom thus pointing to the regioselective 5-phosphorylation of imidazole **1b**. ^{13}C NMR chemical shifts are rather close for **8b** (126.6 ppm) and **8a,c,d** (122–125 ppm) as well as for **2b** (128.7 ppm) and **2a,c,d** (127–129 ppm), which suggests that imidazoles **1a,c** are also phosphorylated at position 5.

We attempted the preparation of bis(imidazol-5-yl)phosphinous chloride analogous to **15** by phosphorylation of imidazoles **1a–c** with PCl_3 in a 4:1 ratio, but the desired products could not be isolated as individual compounds from the resulting mixture of mono-, di-, and trihalosubstituted derivatives. However, the compound of this type,



3, 8–10: R' = R" = Et_2N (**a–c**), Me_2N (**d**), *i*-PrO (**e, f**); R=NMe_2 (**a, e**), SMe (**b, f**), Ph (**c, d**)
6: R' = R" = *i*-PrO; R = NMe_2 (**a**), SMe (**b**)
5, 11: R' = Me_2N, R" = CF_3CCl_2; R = NMe_2
12: R = NMe_2 (**a**), SMe (**b**)

SCHEME 2

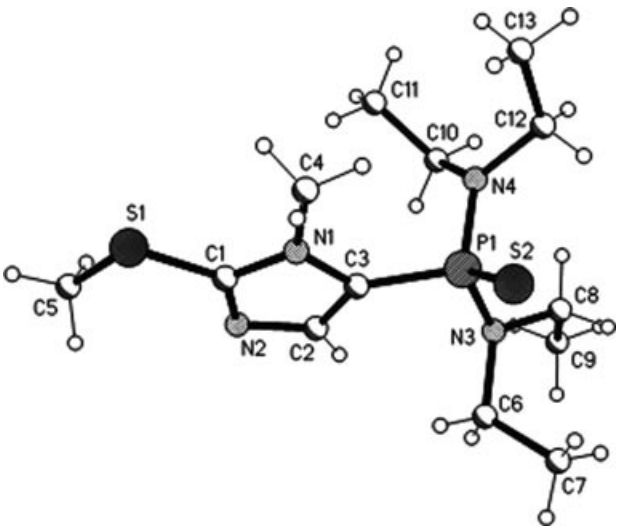
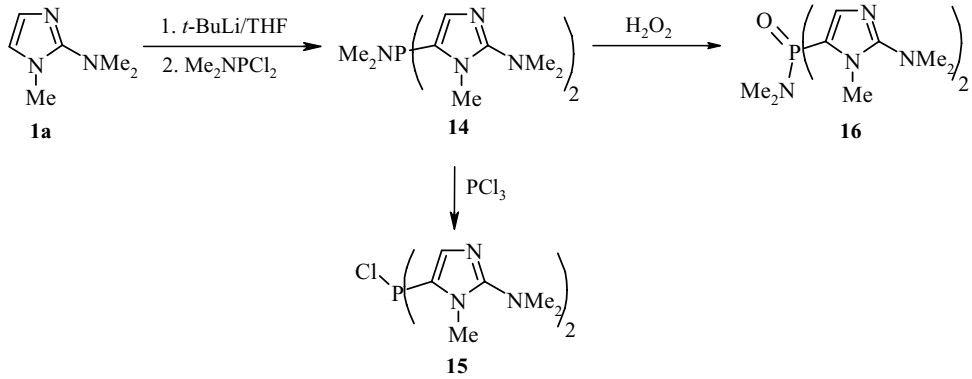


FIGURE 1 Molecular structure of compound **8b**.

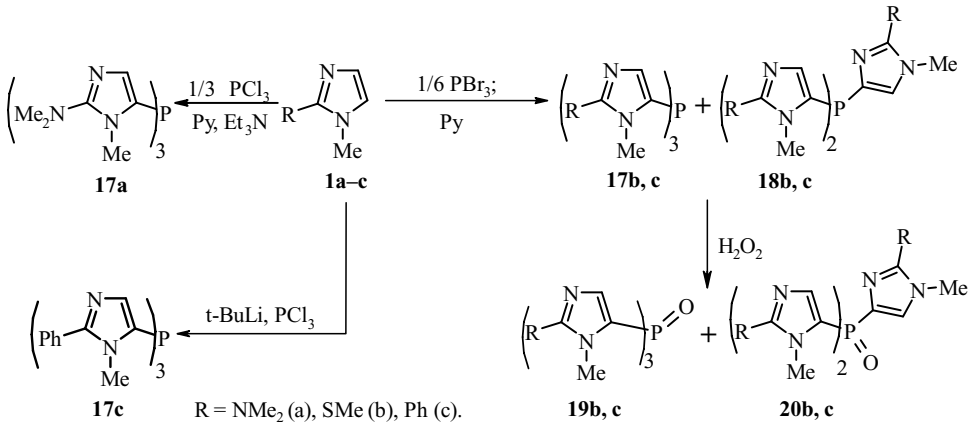
chloride **15**, was obtained by reaction of 5-lithiated imidazole **1a** with dimethylphosphoramidous dichloride, Me_2NPCl_2, followed by treatment of phosphine amide **14** with PCl_3 (Scheme 3). Remarkably, imidazole **1a** remains unreactive toward Me_2NPCl_2 at 20°C, whereas rise of temperature results in the ^{31}P NMR-detected mixture of **2a** and **17a** obviously generated in the reaction between **1a** and PCl_3 formed during Me_2NPCl_2 disproportionation. The structures of product **14** and its oxide **16** were confirmed by ^1H and ^{13}C NMR spectra. When distilled, chloride **15** partially (up to a 10% degree) disproportionates to phosphonous dichloride **2a** and tris(imidazol-5-yl)phosphine **17a**.

Synthesis of Tris(imidazolyl)Phosphines

The most reactive imidazole **1a** is phosphorylated with PCl_3 regioselectively in a 3:1 ratio in the presence of triethylamine to produce tris(imidazol-5-yl)phosphine **17a** (δ_P −85.4 ppm) in about 70% yield; the reaction is completed at 25°C within 30 h. For the phosphorylation of imidazoles, **1b,c** was applied PBr_3 in a 6:1 ratio (see Scheme 4) and reaction proceeds regiospecifically to yield, in each case, a mixture of two isomeric tertiary phosphines, **17** and **18**. As evidenced by ^{31}P NMR spectra (in pyridine),



SCHEME 3



SCHEME 4

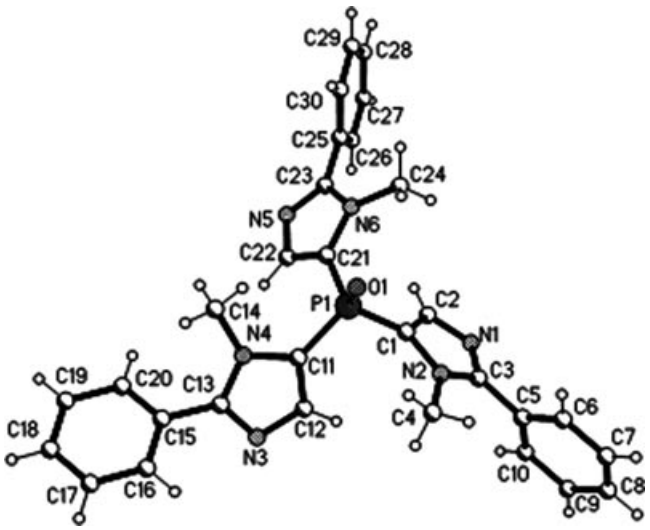


FIGURE 2 Molecular structure of compound **19c**.

there are two upfield signals, which correspond to **17b** (δ_P −86.0 ppm) and **18b** (δ_P −83.0 ppm) or to **17c** (δ_P −85.0 ppm) and **18c** (δ_P −82.0 ppm) and exhibit an approximately 3:1 integral intensity ratio for **17** and **18**. Isomers **17b** and **18b** were separated by chromatography on silica gel. Compound **17c** was isolated by crystallization and oxidized to phosphine oxide **19c** then the remaining mixture enriched in phosphine **18c** was treated with hydrogen peroxide followed by chromatographic isolation of the corresponding phosphine oxide **20c** (see Scheme 4). The structure of phosphine oxides **19c** and **20c** was determined by X-ray diffraction analysis (Figs. 2 and 3), which also supported the structures of starting phosphines **17c** and **18c**. Regarding phosphines **17b** and **18b** as well as the corresponding phosphine oxides **19b** and **20b**, their structures appear to be undoubtedly agree well with ^{31}P, ^{1}H, and ^{13}C NMR spectral data (Tables 2–4).

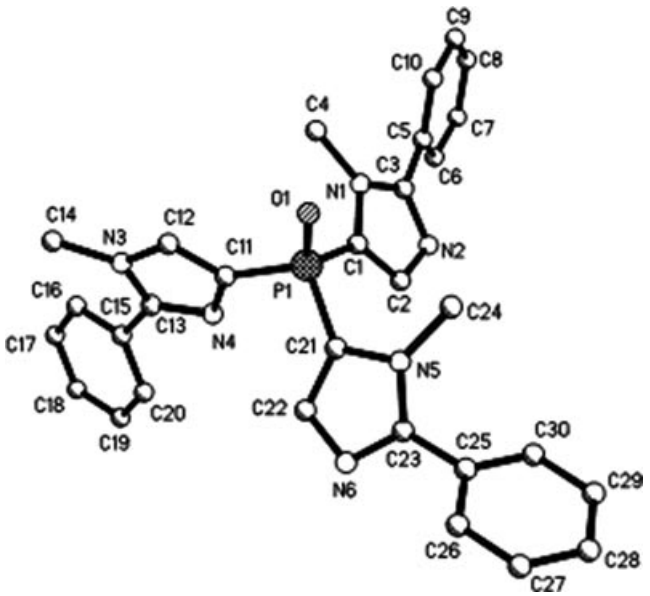


FIGURE 3 Molecular structure of compound **20c**.

It has been found that phosphorylation of imidazoles **1b,c** is favored in the presence of 1 equiv of LiBr. In this case, the reaction requires much milder conditions: for **1b** at 30°C for 7 days against heating at 70°C for 4 days and for **1c** 3 days against 7 days at 75°C, with the **17**:**18** isomer ratio remaining unchanged. It should be noted that the lithiated derivative of imidazole **1c** reacts regioselectively with PCl_3 to give only phosphine **17c**, which is spectrally identical to the tertiary phosphine obtained by direct phosphorylation. Since lithiation of imidazole **1b** is impossible without the SMe group involving, the metal-mediated synthesis cannot afford phosphines **17b** and **18b**, so that direct phosphorylation is the only accessible to these compounds.

Comparing the NMR spectra of compounds **17b,c**, and **18b,c**, it is obvious that phosphorylation even of a single imidazolyl residue at position 4 causes a 2–3 ppm downfield shift of ^{31}P NMR signals, which indicates less electron density on the 4-C than on 5-C atom. The same trend holds for ^{13}C resonances in these tertiary phosphines: The doublet peak of the quaternary 4′-C atom (δ_C 132.9 ppm) is shifted downfield from the analogous signal of the quaternary 5-C atom (δ_C 123–124 and 129.7 ppm for **17b,c** and **18b,c**, respectively). Thus, ^{31}P and ^{13}C NMR chemical shifts provide a reliable criterion to distinguish between 4- and 5-phosphorylated 1,2-disubstituted imidazoles.

Starting from tris(imidazol-5-yl)phosphines **17**, phosphorus(V) derivatives **21** and **22** were also prepared (see Scheme 5).

