Ambident Reactivity of Chloro(dialkylamino)-(diphenylphosphinoyl)methanes

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The chemical properties of chloro(dialkylamino)(diphenylphosphinoyl)methanes have been studied using the simplest compound of this series, chloro(dimethylamino)(diphenylphosphinoyl)methane, as an example. Chloro-(dimethylamino)(diphenylphosphinoyl)methane shows ambident reactivity when reacting with electrophiles and nucleophiles depending on coreactant nature, it behaves as either electrophilic substrate or phosphorus nucleophile. This fact can be explained by its dissociation in solutions with both C–Cl bond cleavage to give (dimethylamino)-(diphenylphosphinoyl)methyl cation and Cl^- anion and C–P bond cleavage to form chloro(dimethylamino)methyl cation and diphenylphosphinite anion. The capability of chloro(dimethylamino)(diphenylphosphinoyl)methane to produce spontaneously Ph_2PO–anion allows us to recommend application in organic and organophosphorus synthesis as a synthetic equivalent (synthon) of diphenylphosphinite anion.

Among organic phosphorus compounds, there are phosphorus-substituted derivatives of triply functionalized methanes that show a number of interesting properties allowing their use in organic and organophosphorus syntheses. In these compounds, carbon atom is bound to P,P-disubstituted atoms of tricoordinated[1,2] or tetracoordinated[1e–1g,3] phosphorus as well as to a halogen atom and alkoxy or dialkylamino groups (Figure 1).

In recent time, there has been increasing interest in these derivatives of three-coordinated phosphorus because they have proven to be promising reagents in carbene syntheses.[2] The chemistry of three-substituted methanes functionalized with phosphinoyl groups was intensively developed in the 1960s through the 1980s.[1e–1g,3,4] These compounds were shown to exhibit high reactivity. Treatment with strong acids and bases leads to the cleavage of the phosphorus–carbon bond,[4] which is used in contemporary synthetic chemistry. Thus, phosphinoyl-substituted dialkoxymethanes undergo Wittig–Horner reaction with aldehydes and ketones to give ketene acetals and thio acetals.[5] Derivatives of dialkyl(dialkoxymethyl)phosphonates are used in bioorganic and medicinal chemistry for temporary protection of hydrophosphinoyl groups[6] and as a synthetic equivalent of formyl anion in the synthesis of carbonyl compounds.[7] However, at present, there is only episodical interest in phosphinoyl-containing trisubstituted methanes functionalized with substituents different from two alkoxy groups.[8]

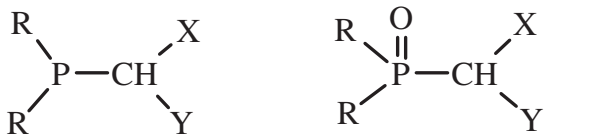
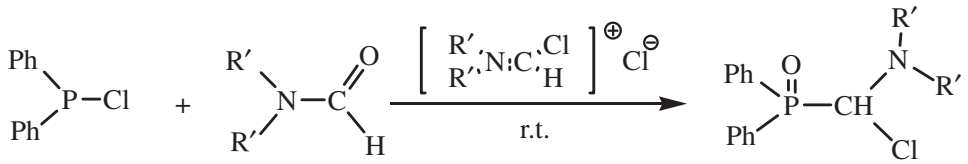


Figure 1. Molecular structure of phosphorus-substituted derivatives of triply functionalized methanes, where R = R′O, R′$_2$N, R′S, Ph (R′: alkyl); X and Y = halogen, R′O, R′$_2$N, R′S, CN.