Reactions of 1,2-Disubstituted Imidazoles **1a–c** *with* $RPCl_2$

Imidazoles **1a–c** are phosphorylated with $PhPCl_2$ to yield phosphine chlorides **23a–c** (Scheme 6). The ease of the reaction is less than with $PHal_3$ and strongly dependent on the electronic nature of the 2-substituent. With a two-fold excess of $PhPCl_2$, ensured only monosubstitution to occur, phosphorylation is completed within 4 h for imidazole **1a** (20°C), 48 h for **1b** (65°C), and 72 h for **1c** (130°C). Just as in the reaction with $PHal_3$, under such conditions imidazole **1c** is phosphorylated with an equimolar amount of $PhPCl_2$ and pyridine in place of starting imidazole acts as a hydrogen chloride acceptor.

TABLE 3 Spectroscopic Data of 5-Phosphorylated-1,2-Disubstituted Imidazoles

Compound	Solvent	^{31}P NMR δ (ppm)	^{1}H NMR, δ (ppm), J (Hz)		
			N-CH_3	4-H	Other Signals
2a	C_6D_6	126.90	3.30 (s, 3H)	7.22 (s, 1H)	2.35 (s, 6H, NCH_3)
2b	C_6D_6	120.50	3.32 (s, 3H)	7.35 (s, 1H)	2.34 (s, 3H, SCH_3)
2c	C_6D_6	128.70	3.41 (s, 3H)	7.52 (s, 1H)	7.39 (t, 2H, 3.5, 2,6-H-Ph); 7.08–7.09 (m, 3H, 3,5- and 4-H-Ph)
2d	C_6D_6	104.30	3.41 (s, 3H)	7.47 (s, 1H)	7.35 (m, 2H, 2,6-H-Ph); 7.05–7.07 (m, 3H, 3,5- and 4-H-Ph)
3a	C_6D_6	75.2	3.23 (s, 3H)	7.25 (d, 1H, 2.5)	2.62 (s, 6H, NCH_3); 0.94 (t, 12H, 7.2, $PNCH_2\underline{CH_3}$); 3.03 (m, 8H, $PN\underline{CH_2}$)
3b	C_6D_6	74.7	3.25 (s, 3H)	7.40 (d, 1H, 2.5)	2.45 (s, 3H, SCH_3); 0.89 (t, 12H, 7.2, $PNCH_2\underline{CH_3}$); 2.95 (m, 8H, $PN\underline{CH_2}$)
3c	C_6D_6	75.1	3.30 (s, 3H)	7.50 (d, 1H, 2.5)	7.68 (d, 2H, 7.5, 2,6-H-Ph) 2.99 (m, 8H, $PN\underline{CH_2}$); 7.16 (t, 1H, 7.5, 4-H-Ph); 7.09 (m, 2H, 3,5-H-Ph); 0.91 (t, 12H, 7.0, $NCH_2\underline{CH_3}$)
3d	C_6D_6	81.9	3.20 (s, 3H)	7.41 (d, 1H, 2.5)	2.55 (d, 12H, 9.5, $PN\underline{CH_3}$); 7.10 (m, 2H, 3,5-H-Ph); 7.17 (t, 1H, 7.5, 4-H-Ph); 7.63 (d, 2H, 7.5, 2,6-H-Ph)
4	C_6D_6	120.90	3.05 (s, 3H)	7.55 (s, 1H)	2.36 (d, 6H, 13.5, P-NCH_3); 2.53 (s, 6H, NCH_3)
5	C_6D_6	51.50	3.35 (s, 3H)	7.90 (s, 1H)	2.50 (s, 6H, NCH_3); 2.50 (d, 6H, 9.30, P-NCH_3)
6a	C_6D_6	144.7	3.40 (s, 3H)	7.53 (s, 1H)	2.52 (s, 6H, NCH_3); 1.10 (dd, 12H, 9.0, $POCH\underline{CH_3}$); 4.20 (m, 2H, $PO\underline{CH}$)
6b	C_6D_6	145.2	3.38 (s, 3H)	7.62 (s, 1H)	2.40 (s, 3H, SCH_3); 1.05 (dd, 9H, 21.0, $POCH\underline{CH_3}$); 4.12 (m, 2H, $PO\underline{CH}$)
7a	$CDCl_3$	−33.2	3.40 (s, 3H)	6.50 (s, 1H)	2.80 (s, 6H, NCH_3); 7.33 (br s, 10H, H-Ph)
7b	$CDCl_3$	−33.5	3.45 (s, 3H)	6.71 (s, 1H)	2.62 (s, 3H, SCH_3); 7.34 (d, 3.9, 10H, H-Ph)
7c	$CDCl_3$	−33.0	3.66 (s, 3H)	6.75 (s, 1H)	7.38 (br s, 10H, H-Ph-P); 7.62 (d, 1.2, 2,6-H-Ph); 7.40–7.50 (m, 3,5- and 4-H-Ph)
8a	$CDCl_3$	59.8	3.68 (s, 3H)	7.00 (s, 1H)	2.89 (s, 6H, NCH_3); 1.09 (t, 12H, 7.0, $PNCH_2\underline{CH_3}$); 3.19 (q, 8H, 12.50, $PN\underline{CH_2}$)
8b	$CDCl_3$	63.3	3.67 (s, 3H)	7.21 (s, 1H)	2.64 (s, 3H, SCH_3); 1.10 (t, 12H, 7.0, $PNCH_2\underline{CH_3}$); 3.20 (q, 8H, 12.50, $PN\underline{CH_2}$)
8c	$CDCl_3$	58.9	3.75 (s, 3H)	7.39 (s, 1H)	1.13 (t, 12H, 7.0, $PNCH_2\underline{CH_3}$); 3.25 (q, 8H, 12.50, $PN\underline{CH_2}$); 7.45–7.50 (m, 3H, 3,5- and 4-H-Ph); 7.6 (d, 2H, 7.5, 2,6-H-Ph)
8d	$CDCl_3$	64.7	3.92 (s, 3H)	7.38 (s, 1H)	2.75 (d, 6H, 5.0, $PN\underline{CH_3}$); 7.1 (m, 2H, 3,5-H-Ph); 7.2 (t, 1H, 7.5, 4-H-Ph); 7.6 (d, 2H, 7.5, 2,6-H-Ph)
8e	$CDCl_3$	68.9	3.89 (s, 3H)	7.30 (s, 1H)	1.31 (dd, 12H, 6.0, 46.0, $POCH\underline{CH_3}$); 2,78 (s, 6H, NCH_3); 4.86 (q, 2H, 6.0, $PO\underline{CH}$)
8f	$CDCl_3$	68.1	3.69 (s, 3H)	7.53 (s, 1H)	1.31 (dd, 12H, 6.0, 50.10, $POCH\underline{CH_3}$); 2,66 (s, 3H, SCH_3); 4.87 (q, 2H, 6.0, $PO\underline{CH}$)
10a	$CDCl_3$	16.9	3.60 (s, 3H)	6.96 (s, 1H)	2.75 (s, 6H, NCH_3); 1.09 (t, 12H, 7.0, $PNCH_2\underline{CH_3}$); 3.19 (m, 8H, $PN\underline{CH_2}$)
10b	$CDCl_3$	17.3	3.61 (s, 3H)	7.22 (s, 1H)	2.64 (s, 3H, SCH_3); 1.07 (t, 12H, 7.0, $PNCH_2\underline{CH_3}$); 3.08 (m, 8H, $PN\underline{CH_2}$)
10c	$CDCl_3$	16.3	3.73 (s, 3H)	7.33 (s, 1H)	7.60 (d, 2H, 6.5, 2,6-H-Ph); 7.41–7.50 (m, 3H, 6.5, 3,5- and 4-H-Ph); 1.11 (t, 12H, 7.0, $PNCH_2\underline{CH_3}$); 3.15 (m, 8H, $PN\underline{CH_2}$)
10e	$CDCl_3$	6.9	3.89 (s, 3H)	7.32 (s, 1H)	2.78 (s, 6H, NCH_3); 1.30; (dd, 12H, 40.5, $POCH\underline{CH_3}$); 4.67 (q, 2H, 2.50, $PO\underline{CH}$)
10f	$CDCl_3$	6.4	3.58 (s, 3H)	7.44 (s, 1H)	2.57 (s, 3H, SCH_3); 1.24 (dd, 12H, 45.0, $POCH\underline{CH_3}$); 4.62 (q, 2H, 2.50, $PO\underline{CH}$)
11	$CDCl_3$	20.00	3.65 (s, 3H)	7.63 (s, 1H)	2.85 (s, 6H, NCH_3); 2.87 (d, 6H, 9.30, P-NCH_3)
12a	CD_3CN	44.00	3.50 (s, 3H)	7.39 (d, 1.5, 1H)	1.18 (t, 12H, 7.2, $PNCH_2\underline{CH_3}$); 2.22 (d, 3H, 13.50, P^+-CH_3); 2.86 (s, 6H, NCH_3); 3.18 (q, 8H, 10.50, $PN\underline{CH_2}$)
12b	CD_3CN	43.40	3.56 (s, 3H)	7.61 (d, 1.2, 1H)	1.84 (t, 12H, 7.2, $PNCH_2\underline{CH_3}$); 2.24 (d, 3H, 13.50, P^+-CH_3); 2.69 (s, 3H, SCH_3); 3.18 (m, 8H, $PN\underline{CH_2}$)

(Continued)

TABLE 3 Continued

Compound	Solvent	^{31}P NMR δ (ppm)	^{1}H NMR, δ (ppm), J (Hz)		
			N-CH_3	4-H	Other Signals
13	$CDCl_3$	31.1	3.68 (s, 3H)	7.22 (s, 1H)	2.82 (s, 6H, NCH_3); 1.33 (dd, 12H, 6.3, POCH$\underline{CH_3}$); 1.68 (d, 3H, 15.0, CH_3); 4.67 (m, 2H, PO$\underline{CH}$)
14	C_6D_6	13.40	3.04 (s, 6H)	7.20 (s, 2H)	2.45 (d, 6H, 10.0, $PNCH_3$); 2.55 (s, 12H, $\overline{NCH_3}$)
15	C_6D_6	31.50	3.29 (s, 6H)	7.24 (s, 2H)	2.47 (s, 12H, NCH_3)
16	$CDCl_3$	10.70	3.25 (s, 6H)	6.76 (d, 2H, 1.50)	2.61 (d, 6H, 10.0, $PNCH_3$); 2.67 (s, 12H, NCH_3)
17a	$CDCl_3$	- 84.0	3.50 (s, 9H)	6.56 (s, 3H)	2.66 (s, 18H, NCH_3)
17b	$CDCl_3$	- 85.8	3.32 (s, 9H)	6.93 (s, 3H)	2.84 (s, 9H, SCH_3)
17c	$CDCl_3$	- 84.8	3.50 (s, 9H	7.10 (s, 3H)	7.39 (d, 3H, 4-H-Ph); 7.44 (t, 6H, 2,6-H-Ph); 7.61 (d, 6H, 3,5-H-Ph)
18b	$CDCl_3$	−83.4	3.56 (s, 6H)	6.15 (s, 2H)	2.60 (s, 6H, SCH_3); 2.62 (s, 3H, SCH_3); 3.53 (s, 3H, NCH_3); 7.03 (s, 1H, 5-H)
19b	$CDCl_3$	−8.2	3.57 (s, 9H)	6.94 (s, 3H)	2.70 (s, 9H, SCH_3)
19c	$CDCl_3$	−4.8	3.73 (s, 9H)	7.15 (s, 3H)	7.50 (m, 9H, 2,6+4-H-Ph); 7.66 (d, 6H, 3,5-H-Ph, 7.00)
20b	$CDCl_3$	−3.9	4.00 (s, 6H)	7.28 (s, 2H)	2.69 (s, 6H, SCH_3); 2.61 (s, 3H, SCH_3); 3.61 (s, 3H, NCH_3); 7.52 (s, 1H, 5-H)
20c	$CDCl_3$	−2.8	3.73 (s, 6H)	7.40 (s, 2H)	7.36 (m, 9H, 2,6+4-H-Ph); 7.55 (d, 6H, 3,5-H-Ph, 7.00); 7.66 (s, 1H, 5-H)
21a	$CDCl_3$	−6.6	3.88 (s, 9H)	6.59 (s, 3H)	2.72 (s, 18H, NCH_3)
21b	$CDCl_3$	−9.2	3.74 (s, 9H)	6.90 (d, 1.80, 3H)	2.68 (s, 9H, SCH_3)
21c	$CDCl_3$	−5.0	4.02 (s, 9H)	7.10 (s, 3H)	7.50 (br s, 9H, *o*- and *p*-H-Ph); 7.66 (br s, 6H, m-Ph)
22b	$CDCl_3$	−40.4	3.55 (s, 9H)	7.09 (s, 3H)	2.65 (s, 9H, SCH_3); 3.72 (s, 3H, OCH_3); 6.60 (q, 4H, 15.60, 2,6 and 3,5-H-Ar)
22c	$CDCl_3$	−37.8	3.87 (s, 9H)	7.33 (s, 3H)	3.72 (s, 3H, OCH_3); 6.70 (s, 4H, 2,6- and 3,5-H-Ar); 7.50 (d, 9H, 7.50, 2,6- and 4-H-Ph); 7.66 (d, 6H, 7.50, 3,5-H-Ph)
23a	C_6D_6	54.80	3.34 (s, 3H)	7.02 (s,1H)	2.82 (s, 6H, NCH_3); 7.41 (br s, 3H, 2,6-H-Ph, 4-H-Ph); 7.60 (d, 2H, 7.5, 3,5-H-Ph)
23b	C_6D_6	53.00	3.00 (s, 3H)	7.31 (s, 1H)	2.37 (s, 3H, SCH_3); 7.02 (br s, 3H, 2,6- and 4-H-Ph); 7.46 (d, 2H, 7.5, 3,5-H-Ph)
23c	C_6D_6	54.55	3.18 (s, 3H)	7.45 (s, 1H)	7.10 (m, 6H, 3,4,5-Ph and 3,4,5-PhP); 7.47 (m, 2H, 2,6-H-PhP); 7.61 (m, 2H, 2,6-H-Ph)
25	$CDCl_3$	9.70	3.63 (s, 6H)	6.61 (s, 2H)	2.83 (s, 12H, NCH_3); 7.54 (m, 2H, 3,5-Ph); 7.59 (m, 1H, 4-Ph); 7.87 (dd, 2H, 7.0; 15.0, 2,6-Ph)
26	C_6D_6	75.50	3.70 (s, 3H)	7.82 (s, 1H)	2.87 (s, 6H, NCH_3)
27	C_6D_6	49.70	3.48 (s, 3H)	7.45 (s, 1H)	2.43 (s, 6H, NCH_3)
28	C_6D_6	−50.20	3.12 (s, 6H)	7.29 (s, 2H)	2.51 (s, 12H, NCH_3)
29	C_6D_6	39.30	3.15 (s, 3H)	7.23 (s, 1H)	2.57 (d, 6H, 9.50, $PNCH_3$); 2.62 (s, 6H, NCH_3)
30	$CDCl_3$	48.00	3.45 (s, 6H)	7.00 (s, 2H)	2.77 (br s, 12H, NCH_3)
31	$CDCl_3$	49.20	3.65 (s, 3H)	7.17 (s, 1H)	2.66 (d, 6H, 12.00, P-NCH_3); 2.74 (s, 12H, C=CNCH_3); 2.78 (s, 6H, NCH_3)
32a	$CDCl_3$	4.70	3.61 (s, 6H)	6.90 (d, 1.50, 2H)	2.79 (s, 12H, NCH_3)
32b	$CDCl_3$	13.00	3.23 (s, 6H)	6.90 (d, 2H, 1.80)	2.86 (s, 12H, NCH_3)
32c	$CDCl_3$	−29.70	3.70 (s, 6H)	7.62 (s, 2H)	2.48 (s, 12H, NCH_3); 6.71 (t, 1H, 7.5, 4-H-Ph); 6.90 (d, 2H, 7.5, 2,6-H-Ph); 7.10 (d, 2H, 7.5, 3,5-H-Ph);
33a	$CDCl_3$	6.10	3.30 (s, 6H)	6.66 (s, 2H)	2.58 (s, 12H, NMe_2); 2.62 (d, 12H, 15.00, C=CNCH_3)
33b	$CDCl_3$	11.30	3.39 (s, 6H)	6.70 (s, 2H)	2.47 (d, 12H, 3.50, C=CNCH_3); 2.50 (s, 12H, NCH_3)
34a	CD_3CN	7.89	3.35 (s, 3H)	7.12 (s, 1H)	2.88 (s, 6H, NCH_3); 2.83 (br d, 3H, 12.50, PCH_3); 7.76 (br s, 8H, 2,6- and 3,5-H-Ph); 7.9 (s, 2H, 4-H-Ph)
35a	$CDCl_3$	17.7	3.50 (s, 3H)	6.58, (s 1H)	2.80 (s, 3H, NCH_3); 7.47–7.53 (m, 4H, 3,5-H-Ph); 7.56 (d, 2H, 7.00, 4-H-Ph); 7.70 (q, 4H, 12.50, 2,6-H-Ph)
35b	$CDCl_3$	17.1	3.60 (s, 3H)	6.82 (s, 1H)	2.70 (s, 3H, SCH_3); 7.51 (m, 4H, 3,5-H-Ph); 7.60 (t, 4H, 7.50, 4-H-Ph); 7.71 (q, 4H, 13.00, 2,6-H-Ph)
35c	$CDCl_3$	17.9	3.73 (s, 3H)	6.90 (s, 1H)	7.50 (m, 12H, Ph and 3,5-H-PhP); 7.60 (d, 2H, 7.50, 4-H-PhP); 7.75 (q, 4H, 12.50, 2,6-H-PhP)

(Continued)

TABLE 3 Continued

Compound	Solvent	^{31}P NMR δ (ppm)	^{1}H NMR, δ (ppm), J (Hz)		
			N-CH_3	4-H	Other Signals
36a	$CDCl_3$	26.7	3.73 (s, 3H)	6.40 (s, 1H)	2.80 (s, 3H, NCH_3); 7.43–7.56 (m, 6H, 3,5- and 4-H-Ph); 7.80 (q, 4H, 13.80, 2,6-H-Ph)
36b	$CDCl_3$	26.1	3.50 (s, 3H)	6.65 (s, 1H)	2.70 (s, 3H, SCH_3); 7.50 (m, 4H, 3,5-H-PhP); 7.58 (t, 8.0, 4-H-Ph); 7.80 (q, 4H, 13.00, 2,6-H-Ph)
36c	$CDCl_3$	27.3	3.60 (s, 3H)	6.75 (s, 1H)	7.45 (br s, 12H, Ph+3,5-H-PhP); 7.55 (dd, 2H, 4-H-PhP); 7.80 (q, 4H, 13.50, 2,6-H-PhP)
37a	$CDCl_3$	−16.0	3.35 (s, 3H)	6.80 (s, 1H)	2.78 (s, 3H, NCH_3); 3.71 (s, 3H, OCH_3); 6.64 (d, 2H, 8.5, 3,5-H-Ar); 6.75 (d, 2H, 8.5, 2,6-H-Ar); 7.45 (m, 4H, 3,5-H-Ph); 7.52 (t, 2H, 7.5, 4-H-Ph); 7.78 (q, 4H, 12.50, 2,6-H-Ph)
37b	$CDCl_3$	−10.6	3.28 (s, 3H)	7.03 (s, 1H)	2.63 (s, 3H, SCH_3); 3.37 (s, 3H, OCH_3); 6.64 (d, 2H, 8.5, 3,5-H-Ar); 6.75 (d, 2H, 8.5, 2,6-H-Ar); 7.42 (m, 4H, 3,5-H-Ph); 7.50 (t, 2H, 7.5, 4-H-Ph); 7.78 (q, 4H, 12.50, 2,6-H-Ph)
38a	CD_3CN	14.60	3.66 (s, 3H)	7.31 (s, 1 H)	1.10 (t, 12H, 12.00, $PNCH_2\underline{CH_3}$); 3.05 (s, 6H, NCH_3); 3.10 (m, 8H, $PN\underline{CH_2}$); 3.74 (s, 3H, N^+-CH_3)
38b	DMSO	55.20	3.94 (s, 3H)	8.10 (s, 1H)	1.01 (t, 12H, 6.70, $PNCH_2\underline{CH_3}$); 2.58 (s, 3H, SCH_3); 3.18 (m, 8H, 6.70, $PN\underline{CH_2}$); 4.00 (s, 3H, N^+-CH_3)
38c	CD_3CN	61.40	3.68 (s, 3H)	7.90 (s, 1H)	2.80 (d, 12H, 12.50, $PNCH_3$); 3.78 (s, 3H, N^+-CH_3); 7.68 (d, 2H, 7.50, 2.6-H-Ph); 7.73 (t, 1H, 7.50, 4-H-Ph); 7.80 (t, 2H, 7.50, 3,5-H-Ph)
38d	$CDCl_3$	17.10	3.60 (s, 3H)	6.63 (d, 2.5, 1H)	3.22 (s, 3H, NCH_3); 3.81 (s, 3H, N^+-CH_3); 7.62 (m, 6H, 3,5- and 4-H-Ph); 8.05 (dd, 13.20, 6.60, 4H, 2,6-H-Ph)
38e	$CDCl_3$	28.20	3.90 (s, 3H)	6.90 (d, 2.1, 1H)	2.80 (s, 3H, SCH_3); 4.04 (s, 3H, N^+-CH_3); 7.63 (m, 6H, 3,5- and 4-H-Ph); 8.25 (dd, 14.70, 7.80, 4H, 2,6-H-Ph)
38f	$CDCl_3$	16.50	3.64 (s, 3H)	7.13 (d, 2.1, 1H)	3.85 (s, 3H, N^+-CH_3); 7.66 (m, 9H, 3,5-H-PhP+H-Ph); 7.92 (d, 2H, 6.60, 4-H-PhP); 8.18 (dd, 13.20, 8.00, 4H, 2,6-H-PhP)

Chlorides **23a–c** appear as air-sensitive yellow liquids distillable in vacuo and represent quite reactive compounds. For instance, compound **23a** reacts with **1a** in a 1:2 ratio to afford bis(imidazol-5-yl)phenylphosphine **24a**, which exhibits a ^{31}P NMR chemical shift (δ_P −81 ppm) being characteristic of tertiary phosphines. Compound **24a** was transferred to phosphine sulfide **25a**, with its structure confirmed by ^{1}H and ^{13}C NMR and mass spectral data.

We studied the chemical behavior of the most reactive imidazole **1a** toward other phosphine dichlorides $RPCl_2$ containing electron-withdrawing groups (R=CCl_3; CCl_2=CCl–). Compound **1a** reacts with trichloromethylphosphine dichloride in pyridine at 60°C, but the reaction results in a low yield of product **26** (26%) and is accompanied by tar formation (Scheme 7). Phosphine chloride **26** is thermally unstable and partially decomposes on vacuo distillation to form phosphine dichloride **2a**. Nevertheless, by treatment of the latter **2a** with trichloromethane ion CCl_3^- [18] chloride **26** is formed in a moderate yield (61%) and does not need to be purified by distillation.

Imidazole **1a** readily reacts with trichlorovinylphosphine dichloride CCl_2=$CClPCl_2$ [19] in a 2:1 or 4:1 ratio producing monohalo- (**27**) or dihalo-substituted product (**28**), respectively (Scheme 8). Phosphine chloride **27** enters into the reaction with dimethyl(trimethylsilyl)amine to give amide **29**. It is notable that phosphine sulfide **30** reacts with dimethylamine so that the β-chlorine atoms in the trichloroethenyl residue are substituted by dimethylamino groups and tetramethylethylendiamino derivative **31** is formed. Tertiary phosphine **28** is easily oxidized with hydrogen peroxide, adds sulfur, and undergoes the Staudinger reaction with phenylazide, thus affording phosphorus(V) compounds **32a–c**. Like compound **30**, they are converted to ethylendiamino derivatives **33a,b** by the reaction with dimethylamine.