In the previous report[9,10] we have shown that the reaction of chlorodiphenylphosphine with dialkylformamides in the presence of $(COCl)_2$, $SOCl_2$, PCl_5, and $PhP(O)Cl_2$, resulted in chloro(dialkylamino)(diphenylphosphinoyl)methane **1** (Scheme 1) in high yield. Compounds **1** are products of autocatalytic reaction comprising two stages:

1. Synthesis of [chloro(dimethylamino)methyl](dichloro)-(diphenyl)phosphorane (**2**) by reaction of Ph_2PCl and chloro-(dialkylamino)methylium chloride $[R_2N{=}C(H)Cl]^+Cl^-$ **3**.



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Scheme 1. Synthesis of chloro(dialkylamino)(diphenylphosphinoyl)methanes **1**.[9]

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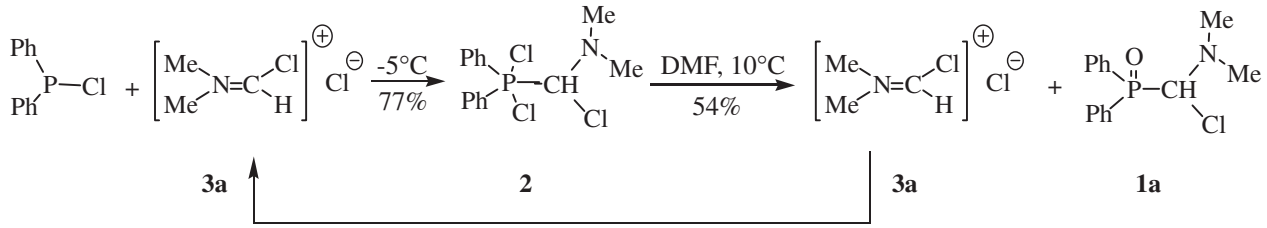


Scheme 2. Autocatalytic syntheses of chloro(dimethylamino)(diphenylphosphinoyl)methane (**1a**).

2. Synthesis of final products, chloro(dialkylamino)(diphenylphosphinoyl)methane **1** by reaction of **2** with dialkylformamides with regeneration of $[R_2N{=}C(H)Cl]^+Cl^-$ **3** providing the next reaction cycle.

Using chloro(dimethylamino)(diphenylphosphinoyl)methane (**1a**) as an example, its previously suggested reaction scheme[9,10] was confirmed experimentally with isolation of reaction products[11] (Scheme 2).

In this context, the role of $(COCl)_2$, $SOCl_2$, PCl_5, and $PhP(O)Cl_2$ consists of the production of $[R_2N{=}C(H)Cl]^+Cl^-$ **3** from dialkylformamides in reaction medium. For example:[12]

$$(COCl)_2 + Me_2NC(H)O \rightarrow [Me_2N{=}C(H)Cl]^+Cl^- \ (\mathbf{3a}) \quad (1)$$

Compounds **1** structurally related to the trisubstituted methanes functionalized with dialkoxyphosphinoyl or bis(dialkylaminophosphinoyl) groups as well as a halogen atom and an *N*,*N*-dialkylamino group[8] were unknown previously. Therefore, the chemical properties of this new type of organophosphorus compounds are of great interest and have been studied using the simplest compound of this series, chloro(dimethylamino)(diphenylphosphinoyl)methane (**1a**), (Scheme 1, R = Me), as an example.

Results and Discussion

Reactions of Chloro(dimethylamino)(diphenylphosphinoyl)methane (1a) with Nucleophiles. In terms of structure, compound **1a** is a phosphorylated chloroaminal of formaldehyde where one hydrogen atom is substituted with diphenylphosphinoyl group $Ph_2P(O)$. Taking into account this feature, one could expect that **1a** will behave as electrophilic substrate in reactions with nucleophiles.

Indeed, the study of reaction of **1a** with phosphorus nucleophiles showed that the chlorine atom in the chloro(dimethylamino)methyl group is rather labile and readily displaced by diethoxyphosphinoyl, dimethoxyphosphinoyl, and diphenylphosphinoyl groups. Therefore compound **1a** easily reacts with diethyl trimethylsilyl phosphite via Arbuzov-type reaction to form (diethoxyphosphinoyl)(dimethylamino)(diphenylphosphinoyl)methane (**4**).[3k] Compound **1a** also reacts with hydrophosphinoyl compounds—diethyl phosphite, dimethyl phosphite, and diphenylphosphine oxide—according to the Michaelis–Becker-type reaction to give corresponding products of chlorine atom displacement: compound **4**, (dimethoxyphosphinoyl)(dimethylamino)(diphenylphosphinoyl)-methane (**5**), and (dimethylamino)bis(diphenylphosphinoyl)-methane (**6**).[3k] In contrast to the classical variant of the Michaelis–Becker reaction,[13] the reaction of **1a** with the hydrophosphinoyl compounds requires no presence of an equivalent amount of a strong base. The reaction proceeds spontaneously with marked heat evolution (Scheme 3).

Since the chloro(dimethylamino)methyl group in compound **1a** is structurally related to the halo(dialkylamino)methyl group of the Vilsmeier–Haak reagents,[14] one can expect that **1a** will react similarly with *N*,*N*-dimethylaniline, a highly nucleophilic substrate used in the studies of such reactions. Compound **1a** was found to react with *N*,*N*-dimethylaniline vigorously with marked heat evolution. In this case, as distinct from the reaction of **1a** with phosphorus nucleophiles, both chlorine atom and *N*,*N*-dimethylamino group undergo displacement in the chloro-(dimethylamino)methyl group of compound **1a**. The reaction produces bis(*p*-dimethylaminophenyl)(diphenylphosphinoyl)-methane[15] (**9**) (Scheme 3).

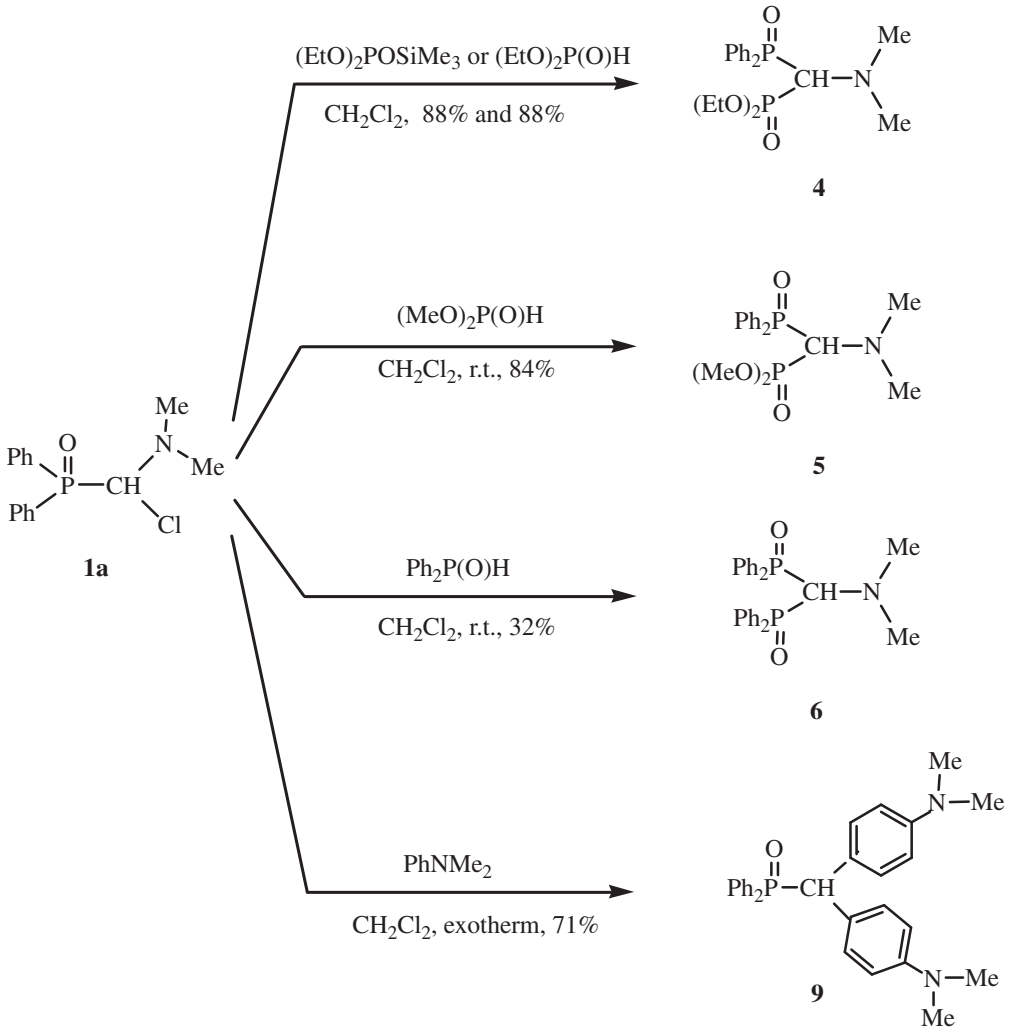
C–P and C–Cl Bond Cleavage. However, an attempt to displace the chlorine atom in the chloro(dimethylamino)methyl group of compound **1a** by amino group upon treatment with secondary amines, diethylamine or piperidine, led to (dimethylamino)bis(diphenylphosphinoyl)methane (**6**) as a sole product instead of expected diphenylphosphinoyl-substituted formaminals **10** (Scheme 4). This product was also obtained by the reaction of compound **1a** with triethylamine. This fact possibly indicates that the amines in the reaction with **1a** facilitate its cleavage at the C–P bond to form diphenylphosphinite anion Ph_2PO^- (**8**) that further combines with unreacted **1a** to give **6** (Scheme 4).