Synthesis of Diphenyl(imidazolyl)Phosphines

Diphenylphosphine halides Ph_2PHal (Hal=Cl, Br) are the less reactive phosphorylating agents among those involved in the present study and,

TABLE 4 Spectroscopic Data of 5-Phosphorylated-1,2-Disubstituted Imidazoles: ^{13}C NMR δ (Multiplicity in ppm) and J_{PC} (Hz)

		^{13}C NMR				
No	Solvent	N-CH_3	C-2	C-4	C-5	Other Signals
2a	C_6D_6	32.07, s	161.12, d, 2.50	140.50, d, 52.82	128.85, d, 76.71	42.36, s
2b	C_6D_6	31.86, s	155.08, d, 2.00	141.50, d, 57.85	128.70, d, 78.0	14.38, s
2c	C_6D_6	34.36, d, 3.77	157.34, d, 3.77	141.40, d, 50.3	127.08, d, 8.8	129.11 (d, 27.7, *i*-Ph); 130.20 (s, 2,6-Ph); 130.52 (s, 4-Ph); 129.33 (s, 3,5-Ph).
2d	C_6D_6	33.72, d, 2.52	156.1, d, 3.77	141.01, d, 52.82	128.85, d, 46.53	129.35 (d, 11.3, *i*-Ph); 129.61 (s, 2,6-Ph); 129.90 (s, 4-Ph); 128.7(s, 3,5-Ph).
3a	C_6D_6	30.80, d, 7.54	156.45, d, 6.3	131.54, d, 5.03	127.66, d, 24.00	42.65 (s, NCH_3); 14.5 (d, 3.77, $PNCH_2\underline{CH_3}$); 42.74 (d, 17.6, $PN\underline{CH_2}$)
3b	C_6D_6	31.15, d, 6.30	146.0, d, 6.3	135.0, d, 5.03	132.3, d, 1.26	14.36 (d, 3.77, $PNCH_2\underline{CH_3}$); 42.74 (d, 16.35, $PN\underline{CH_2}$)
3c	C_6D_6	33.94, d, 8.80	151.8, d, 6.29	135.94, d, 5.03	133.44, d, 1.26	132.75(s, *i*-Ph); 130.0 (s, 2,6-Ph); 129.0 (s, 4-Ph); 129.22 (s, 3,5-Ph); 15.43 (d, 3.8, $PNCH_2\underline{CH_3}$); 43.9 (d, 17.6, $PN\underline{CH_2}$)
3d	C_6D_6	33.60, d, 7.54	151.9, d, 5.03	132.35, d, 5.03	136.24, d, 6.30	132.37 (s, *i*-Ph-P);130.0 (s, 2,6-Ph-P); 129.0 (s, 4-Ph-P); 29.22 (s, 3,5-Ph-P); 41.77 (d, $PN\underline{CH_3}$)
4	C_6D_6	30.78, s	157.70, d, 5.03	134.57, d, 6.30	125.30, d, 20.10	39.10 (d, 11.30, $PNCH_3$); 42.55 (s, NCH_3)
5	C_6D_6	30.70, s	156.90, d, 8.80	135.43, s	119.78, d, 13.80	41.10 (d, 19.00, $PNCH_3$); 42.53 (s, NCH_3); 84.80 (m, CF_3); 123.90 (dd, 16.35; 287.0, $P\underline{C}Cl_2CF_3$)
6a	C_6D_6	31.06, d, 5.03	157.02, d, 5.03	135.45, d, 2.64	129.70, d, 21.38	42.47 (s, NCH_3); 3.48 (d, 3.77); 23.90 (d, 5.03, $POCH(\underline{CH3})_2$); 70.19 (d, 15.09, $PO\underline{CH}$)
6b	C_6D_6	31.63, d, 5.03	147.76, d, 2.51	136.28, d, 22.64	134.10, d, 26.41	15.10 (s, SCH_3); 24.15 (d, 3.77); 24.45 (d, 6.3, $POCH(\underline{CH3})_2$); 70.58 (d, 13.83, $PO\underline{CH}$)
7a	$CDCl_3$	42.74, s	157.17, d, 5.00	128.9, s	123.90, d, 5.00	31.20 (s, NCH_3); 133.20 (d, 20.12, *i*-Ph-P); 134.40 (d, 6.3, 2,6-Ph-P); 135.33 (d, 6.3, 4-Ph-P); 128.53 (d, 7.54, 3,5-Ph-P)
7b	$CDCl_3$	31.83, d, 6.3	147.60, d, 8.80	137.81, d, 5.03	134.80, d, 6.30	15.77 (s, SCH_3); 128.90 (d, 7.6, *i*-Ph); 133.22 (d, 20.12, 2,6-Ph); 129.15 (s, 4-Ph); 128.68 (d, 18.86, 3,5-Ph)
7c	$CDCl_3$	33.32, d, 12.6	151.85, d, 2.50	137.30, d, 2.50	128.57, s	128.88 (s, 4-Ph); 128.92 (s, 3,5-Ph-P); 128.72 (s, 3,5-Ph); 128.78 (s, 2,6-Ph); 129.24 (s, 4-Ph-P); 130.73 (s, *i*-Ph); 133.37; 133.53 (s, 2,6-Ph-P); 134.96 (d, 6.30, *i*-Ph-P)
8a	$CDCl_3$	32.34, s	158.05, d, 13.8	134.07, d, 50.3	121.90, d, 162,2	13.80 (d, 2.5, $PNCH_2\underline{CH_3}$); 39.76 (d, 5.03, $PN\underline{CH_2}$); 42.50 (s, NCH_3)
8b	$CDCl_3$	38.50, s	150.0, d, 11.0	136.95, d, 15.1	126.62, d, 157.2	13.8(d, 3.0, $PNCH_2\underline{CH_3}$); 15.23 (s, SCH_3); 39.8 (d, 5.0, $PN\underline{CH_2}$)
8c	$CDCl_3$	34.20, d, 2.50	153.00, d, 12.6	137.00, d, 15.0	125.2, d, 155.9	13.8 (s, $PNCH_2\underline{CH_3}$); 39.9 (d, 3.77, $PN\underline{CH_2}$); 130.20 (d, 2.5, *i*-Ph); 129.11 (s, 2,6-Ph); 129.21 (s, 4-Ph); 128.52 (s, 3,5-Ph)
8d	$CDCl_3$	34.10, s	153.03, d, 11.32	137.26, d, 18.86	123.91, d, 30.18	37.15 (d, 2.52, $PNCH_3$); 128.28 (s, 3,5-Ph); 129.12 (s, 2,6-Ph); 129.32 (s, 4-Ph); 129.95 (s, *i*-Ph)
8e	$CDCl_3$	30.04, s	158.02, d, 15.09	137.43, d, 20.12	122.89, d, 152.17	24.36 (d, 3.77), 24.08 (d, 5.03, $POCH(\underline{CH3})_2$); 42.51 (s, NCH_3); 71.76 (d, 3.77, $PO\underline{CH}$)
8f	$CDCl_3$	32.41, s	150.13, d, 13.83	140.05, d, 21.40	127.48, d, 188.64	15.26 (s, SCH_3); 23.46 (d, 5.03), 23.85 (d, 5.03, $POCH(\underline{CH3})_2$); 71.96 (d, 5.03, $PO\underline{CH}$)
10a	$CDCl_3$	31.86, s	157.606 d, 13.83	134.97, d, 16.35	120.87, d, 190.0	42.42 (s, NCH_3); 14.07 (d, 1.26, $PNCH_2\underline{CH_3}$); 38.86 (d, 6.30, $PN\underline{CH_2}$)
10b	$CDCl_3$	32.30, s	149.21, d, 13.00	137.60, d, 16.00	125.60, d, 187.0	15.33 (s, SCH_3); 14.09 (d, 1.26, $PNCH_2\underline{CH_3}$); 39.86, (s, $PN\underline{CH_2}$)
10c	$CDCl_3$	33.88, s	152.60, d, 12.57	137.77, d, 17.61	125.20, d, 184.90	14.14 (d, 2.51, $PNCH_2\underline{CH_3}$); 39.06 (d, 5.03, $PN\underline{CH_2}$); 130.27(s, *i*-Ph); 129.07 (s, 2,6-Ph); 129.16 (s, 4-Ph); 128.53 (s, 3,5-Ph);
10e	$CDCl_3$	31.90, s	157.90, d, 16.35	137.07, d, 17.61	117.7, d, 104.38	23.78, 24.08 (d, 5.03, d, 5.03, $POCH(\underline{CH_3})_2$); 42.51 (s, NCH_3); 71.18 (d, 5.03, $PO\underline{CH}$)

(Continued)