The reaction of **1a** with *N*,*N*-dimethylaniline indicates the presence of highly reactive (dimethylamino)(diphenylphosphinoyl)methyl cation (**11**) in reaction medium. Therefore, taking into account the results of reactions of **1a** with nucleophilic substrates and amines, one can suppose that **1a** in solutions can simultaneously dissociate with both C–Cl bond cleavage to give (dimethylamino)(diphenylphosphinoyl)methyl cation (**11**) and Cl^- anion and C–P bond cleavage to form chloro(dimethylamino)methyl cation $[Me_2N{=}C(H)Cl]^+$ (**3b**) and diphenylphosphinite anion (**8**) (Scheme 5).

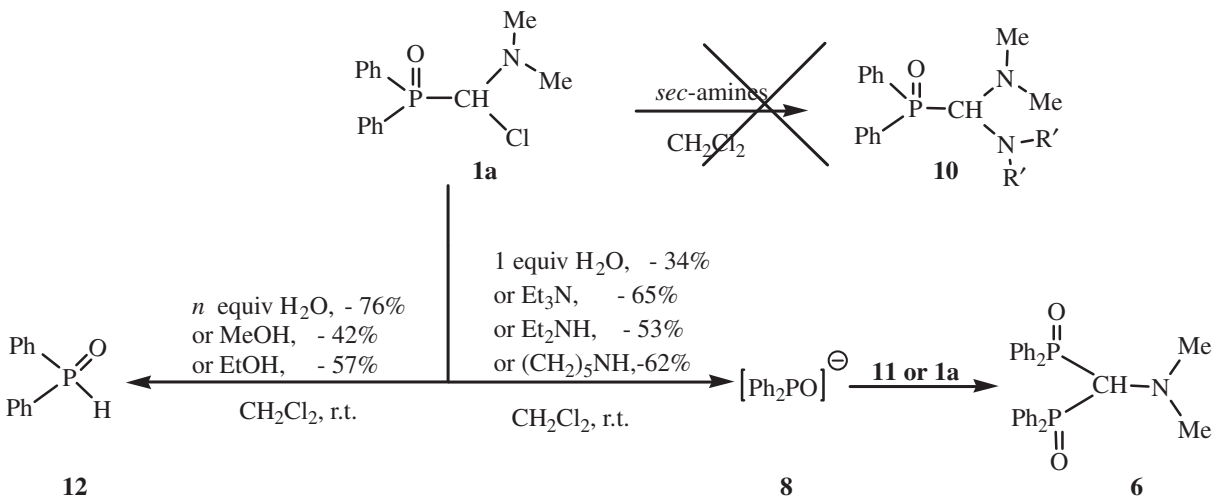
The results of subsequent reactions are determined by the type of coreactant. Phosphorus nucleophiles in the form of dialkyl phosphite anion[16a] **7** and diphenylphosphinite anion[16b] (**8**) apparently can quickly react with unreacted **1a** (or with the cation **11**) to give compounds **4**, **5**, and **6**.