TABLE 4 Continued

		^{13}C NMR				
No	Solvent	N-CH_3	C-2	C-4	C-5	Other Signals
10f	$CDCl_3$	32.01, s	149.71, d, 16.35	139.46, d, 18.86	122.50, d, 227.62	14.93 (s, SCH_3); 23.51, 23.79 (d, 5.03, d, 5.03, $POCH(\underline{CH_3})_2$); 71.09 (d, 5.03, $PO\underline{CH}$)
13	$CDCl_3$	32.07, s	157.80. d, 13.83	135.73, d, 15.09	121.0, d, 155.94	17.53 (d, 109.41, $P(O)CH_3$); 23.87 (d, 6.3), 24.53 (d, 2.51, $POCH(\underline{CH_3})_2$); 42.46 (s, NCH_3); 69.80 (d, 6.30, $PO\underline{CH}$)
12a	CD_3CN	33.83, s	161.84, d, 13.80	143.30, d, 16.35	111.50, d, 157.20	13.00 (d, 96.80, P^+CH_3); 14.04 (d, 2,50, $P^+NCH_2\underline{CH_3}$); 41.08 (d, 5.03, $P^+N\underline{CH_2}$); 42.40 (s, NCH_3)
12b	CD_3CN	33.90, s	155.68, d, 12.75	144.90, d, 18.90	116.55, d, 152.20	13.00 (d, 95.60, P^+CH_3); 14.00 (d, 2,50, $P^+NCH_2\underline{CH_3}$); 15.44 (s, SCH_3); (d, 3.80, $P^+N\underline{CH_2}$)
11	$CDCl_3$	32.50, s	158.60, d, 16.35	139.40, d, 15.09	112.00, d, 174.80	37.37 (d, 3.80, $PNCH_3$); 42.26 (s, NCH_3); 80.00 (m, CF_3); 121.75 (qd, 5.03; 283.0, $P\underline{CCl_2}CF_3$)
17a	$CDCl_3$	31.21, d, 8.80	157.65, d, 5.03	134.40, d, 8.80	119.00, d, 6.30	42.50 (s, NCH_3)
17b	$CDCl_3$	31.84, d, 8.8	149.05, d, 5.03	138.10, d, 7.5	123.13, d, 5.03	15.57 (s, SCH_3)
17c	$CDCl_3$	33.43, d, 12.57	152.85, d, 3.77	138.0, d, 5.03	123.61, d, 7.54	130.25 (s, *i*-Ph); 128.90 (s, 2,6-Ph); 129.20 (s, 4-Ph); 128.66 (s, 3,5-Ph)
18b	$CDCl_3$	32.02, d, 8.80	147.80, d, 3.80	138.15, d, 13.80	129.74, d, 40.24	33.00 (s, NCH_3); 125.99 (d, 2.50, P-CC-5′); 132.94 (d, 17.60, P-C-4′); 146.44 (d, 12.75, C-2′)
19b	$CDCl_3$	32.95, s	152.40, d, 11.32	140.07, d, 18.86	124.04, d, 144.62	15.16 (s, SCH_3)
19c	$CDCl_3$	34.69, s	154.80, d, 11.32	140.10, d, 17.61	124.02, d, 144.62	128.82 (s, 3,5-C-Ph); 129.20 (s, *i*-C-Ph); 129.26 (2,6-C-Ph); 129.90 (s, 4-C-Ph)
20b	$CDCl_3$	32.75, s	150.92, d, 11.32	140.14, d, 17.61	124.93, d, 139.60	15.27 (s, SCH_3); 15.47 (s, SCH_3'); 33.28 (NCH_3); 131.46 (d, 31.44, C-5′); 132.95 (d, 168.50, PC-4′); 147.65 (d, 22.64, C-2′)
20c	$CDCl_3$	38.48, s	153.70, d, 11.32	140.12, d, 16.35	124.98, d, 137.08	35.13 (NCH_3); 128.62 (s, 3,5-CPh); 128.68 (s, 3,5-C′Ph); 128.87 (2,6-C′Ph); 129.20 (2,6-CPh); 129.34 (s, *i*-C′Ph); 129.49 (4-CPh); 129.51 (5-C′Ph); 129.58 (*i*-CPh); 132.17 (d, 35.20, C′-5); 132.90 (d, 207.0, PC′-4); 150.86 (d, 20.12, C′-2)
21a	$CDCl_3$	32.82, s	159.38, d, 12.75	136.90, d, 15.09	117.22, d, 124.50	42.47 (s, NCH_3)
21b	$CDCl_3$	33.15, s	152.90, d, 11.32	139.50, d, 17.61	122.14, d, 122.00	15.13 (s, SCH_3)
21c	$CDCl_3$	34.94, s	155.25 d, 11.32	139.43 d, 16.35	122.00, d, 122.00	128.81 (s, 3,5-C-Ph); 129.27 (s, *i*-C-Ph); 129.33 (2,6-C-Ph); 129.93 (s, 4-C-Ph)
22b	$CDCl_3$	32.94, s	152.15, d, 10.06	140.35, d, 13.83	122.25, br s	15.10 (s, SCH_3); 55.46 (s, OCH_3); 114.57 (3,5-C-Ar); 123.20 (d, 16.35, 2,6-C-Ar); 141.92 (s, *i*-C-Ar); 152.94 (s, 4-C-Ar)
22c	$CDCl_3$	34.78, s	154.60, d, 11.32	140.30, d, 17.60	123.10, d, 134.56	55.56 (s, OCH_3); 114.71 (3,5-C-Ar); 123.30 (d, 17.60, 2,6-C-Ar); 128.78 (s, 3,5-C-Ph); 129.28 (s, 2,6-C-Ph); 129.32 (s, *i*-C-Ph); 129.84 (s, 4-C-Ph); 142.20 (s, *i*-C-Ar); 152.91 (s, 4-C-Ar)
23a	C_6D_6	31.86, s	158.97, d, 2.50	138.75, d, 35.21	124.36, d, 49.00	42.25 (s, NCH_3); 128.60 (d, 6.2, 3,5-Ph); 129.88 (s, 4-Ph); 130.56 (d, 22.64, 2,6-Ph); 135.60 (d, 25.16, *i*-Ph)
23b	C_6D_6	31.32, s	151.87, d, 3.77	142.00 d, 32.70	128.58 d, 47.80	14.75 (s, SCH_3); 136.23 (d, 25.15, *i*-Ph); 128.67 (d, 6.3, 3,5-Ph); 129.85 (s, 4-Ph); 130.71 (d, 22.64, 2,6-Ph).
23c	C_6D_6	33.04, s	153.96, d, 2.50	140.95 d, 24.00	129.94 d, 87.00	128.41 (s, 3,5-Ph); 128.78 (d, 6.30, 3,5-PhP); 129.07 (s, 4-Ph); 129.20 (s, 2,6-Ph); 130.30 (s, 4-PhP); 130.36 (s, *i*-Ph); 131.27 (d, 24.00, 2,6-PhP); 135.66 (d, 24.00, *i*-PhP)
25a	$CDCl_3$	32.85, s	159.30, d, 12.75	132.30, d, 10.10	118.56, d, 108.80	42.36 (s, NCH_3); 128.60 (d, 12.75, 3,5-C-Ph); 130.20 (d, 95.60, *i*-C-Ph); 132.36 (s, 4-C-Ph); 136.62 (d, 13.83, 2,6-C-Ph)

(Continued)

TABLE 4 Continued

		^{13}C NMR				
No	Solvent	N-CH_3	C-2	C-4	C-5	Other Signals
14	C_6D_6	30.60, s	156.92, d, 6.30	133.50, s	124.35, d, 2.50	40.24 (d, 16.35, $PNCH_3$); 42.61 (s, NCH_3)
15	C_6D_6	31.97, d, 6.30	159.53, d, 5.03	137.80, d, 28.00	121.73, d, 33.00	42.02 (s, NCH_3)
16	$CDCl_3$	32.10, s	158.25, d, 13.83	136.41, d, 17.60	119.78, d, 37.73	36.39 (s, $P(O)NCH_3$); 42.28 (s, NCH_3)
27	C_6D_6	31.82, d, 7.54	159.50, d, 6.30	139.22, d, 28.92	120.22, d, 39.00	41.94 (s, NCH_3); 129.07 (d, 45.27,C=$\underline{C}Cl_2$); 130.92 (d, 71.70, P$\underline{C}$=C)
29	C_6D_6	30.40, d, 10.0	158.20, d, 6.30	133.60, s	121.65, d, 10.0	40.45 (d, 16.34, $PNCH_3$); 42.50 (s, NCH_3); 122.60, (d, 34.0, C=$\underline{C}Cl_2$); 136.00 (d, 74.0, P$\underline{C}$=C)
28	C_6D_6	30.91, s	157.78, d, 6.30	136.40, d, 7.54	117.45, d, 7.54	42.42 (s, NCH_3); 126.80 (d, 42.75, C=$\underline{C}Cl_2$); 131.19 (d, 50.30, P$\underline{C}$=C)
30	$CDCl_3$	32.53, s	159.07, d, 15.09	136.41, d, 15.09	117.34, d, 150.91	37.20 (d, 16.35, $PNCH_3$); 42.34 (s, NCH_3); 128.70 (d, 94.32, P$\underline{C}$=Cl; 130.68 (d, 17.61, C=$\underline{C}Cl_2$)
32a	$CDCl_3$	32.75, s	159.27, d, 13.80	138.30, d, 17.60	117.54, d, 153.40	42.27 (s, NCH_3); 125.20 (d, 115.70, P$\underline{C}$=C); 134.64 (d, 17.60, C=$\underline{C}Cl_2$)
32b	$CDCl_3$	32.92, s	159.55, d, 12.57	137.76, d, 16.35	116.28, d, 128.27	42.19 (s, NCH_3); 125.67 128.70 (d, 90.54, P$\underline{C}$=C); 132.60 (d, 17.60, C=$\underline{C}Cl_2$)
32c	$CDCl_3$	32.35, s	159.42, d, 13.83	138.64, d, 17.60	116.38, d, 152.17	42.10 (s, NCH_3); 119.00 (s, 4-Ph); 123.27 (d, 18.86, 2,6-Ph); 129.00 (s, 3,5-Ph); 129.40 (d, 56.60, P$\underline{C}$=C); 132.18 (d, 16.35, C=$\underline{C}Cl_2$); 149.18 (s, *i*-Ph)
31	$CDCl_3$	32.00, s	157.70, d, 11.30	136.57, d, 13.80	121.00, d, 138.30	37.45 (s, $PNCH_3$); 40.30 (s, C=CN$\underline{C}H_3$); 42.50 (s, NCH_3); 73.00 (d, 138.00, P$\underline{C}$=C); 165.25 (d, 24.00, C=$\underline{C}NCH_3$)
33a	$CDCl_3$	32.00, s	157.30, d, 12.75	135.80, d, 15.10	121.80, d, 143.40	39.90; 41.50 (s, C=CN$\underline{C}H_3$); 42.20 (s, NCH_3); 70.00 (d, 161.00, P$\underline{C}$=C); 164.35 (d, 20.10, C=$\underline{C}NCH_3$)
33b	$CDCl_3$	32.43, s	158.00, d, 11.30	136.05, d, 15.09	120.20, d, 123.24	40.28; 42.00 (s, C=CN$\underline{C}H_3$); 42.44 (s, NCH_3); 68.05 (d, 132.00, P$\underline{C}$=C); 165.27 (d, 24.00, C=$\underline{C}NCH_3$)
34a	CD_3CN	34.37, s	162.55, d, 12.75	144.67, d, 15.10	105.50, d, 120.73	11.00 (d, 60.40, $P^+\underline{C}H_3$); 42.30 (s, NCH_3); 119.90 (d, 93.00, *i*-PhP); 130.93 (d, 7.50, 3,5-PhP); 133.77 (d, 11.32, 2,6-PhP); 135.80 (d, 2.50, 4-PhP)
35a	$CDCl_3$	32.52, s	158.64, d, 11.32	127.80, d, 15.09	120.90, d, 127.00	42.40 (s, NCH_3); 131.52 (d, 110.60, *i*-Ph); 131.80 (d, 11.32, 2,6-Ph); 132.27 (d, 3.8, 4-Ph); 128.53 (d, 12.5, 3,5-Ph)
35b	$CDCl_3$	32.88, s	151.30, d, 11.32	140.06, d, 15.09	125.70, d, 123.20	15.43 (s, SCH_3); 130.91(br s, *i*-Ph); 131.80 (d, 10.06, 2,6-Ph); 132.48 (d, 3.77, 4-Ph); 128.75 (d, 12.57, 3,5-Ph)
35c	$CDCl_3$	34.25, s	153.85, d, 8.8	140.24, d, 16.36	125.20, d, 121.98	129.25 (s, *i*-PhP); 120.07 (s, 2,6-Ph); 129.50 (s, 4-Ph); 128.73 (s, 3,5-Ph); 131.41 (d, 111.92, *i*-PhP); 131.70 (d, 10.06, 2,6-PhP); 132.38 (d, 2.5, 4-PhP); 128.60 (d, 10.06, 3,5-PhP)
36a	$CDCl_3$	32.60, s	159.03, d, 11.32	136.80, (d, 13.8	119.40, d, 109.41	42.10 (s, NCH_3); 128.6 (d, 12.6, 3,5-Ph); 131.3 (br s, *i*-Ph); 132.0 (d, 8.8, 2,6-Ph); 132.1 (s, 4-Ph)
36b	$CDCl_3$	33.04, s	151.54, d, 10.06	138.79, (s	124.00, d, 105.64	15.43 (s, SCH_3); 128.8 (d, 12.6, 2,6-Ph); 131.05 (d, 89.3, *i*-Ph); 132.03 (d, 12.6, 3,5-Ph); 132.27 (br s, 4-PhP);
36c	$CDCl_3$	34.42, s	154.3, d, 10.06	139.56, d, 15.09	123.85, d, 105.64	128.70 (d, 10.0, 3,5-PhP); 128.85 (s, 3,5-Ph); 129,22 (s, 2,6-Ph); 129.57 (s, 4-Ph); 129.64 (s, *i*-PhP); 131.48 (d, 89.3, *i*-PhP); 132.09 (d, 11.32, 2,6-PhP); 132.20 (d, 3,77, 4-PhP);
37b	$CDCl_3$	32.50, s	151.34, d, 8.80	141.15, d, 13.80	123.50, d, 105.64	15.30 (s, SCH_3); 55.54 (s, OCH_3); 114.45 (3,5-C-Ar); 123.35 (d, 17.60, 2,6-CPh); 128.77 (d, 13.80, 3,5-CPh); 130.85 (d, 109.50, *i*-CPh); 131.94 (s, 4-CPh); 132.00 (2,6-C-Ar); 144.00 (d, 2.50, *i*-C-Ar); 152.26 (s, 4-C-Ar)

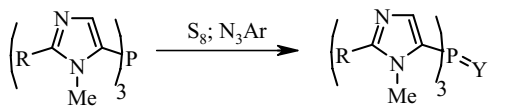
(Continued)

TABLE 4 Continued

No	Solvent	^{13}C NMR				
		N-CH_3	C-2	C-4	C-5	Other Signals
37a	$CDCl_3$	32.15, s	159.00, d, 11.30	138.63, d, 13.80	118.74, d, 110.64	42.45 (s, NCH_3); 55.54 (s, OCH_3); 114.40 (3,5-C-Ar); 123.25 (d, 17.60, 2,6-CPh); 128.65 (d, 12.75, 3,5-CPh); 131.80 (d, 2.50, 4-CPh); 131.22 (d, 109.50, *i*-CPh); 132.00 (d, 10.20, 2,6-C-Ar); 144.00 (d, 2.50, *i*-C-Ar); 152.26 (s, 4-C-Ar)
38a	$CDCl_3$	34.73, s	150.95, d, 6.30	133.40, br s	123.90, d, 115.70	37.50 (s, N^+CH_3); 42.13 (s, NCH_3); 128.28 (s, 4-C-Ph); 128.50 (d, 113.20, *i*-C-Ph); 129.40 (d, 13.80, 2,6-C-Ph); 132.22 (d, 11.30, 3,5-C-Ph)
38b	$CDCl_3$	36.05, s	147.40, d, 5.00	133.33, d, 3.80	121.70, d, 106.90	19.43 (s, SCH_3); 38.58 (s, N^+CH_3); 127.88 (d, 91.80, *i*-C-Ph); 129.05 (d, 12.75, 3,5-C-Ph); 129.58 (d, 13.80, 2,6-C-Ph); 132.68 (d, 2.5, 4-C-Ph);
38c	$CDCl_3$	35.73, s	149.70, d, 5.00	132.22, d, 17.60	128.26, d, 114.45	37.86 (s, N^+CH_3); 120.05 (s, *i*-C-Ph); 128.20 (d, 110.70, *i*-C-PhP); 129.56 (d, 13.80, 3,5-C-PhP); 129.96 (s, 3,5-C-Ph); 131.20 (s, 2,6-C-Ph); 132.30 (d, 12.75, 2,6-C-PhP); 133.25 (s, 4-C-Ph); 133.64 (d, 3.80, 4-C-PhP)
38d	CD_3CN	34.35, s	150.97, d, 8.80	128.07, d, 18.90	123.42, d, 182.35	14.30 (s, $PNCH_2\underline{CH_3}$); 35.97 (s, N^+CH_3); 39.44 (d, 3.80, $PN\underline{CH_2}$); 41.14 (s, NCH_3)
38e	$CDCl_3$	35.63, s	145.93, d, 5.00	130.53, d, 16.35	131.57, d, 144.60	14.23 (s, $PNCH_2\underline{CH_3}$); 19.21 (s, SCH_3); 38.50 (s, N^+CH_3); 40.54 (d, 3.80, $PN\underline{CH_2}$)
38f	CD_3CN	35.76, s	149.70, d, 5.00	130.90, d, 17.60	127.90, d, 149.65	36.97 (s, N^+CH_3); 37.37 (d, 5.00, CH_3N); 121.66 (s, *i*-C-Ph); 130.30 (s, 3,5-C-Ph); 131.53 (s, 2,6-C-Ph); 133.54 (s, 4-C-Ph)

accordingly, they require more severe conditions for interaction with imidazoles **1a–c** to form corresponding diphenyl(imidazol-5-yl)phosphines **7a–c** (Scheme 9 and Table 1). The readiness of the reaction regularly decreases together with the electron-donating ability of the 2-substituent in the imidazole ring. Application of second mole of imidazole as HCl acceptor is also reasonable to advance its purity.

Starting from compounds **7a–c** a number of phosphorus(V) derivatives **35–37** have been obtained by standard procedures (Scheme 9). As evidenced by ^{31}P NMR spectral data, phosphines **7a–c** are alkylated with CH_3I not only at the phosphorus atom but also at the heterocyclic imine nitrogen atom to form a mixture of compounds (δ_P(Py) 8–10 and 13–14 ppm, respectively) from which in the case of **7a** only we managed to isolate phosphonium salt **34a** by crystallization.



17a–c **21a–c** Y = S; **22b, c** Y = N-Ar

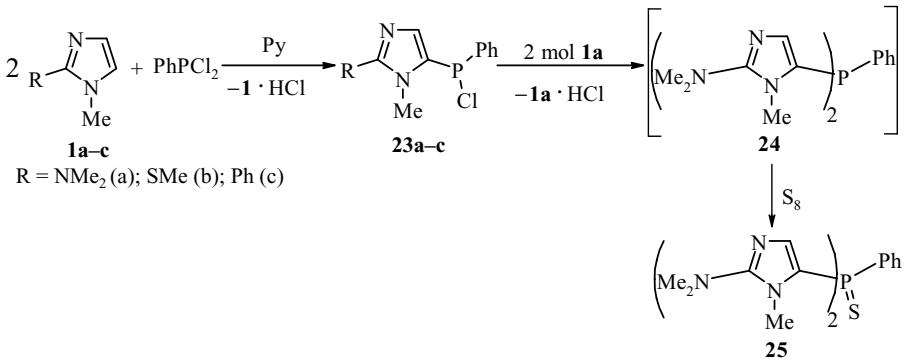
R = NMe_2 (a), SMe (b), Ph (c)
Ar = C_6H_4-OCH_3-p

SCHEME 5

EXPERIMENTAL

General

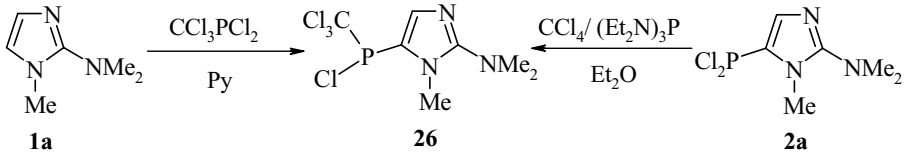
All procedures with air and moisture sensitive compounds were performed under an atmosphere of dry argon in flame-dried glassware. Solvents were purified and dried by standard methods. Melting points were determined with an electro-thermal capillary melting point apparatus and were uncorrected. Yields, crystallization solvents, and physical specifications of isolated products are listed in Table 2. All reactions were carried out monitoring by ^{31}P NMR. All organic solutions were dried over anhydrous $MgSO_4$. ^{1}H spectra were recorded on a Bruker Avance DRX 500 (500.13 MHz) or Varian VXR-300 (299.94 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker Avance DRX 500 (125.75 MHz) spectrometer. ^{31}P NMR spectra were recorded on a Varian VXR-300 (121.42 MHz) spectrometer. Chemical shifts (δ) are reported in ppm downfield relative to internal TMS (for ^{1}H, ^{13}C) and external 85% H_3PO_4 (for ^{31}P). Chromatography was performed on silica gel Gerudan SI60. Elemental analyses were performed at the Microanalytical laboratory of the



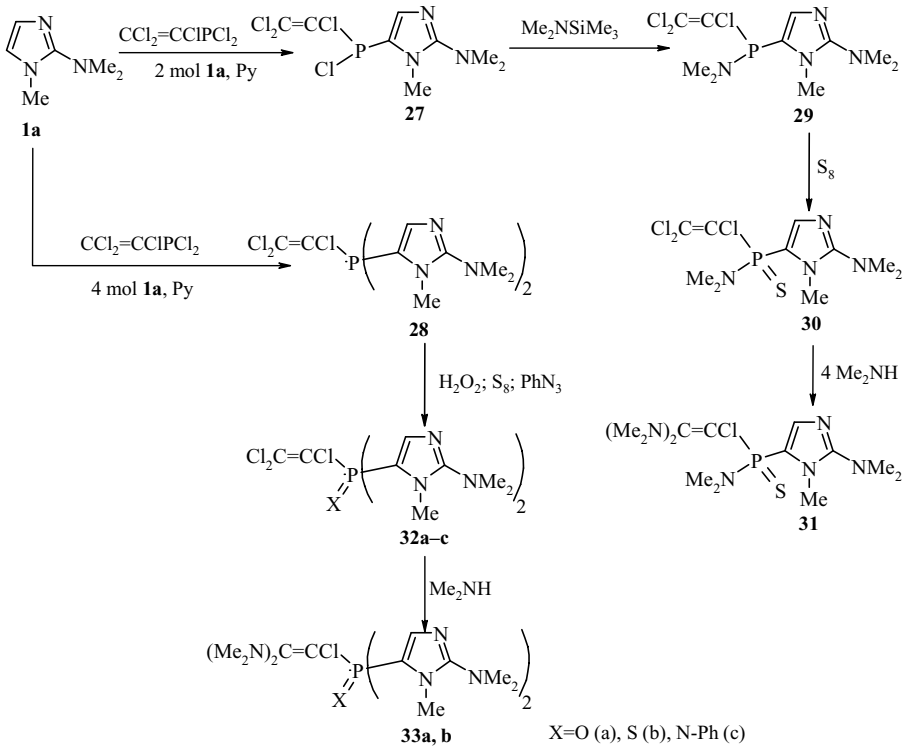
SCHEME 6

Institute of the Organic Chemistry National Academy of Sciences of Ukraine.

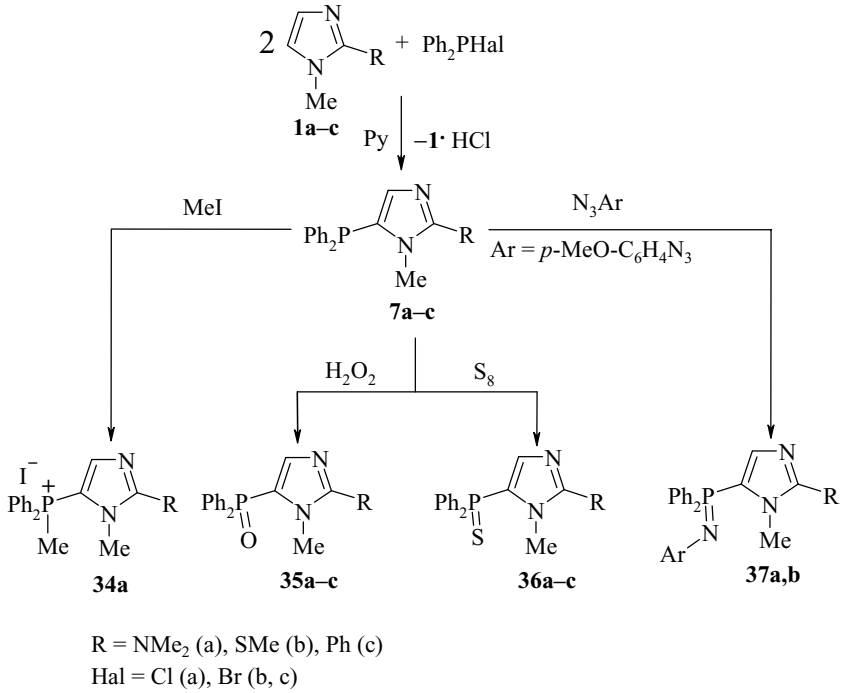
CCDC 643530 (**8b**), 693407 (**19c**), and 693406 (**20c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK;



SCHEME 7



SCHEME 8



SCHEME 9

fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

General Procedure for Preparation of 1-Methyl-2-(R)-1H-imidazol-5-ylphosphonous Dihalides **2a–d**

A solution of imidazole **1a–c** (10 mmol) in pyridine (20 mL) to phosphorus trichloride (or phosphorus tribromide for **1c**; 25 mmol) was added. The reaction mixture was stirred for 2 h at 20°C (**1a)**, for 3 h (**1b)**, or 48 h at 100°C (**1c**). Pyridine was removed in vacuo, then benzene (or diethyl ether for **1a**; 50 mL) was added, and the resulted mixture was heated up to reflux. The precipitate was filtered off, washed with benzene (or diethyl ether for **1a**; 2 × 20 mL), and the filtrate was concentrated in vacuo. The residue was distilled in vacuo to give **2a–d**.