This can be explained by high reactivity of both **1a** or cation **11** and anion **7** and **8**. Low concentration[16c] of **7** and **8** resulting from tautomerism and dissociation of dialkyl phosphites[16a] and diphenylphosphine oxide[16b] in reaction medium:

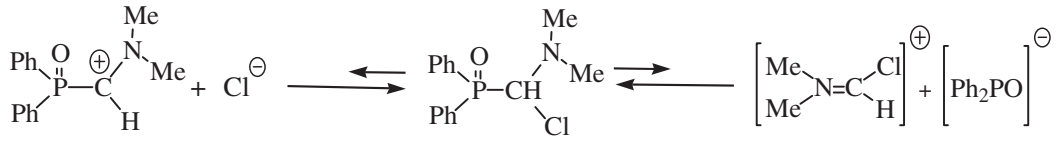
$$(RP(O)H \rightleftharpoons RPOH) \rightarrow RP{-}O^- + H^+; \quad \text{where R = OR′ or Ph} \quad (2)$$



Scheme 3. The reactions of **1a** with nucleophiles.

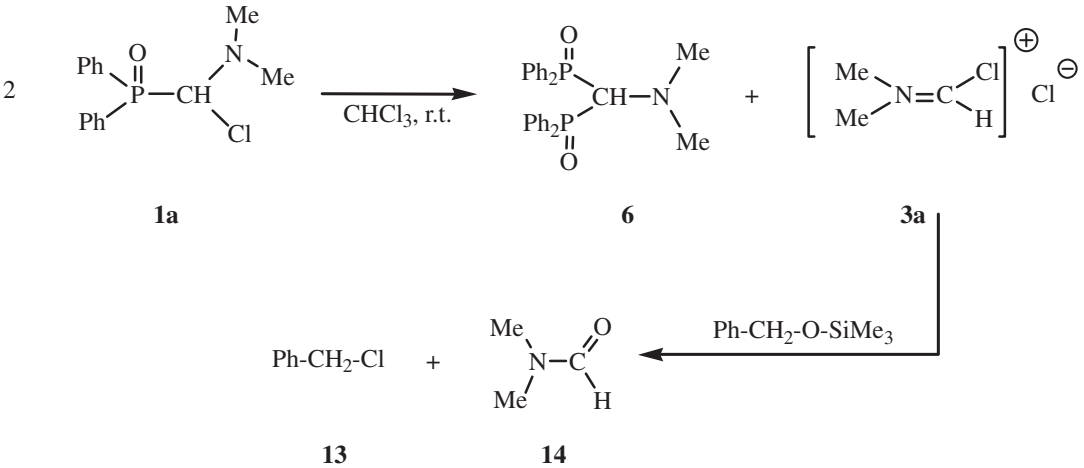


Scheme 4. The reactions of compound **1a** with amines, water, and alcohols.



11 **1a** **3b** **8**

Scheme 5. Dissociation of compound **1a** in solutions.



1a **6** **3a** **13** **14**

Scheme 6. The reaction of compound **1a** with itself.

It is sufficient for their fast reaction with **1a** (or cation **11**). The phosphinoyl group shows rather basicity[16d,16e] therefore dialkyl phosphites and diphenylphosphine oxide can behave as a proton acceptor.

N,*N*-Dimethylaniline reacts with the cation **11** to yield compound **9**, thus facilitating dissociation of **1a** to produce **11**. Amines, by solvating $[Me_2N{=}C(H)Cl]^+$ cation (**3b**), promote the dissociation of **1a** to afford **3b** and diphenylphosphinite anion (**8**) that further react with **1a** to give compound **6**.

The reaction of compound **1a** with 0.5 mol of water was shown to give product **6**, too. This indicates that the reaction of compound **1a** with water also results in the facile cleavage of C–P bond. Probably, diphenylphosphinite anion (**8**) forms initially in this reaction and further combines with cation **11** to yield **6** (Scheme 4). The reaction of **1a** with excess water or alcohol leads only to diphenylphosphine oxide[17] (**12**) (Scheme 4) as product of C–P bond cleavage in **1a**, too.

Schemes 4 and 5 indicate a possible explanation for the mechanism of reaction of compound **1a** with amines. Probably, amines (R_2NH and R_3N) bind chloro(dimethylamino)methyl cation (**3b**) to form di- or trialkyl[chloro(dimethylamino)methyl]ammonium cations **3′**, thus shifting the dissociation equilibrium of **1a** to the right and increasing the concentration of diphenylphosphinite anion (**8**). Anion **8** further combines with cation **11** (or react with unreacted **1a**) to yield compound **6**. However, we failed to isolate di- or trialkyl[chloro(dimethylamino)methyl]ammonium cations **3′** in individual state probably owing to its high reactivity.

The Reaction of Chloro(dimethylamino)(diphenylphosphinoyl)methane (1a) with Itself. It follows from the assumption of partial dissociation of **1a** in solutions that this compound should react with itself by displacing chlorine atom with diphenylphosphinoyl group because it behaves in the dissociated form as an electrophilic substrate (cation **11** and/or unreact **1a**) and as a phosphorus nucleophile (diphenylphosphinite anion (**8**)). The reaction should result in (dimethylamino)bis(diphenylphosphoryl)methane (**6**) and its by-product, chloro(dimethylamino)methylium chloride (**3a**) (Scheme 6).

Indeed, 10 min after dissolution of **1a** in freshly distilled $CHCl_3$, ^{31}P NMR spectra of reaction mixture (using 85% H_3PO_4 as an external standard) show a signal of compound **6** at 27 ppm whose intensity increases rapidly. At the same time, the ^{31}P NMR signal of initial **1a** at 21 ppm decreases and disappears after 18 h. Chloro(dimethylamino)methylium chloride (**3a**) formed simultaneously with **6** is a highly reactive compound and could not be isolated from the reaction mixture. Therefore, to identify the resultant **3a**, the reaction mixture after completion of the reaction was treated with benzyloxytrimethylsilane that reacts with **3a** to afford an equimolar mixture of benzyl chloride (**13**) and dimethylformamide (DMF) (**14**). A workup of the reaction mixture furnished an 85% yield of (dimethylamino)bis(diphenylphosphinoyl)methane (**6**) resulting from the displacement of chlorine atom in initial **1a** with diphenylphosphinite anion (**8**). After separation of **6**, a mixture of benzyl chloride and DMF in 1:0.3 ratio was isolated from filtrate, the ratio was determined by ^1H NMR spectroscopy in $CDCl_3$ (a part of DMF was lost during aqueous treatment of the reaction mixture). After complete removal of DMF by washing with water, pure benzyl chloride (**13**) was isolated in 52% yield (determined by ^1H NMR spectroscopy in $CDCl_3$). Syntheses of benzyl chloride (**13**) and DMF (**14**) confirm the formation of chloro(dimethylamino)methylium chloride (**3a**) as by-product reaction of **1a** with itself thus in turn confirming reaction of **1a** with itself (Scheme 6) (Subsequently, reactivity of **1a** in

solutions is dependent on the present of nucleophilic reagents (for example P-nucleophiles). In the absence of nucleophilic reagents **1a** reacts with itself to form only **6**).