1-Methyl-2-phenyl-1H-imidazol-5-yl-phosphonous dichloride **2d** *(Method B).* To a solution of imidazole **1a** (1.25 g, 10 mmol) and triethylamine (2.0 g, 20 mmol) in pyridine (20 mL), a mixture of phosphorus tribromide (2.7 g, 10 mmol) and phosphorus trichloride (5.5 g, 40 mol) was added. The reaction mixture was heated for 2 h at 120°C. Pyridine was removed in vacuo, and then diethyl ether (50 mL) was added. The precipitate was filtered off, washed with diethyl ether (2 × 20 mL), and the filtrate was concentrated in vacuo. The residue was distilled in vacuo to give **2d** as a light yellow liquid.

General Procedure for Preparation of N,N,N′,N′-Tetraalkyl-P-(1-methyl-2-(R)-1H-imidazol-5-yl)phosphonous Diamide **3a–d**

To a stirred solution of dichlorophosphine **2a–d** (10 mmol) in benzene (15 mL) cooled to 0–5°C, a solution of diethylamine (42 mmol) or dimethylamine (for **2c**) in benzene (20 mL) was added dropwise over 10 min. The reaction mixture was stirred for 2 h (3 h for **2c**) at 20°C. The precipitate was filtered off, washed with benzene (2 × 20 mL), and the filtrate was concentrated in vacuo. The residue was distilled in vacuo to give **3a–d**.

P-[2-(Dimethylamino)-1-methyl-1H-imidazol-5-yl]-N,N-dimethylphosphonamidous Chloride **4**

To dichlorophosphine **2a** (2.3 g, 10 mmol), a solution of *N,N*-dimethyltrimethylsilylamine (1.2 g, 10 mmol) in dichloromethane (15 mL) was added. The reaction mixture was heated for 40 min at 100°C in a sealed tube. The solvent was removed in vacuo; the residue was treated with hot pentane (2 × 10 mL), insoluble impurities were filtered off and the filtrate was evaporated. The crude product was distilled in vacuo to give pure **4** as a pale yellow liquid.

P-(1,1-Dichloro-2,2,2-trifluoroethyl)-P-[2-(dimethylamino)-1-methyl-1H-imidazol-5-yl]-N,N-dimethylphosphinous Amide **5**

To a stirred solution of compound **4** (2.4 g, 1 mmol) and trifluorotrichloroethane (4.5 g, 2.4 mmol) in diethyl ether (40 mL), tris(diethylamino)phosphine (5.9 g, 2.4 mmol) in diethyl ether (15 mL) was added dropwise at −60 to −80°C over 20 min. The reaction mixture was allowed to warm to 25°C and stirred for further 30 min. The precipitate was filtered off, washed with diethyl ether (2 × 20 mL); the filtrate was concentrated in vacuo. The oily residue was treated with hot pentane (30 mL) to afford **5**, precipitating at −7°C as colorless crystals.

General Procedure for Preparation of Diisopropyl[1-methyl-2-(R)-1H-imidazol-5-yl]phosphonite **6a,b**

To a solution of dichlorophosphine **2a,b** (10 mmol) and triethylamine (21 mmol) in benzene (50 mL) cooled to 0–5°C, isopropanol cooled to −30°C (21 mmol) was added. The reaction mixture was stirred for 15 h at 20°C. The precipitate was filtered off, washed with benzene (2 × 20 mL); the filtrate was concentrated in vacuo, and the oily residue was treated with pentane (70 mL). Insoluble impurities were filtered off, and the filtrate was concentrated. The residue was distilled in vacuo to give **6 a,b**.

General Procedure for Preparation of 5-(Diphenylphosphino)-1-methyl-2-(R)-1H-imidazole **7a–c**

To a solution of **1a–c** (22 mmol) in pyridine (30 mL), Ph_2PCl (for **1a**), and Ph_2PBr (for **1b, c**; 10 mmol) was added. The reaction mixture was stirred for 22 h at 20°C (for **1a**), 8 days at 30°C (for **1b**), and 54 h at 100°C (for **1c**). Pyridine was removed in vacuo, then benzene (50 mL) was added, and the resulted mixture was heated up to reflux, the precipitate was filtered off, washed with benzene (2 × 25 mL), the filtrate was concentrated in vacuo. The residue was treated with hot hexane (60 mL); insoluble impurities were filtered off, and the filtrate concentrated. The residue was distilled in vacuo to give **7a–c**.

5-(Diphenylphosphino)-1-Methyl-2-Phenyl-1H-imidazole **7c** *(Method B).* To a stirred solution of bromobenzene (3.2 g, 2 mmol) in THF (10 mL), BuLi (0.8 mL; 2.5 N solutions in hexane) was added dropwise at −80°C over 5 min. The mixture was stirred for 30 min at −60°C, after cooling to −90°C; a solution of dichlorophosphine **2c** (2.6 g, 1 mmol) in THF was added. After stirring for 2.5 h at −40°C, the reaction mixture was allowed to warm to −10°C and water (5 mL) was added. The organic layer was separated and concentrated in vacuo. The residue was treated with hot hexane (2 × 50 mL). The solution was refined with activated charcoal and concentrated to 40 mL. The precipitate formed at −10°C was filtered off and washed with hexane to give **7c** as colorless crystals.

General Procedure for Preparation of P-[1-Methyl-2-(R)-1H-imidazol-5-yl]-N,N,N′,N′-tetraalkyl(thio)phosphonic Diamide **8a–d**, *O,O-Diisopropyl [1-methyl-2-(R)-1H-imidazol-5-yl](thio)phosphonate* **8e, f**, *Tris(1-methyl-2-phenyl-1H-imidazol-5-yl)phosphine Sulfide* **21a–c**, *and Diphenyl(1-methyl-2-R-1H-imidazol-5-yl)phosphine Sulfide* **36a–c**

To a solution of compounds **3a–d, 6a,b, 17a–c**, or **7a–c** (1 mol) in benzene (or dichloromethane for **17a–c**; 3 mL), powdered sulfur (1.1 mol) was added. The mixture was stirred for 3–4 h at 20°C (in case **35a–c)**, for 18 h (**21a**) or heated for 4 h (**21b**), or for 14 h (**21c**) at 40°C. Benzene (dichloromethane) was removed in vacuo. The crude product was crystallized from the appropriate solvent to give **8a–d, 8e,f, 21a**, and **36a–c**, respectively (see Table 1). In the case of **21b,c**, the product precipitated from the concentrated diethyl ether solution (15 mL) preliminarily refined with activated charcoal.

General Procedure for Preparation of P-[1-Methyl-2-(R)-1H-imidazol-5-yl]-N,N,N′,N′-Tetraethylphosphonic Diamide **10a–c**

To a solution of compound **3a–c** (1 mmol) in hexane (25 mL), hexachloroethane (1 mmol) dissolved in hexane (25 mL) was added. In 1 h, the intermediate chlorophosphonium chloride **9** was filtered off, dissolved in dichloromethane (15 mL), and shaken with a saturated solution of Na_2CO_3. The organic layer was separated, washed with water, dried, and concentrated in vacuo. The crude product was crystallized from the appropriate solvent to give **10a–c**.

General Procedure for Preparation of Diisopropyl 2-(Dimethylamino)-1-methyl-1H-imidazol-5-yl-phosphonate **10e,f**, *Tris(1-methyl-2-R-1H-imidazol-5-yl)phosphine Oxide* **19b,c**, *and Diphenyl(1-methyl-2-R-1H-imidazol-5-yl)phosphine Oxide* **35a–c**

To a solution of compounds **6a,b, 17b,c**, or **7a–c** (5 mmol) in dichloromethane (5 mL), hydrogen

peroxide (5 mmol, 30% solution) was added. The reaction mixture was shaken for 15–30 min. The organic layer was separated, washed with water, dried, and concentrated in vacuo affording the residue, which in the case of **10f** was distilled in vacuo to give the target product or crystallized from the appropriate solvent to give **10e, 19b,c**, and **35a–c**, respectively.

P-(1,1-Dichloro-2,2,2-trifluoroethyl)-P-[2-(dimethylamino)-1-methyl-1H-imidazol-5-yl]-N,N-dimethylphosphinic Amide **11**

To a solution of **5** (2.4 g, 1 mmol) in pyridine (8 mL) cooled to 0–5°C, hydrogen peroxide (1 mmol, 30% solution) was added. After stirring for 10–15 min, pyridine was removed in vacuo; the residue was quenched, and then crystallized from diethyl ether (40 mL) to give **11** as colorless crystals.

General Procedure for Preparation of Bis(diethylamino)[1-methyl-2-(R)-1H-imidazol-5-yl]methylphosphonium Iodide **12a,b** *and [2-(Dimethylamino)-1-methyl-1H-imidazol-5-yl](methyl)diphenylphosphonium Iodide* **34a**

To a solution of compound **3 a,b** or **7a (**1 mmol) in benzene (5 mL), methyl iodide (1 mmol) was added. The reaction mixture was stirred for 24 h at 20°C. Benzene was decanted; the oily residue was dried in vacuo. Diethyl ether (15 mL) was added for solidification (**34a**), followed by crystallization of the obtained solid from ethyl acetate to give **12a,b**.

Isopropyl 2-(Dimethylamino)-1-methyl-1H-imidazol-5-yl(methyl)phosphinate **13**

To a solution of phosphonite **6a** (2.73 g, 1 mmol) in diethyl ether (25 mL), methyl iodide (0.16 g, 1.1 mmol) was added. The reaction mixture was stirred for 18 days at 14–16°C. The precipitate was filtered off, and the filtrate concentrated in vacuo. The residue was distilled in vacuo and was crystallized from diethyl ether (5 mL) to give **13**. The product is highly hygroscopic.

P,P-Bis[2-(dimethylamino)-1-methyl-1H-imidazol-5-yl]-N,N-dimethylphosphinous Amide **14**

To a stirred solution of preliminarily dried over P_2O_5 imidazole **1a** (2.5 g, 2 mmol) in THF (50 mL), t-BuLi (1.2 mL, 1.7 N solutions in pentane) at −90°C was added dropwise over 15 min. After stirring for 1.5 h at −80 to −85°C, a solution of dimethylphosphoramidous dichloride (1.46 g, 1 mmol) in pentane (10 mL) at −90°C was added dropwise. The reaction mixture was allowed to warm up to −40°C. After stirring for further 3 h, ammonia (liquid; 2 mL) at −60°C was added. The reaction mixture was concentrated in vacuo; the residue was treated with hot benzene (60 mL). The precipitate was filtered off, washed with benzene (2 × 20 mL), and the filtrate was concentrated in vacuo. The residue was treated with hot hexane (2 × 50 mL), insoluble impurities were filtered off, and the filtrate was evaporated to 40 mL to give **14**, precipitating at −7°C.

Bis[2-(dimethylamino)-1-methyl-1H-imidazol-5-yl]phosphinous Chloride **15**

To phosphorus trichloride (1.65 g, 12 mmol) cooled to −30°C, a solution of **14** (3.20 g, 10 mmol) in benzene (20 mL) was added. The reaction mixture was allowed to warm to 20°C and then heated for 15 min at 50°C. After cooling, benzene was removed in vacuo and the residue was extracted with hot hexane (2 × 60 mL). If needed, insoluble impurities were filtered off; the filtrate was concentrated in vacuo to give the crude product distilled in vacuo to give **15** as a yellow liquid.

Tris[2-(dimethylamino)-1-methyl-1H-imidazol-5-yl]phosphine **17a**

To phosphorus trichloride (1.50 g, 11 mmol), a solution of imidazole **1a** (3.75 g, 30 mmol) and triethylamine (3.0 g, 30 mmol) in pyridine (25 mL) was added. The reaction mixture was stirred for 30 h at 20°C. Pyridine was removed in vacuo, and the residue was heated up in benzene (75 mL) to reflux. The precipitate was filtered off and washed with benzene (2 × 20 mL). The filtrate was concentrated to 1/3 of volume. The precipitate formed under cooling was filtered off and crystallized from diethyl ether (60 mL) to give **17a** as colorless crystals.

Tris[1-methyl-2-(methylthio)-1H-imidazol-5-yl]phosphine **17b** *and [1-Methyl-2-(methylthio)-1H-imidazol-4-yl-]{bis[1-methyl-2-(methylthio)-1H-imidazol-5-yl]phosphine* **18b***; Tris[1-methyl-2-(methylthio)-1H-imidazol-5-yl]phosphine Oxide* **19b***; [1-Methyl-2-(methylthio)-1H-imidazol-4-yl]-{bis[1-methyl-2-(methylthio)-1H-imidazol-5-yl]phosphine Oxide* **20b**

To a solution of imidazole **1b** (7.94 g, 62 mmol) in pyridine (40 mL), phosphorus tribromide (2.71 g, 10 mmol) was added. The reaction mixture was stirred for 4 days at 70°C. Pyridine was removed in

vacuo; the oily residue was heated up in benzene (40 mL) to reflux. The precipitate was filtered off, washed with benzene (2 × 20 mL), and the filtrate was concentrated in vacuo. The residue was treated with hot hexane (4 × 40 mL), the solution was concentrated in vacuo, and the solid residue crystallized from diethyl ether (50 mL). Precipitate formed at −5 to −7°C was filtered off in 24 h to give **17b**. The diethyl ether filtrate was concentrated, and the residue was refined by chromatography on silica gel (eluent EtOAc: CH_3OH = 49:1) to give **18b** (R_f = 0.55). To a solution of the compounds with R_f = 0.38—0.45 in dichloromethane (2 mL) cooled to 0–5°C, hydrogen peroxide (1 mL, 30% solution) was added. The mixture was shaken for 10–15 min, the organic layer was separated, washed with water, and dried and concentrated to afford the residue, which was refined by chromatography on silica gel (eluent $CHCl_3$: CH_3OH = 49:1) to give **19b** (R_f = 0.30) and **20b** (R_f = 0.43).

Tris(1-methyl-2-phenyl-1H-imidazol-5-yl)phosphine **17c** *and (1-Methyl-2-phenyl-1H-imidazol-4-yl)-[bis(1-methyl-2-phenyl-1H-imidazol-5-yl)phosphine Oxide* **20c**

To a solution of imidazole **1c** (9.80 g, 62 mmol) in pyridine (40 mL), phosphorus tribromide (2.71 g, 10 mmol) was added. The reaction mixture was stirred for 7 days at 70°C. Pyridine was removed in vacuo; the oily residue was heated up in benzene (40 mL) to reflux. The precipitate was filtered off and washed with benzene (2 × 20 mL). The filtrate was concentrated to 10 mL, and the precipitate formed under cooling was filtered and dried in vacuo to give **17c**. The filtrate was concentrated affording the residue dissolved in hot benzene (10 mL). To a solution obtained, hydrogen peroxide (3 mL, 30% solution) was added. The mixture was shaken for 10–15 min, the organic layer was separated, washed with water, and dried and concentrated to afford the residue, which was refined by chromatography on silica gel (eluent $CHCl_3$:CH_3OH = 1:9) to give **20c** (R_f = 0.38).

Preparation of Tris(1-Methyl-2-Phenyl-1H-imidazol-5-yl)phosphine **17c** *(Method B).* To a stirred solution of imidazole **1c** (2.37 g, 15 mmol) in THF (30 mL), *t*-BuLi (8.82 mL, 1.7 N solutions in pentane) was added dropwise at −95 to −98°C in 20 min. After stirring for 4 h at −80 to −90°C, a solution of phosphorus trichloride (0.69 g, 5 mmol) in THF (5 mL) at −90 to −60°C was added dropwise over 20 min. The reaction mixture was allowed to warm to −30°C, and degassed water was added. The organic layer was separated and concentrated to give the oily residue, quenched and then treated with hot diethyl ether (3 × 50 mL). The solution was concentrated to 30 mL to give **17c** as colorless crystals precipitating under cooling.

General Procedure for Preparation of (4-Methoxyphenylimino)[tris(1-methyl-2-R-1H-imidazol-5-yl)]phosphorane **22b,c** *and Diphenyl(4-methoxyphenylimino)(1-methyl-2-R-1H-imidazol-5-yl)phosphorane* **37a,b**

To a solution of compound **17b,c** or **7 a,b** (1 mmol) in benzene (20 mL), a solution of 4-methoxyphenyl azide (1 mmol) in benzene (10 mL) was added. The reaction mixture was stirred for 15 min (**22b**), 30 min (**37a**), or 15 h (**37 b**) at 20°C until nitrogen stopped to evolving. In the case of **22c** reflux for 1 h at 80°C is needed. Benzene was removed in vacuo, and the residue was crystallized from diethyl ether to give **22b,c**. In the case of **37a,b**, the oily residue was treated with hot hexane (50 mL) to give the crude product crystallized from the appropriate solvent.

General Procedure for the Preparation of 1-Methyl-2-(R)-1H-imidazol-5-yl(phenyl)phosphinous Chloride **23a–c**

To a solution of imidazole **1a–c** (10 mmol) in pyridine (20 mL), phenylphosphonous dichloride (20 mmol) was added. The reaction mixture was stirred for 4 h at 20°C (**20a**), for 48 h at 65°C (**20b**), for 72 h at 130°C (**20c**). Pyridine was removed in vacuo, the oily residue was treated with diethyl ether (or benzene for **20b,c**; 70 mL), and the precipitate was filtered off and washed with diethyl ether (benzene; 2 × 50 mL). The filtrate was concentrated in vacuo. The residue was distilled to give **20a–c**.

Bis[1-Methyl-2-(Dimethylamino)-1H-Imidazol-5-yl](phenyl)phosphine Sulfide **25**

A solution of imidazole **1a** (0.25 g, 2 mmol) in pyridine (5 mL) was added to **23a** (0.27 g, 1 mmol). The reaction mixture was heated for 30 min at 50°C. Then pyridine was removed in vacuo; the residue was dried in vacuo and dissolved in benzene (10 mL). Then powdered sulfur (0.035 g, 1.1 mmol) was added. The reaction mixture was refluxed for 3 h. After cooling, benzene was concentrated in vacuo and the residue was treated with hot diethyl ether (2 × 10 mL) to give **25** as yellow crystals precipitating under cooling.

General Procedure for Preparation of P,P-Bis[2-(dimethylamino)-1-methyl-1H-imidazol-5-yl]-N,N-dimethylphosphinic Amide **16** *and Bis[2-(dimethylamino)-1-methyl-1H-imidazol-5-yl](trichlorovinyl)phosphine Oxide* **32a**

A solution of compound **14** or **28** (1 mmol) in dichloromethane (5 mL) was shaken with hydrogen peroxide (1.5 mmol, 30% solution) for 10–15 min. The organic layer was separated off, washed with water, and concentrated in vacuo. The residue was treated with hot hexane (40 or 3 × 40 mL, respectively) to give **16** as residue after hexane removal. The solid residue of crude **32a** precipitating from hexane under cooling was recrystallized from diethyl ether (40 mL). The precipitate formed at −7°C was filtered off and dried to give pure **32a**.

2-(Dimethylamino)-1-methyl-1H-imidazol-5-yl(trichloromethyl)phosphinous Chloride **26**

To a stirred solution of **2a** (1.25 g, 10 mmol) and carbon tetrachloride CCl_4 (1.7 g, 11 mmol) in diethyl ether (50 mL), tris(diethylamino)phosphine (2.72 g, 11 mmol) in diethyl ether (20 mL) was added dropwise at −60 to −80°C over 20 min. The mixture was allowed to warm to 20°C and stirred for further 1.5 h at 20°C. The precipitate was filtered off, washed with diethyl ether (2 × 20 mL), and the filtrate was concentrated in vacuo. The oily residue was treated with hot pentane (50 mL). Insoluble impurities were filtered off to give **26** as oil after solvent removal.

2-(Dimethylamino)-1-methyl-1H-imidazol-5-yl(trichlorovinyl)phosphinous Chloride **27**

To trichlorovinyldichlorophosphine (1.16 g, 5 mmol), a solution of imidazole **1a** (1.25 g, 10 mmol) in pyridine (5 mL) cooled to −30 to −10°C was added. The reaction mixture was stirred for 3 h at 20°C. Then pyridine was removed in vacuo; the oily residue was treated with pentane (2 × 40 mL). The precipitate was filtered off and washed with pentane (2 × 20 mL). The filtrate was concentrated, and the residue was distilled in vacuo to give **27** as a clear colorless liquid.

Bis[(2-(dimethylamino)-1-methyl-1H-imidazol-5-yl)](trichlorovinyl)phosphine **28**

To trichlorovinyldichlorphosphine (9.75 g, 42 mmol), a solution of imidazole **1a** (1.25 g, 10 mmol) in pyridine (5 mL) cooled to −30 to −10°C was added. The reaction mixture was stirred for 5 h at 20°C. Then pyridine was removed in vacuo; the residue was treated with warm diethyl ether (50 mL), the precipitate was filtered off, washed with diethyl ether (2 × 30 mL), the filtrate was concentrated in vacuo. The residue was treated with hot hexane (2 × 40 mL); the residue after hexane removal was distilled in vacuo to give **28** as a colorless liquid.

P-[2-(Dimethylamino)-1-methyl-1H-imidazol-5-yl]-N,N-dimethyl-P-(trichlorovinyl)phosphinous Amide **29**

To a solution of **27** (0.64 g, 2 mmol) in pentane (10 mL) cooled to −10°C, a solution of *N,N*-dimethyltrimethylsilylamine (0.23 g, 2 mmol) in pentane (50 mL) was added. The reaction mixture was stirred for 2 h at 25°C. Pentane was removed in vacuo, and the residue was distilled twice in vacuo to give **29** as a clear colorless liquid.

General Procedure for Preparation P-[2-(Dimethylamino)-1-methyl-1H-imidazol-5-yl]-N,N-dimethyl-P-(trichlorovinyl)phosphinothioic Amide **30** *and Bis[2-(dimethylamino)-1-methyl-1H-imidazol-5-yl](trichlorovinyl)phosphine Sulfide* **32b**

To a solution of compound **28, 29** (1 mmol) in benzene (5 mL) powdered sulfur (1.1 mmol) was added. The mixture was refluxed for 17 h (**30**) or 30 h (**32b**). Benzene was concentrated in vacuo. The residue was crystallized from pentane (10 mL) to give **30**, or the residue was treated with hot hexane (2 × 30 mL) and then activated charcoal was added. The filtrate was concentrated in vacuo to give **32b**.

Bis[2-(dimethylamino)-1-methyl-1H-imidazol-5-yl](phenylimino)(trichlorovinyl)phosphorane **32c**

To a solution of **28** (1 mmol) in benzene (5 mL), phenyl azide was added. The reaction mixture was refluxed for 30 h. Benzene was removed in vacuo, and the residue was treated with hot hexane (3 × 40 mL) to give **32c** as oil after solvent removal.

General Procedure for Preparation of 2-Chloro-N,N,N,N-tetramethylethylene-1,1-diamino Phosphorus(V) Derivatives **31, 33a,b**

A solution of compound **30, 32a,b** (1 mmol) in dimethylamine (2 g) was stirred for 3 days at 25°C. Excess of dimethylamine was removed. The residue was crystallized from pentane to give **31** or treated hot hexane (2 × 20 mL) for **33a,b**. Insoluble

impurities were filtered off. Hexane was removed in vacuo to give **33a** or crude **33b** as solid residue, recrystallized from diethyl ether (10 mL).

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