The Reactions of Chloro(dimethylamino)(diphenylphosphinoyl)methane (1a) with Electrophilic Substrates. Unfortunately, the diphenylphosphinite anion[16c] (**8**) is not detected in the ^{31}P NMR spectra of reaction mixtures. Therefore, to confirm the possibility of existence of nucleophilic anion **8** in reaction medium, compound **1a** was also reacted with acetone, acetaldehyde, phenyl isocyanate, dimethylformamide dimethylacetal, triethyl orthoformate, bis(diethylamino)methane, and acetonitrile complex palladium(II) chloride which behave as electrophilic substrates.

In all cases, compound **1a** reacted as it was expected from the assumption of the existence of diphenylphosphinite anion (**8**). The reactions resulted in 2-(diphenylphosphinoyl)propan-2-ol[18] (**15**), 1-(diphenylphosphinoyl)ethan-1-ol[19] (**16**), *N*-phenyl(diphenylphosphinoyl)formamide[20] (**17**), (dimethylamino)-(diphenylphosphinoyl)methoxymethane (**18**), diethoxy(diphenylphosphinoyl)methane[3i] (**19**), (diethylamino)(diphenylphosphinoyl)methane[21] (**20**), and *cis*-dicholoridobis(hydroxydiphenylphosphane)palladium(II)[22] (**21**), respectively (Scheme 7).

The isolated compounds **15**–**20** are the products of addition of diphenylphosphinite anion (**8**) to the electrophilic carbon atoms of the reactants (compounds **15**, **16**, and **17**) or corresponding substitution products (compounds **18**, **19**, **20**, and **21**); this fact provides evidence for the existence of diphenylphosphinite anion (**8**) in the reaction mixture. This, in turn, confirms the dissociation of **1a** with C–P bond cleavage (Scheme 5).

Conclusion

The reactions of **1a** with P-nucleophiles (and *N*,*N*-dimethylaniline), amines, 0.5 equivalents of water, with itself, and electrophilic substrates confirm a complete dissociation of compound **1a** in solutions (Scheme 5). Therefore, we can explain the ambident reactivity of compound **1a** (and chloro-(dialkylamino)(diphenylphosphinoyl)methanes **1** correspondingly) as follows.

With nucleophiles and nucleophile substrates, the reactant is the initial molecular form of **1a**, and/or (dimethylamino)-(diphenylphosphinoyl)methyl cation (**11**); it behaves as an electrophilic substrate to give corresponding products of nucleophilic displacement (compounds **4**–**6** and **9**) in the chloro(dimethylamino)methyl group of **1a**.

With electrophilic substrates, the reacting species is diphenylphosphinite anion Ph_2PO^- (**8**) that behaves as a nucleophile to afford corresponding addition/substitution products (compounds **15**–**21**).

The ease of Ph_2PO^- (**8**) to undergo addition to electrophilic substrates indicates that **1a** in fact is a hidden form of diphenylphosphinite anion (**8**). This allows us to recommend application of **1a** in organic synthesis as a synthetic equivalent (synthon) of diphenylphosphinite anion (**8**). (Examples of compounds capable of generating diphenylphosphinite anion (**8**) in reaction medium are known from the literature. However, this process requires either lithiation of the initial compound at low temperature[7b,7e] or addition of NaI on heating.[23] Compound **1a** is devoid of these drawbacks. **1a** spontaneously produces diphenylphosphinite anion (**8**) upon dissolution, and it can be easily prepared in high yield from available initial compounds.[9]

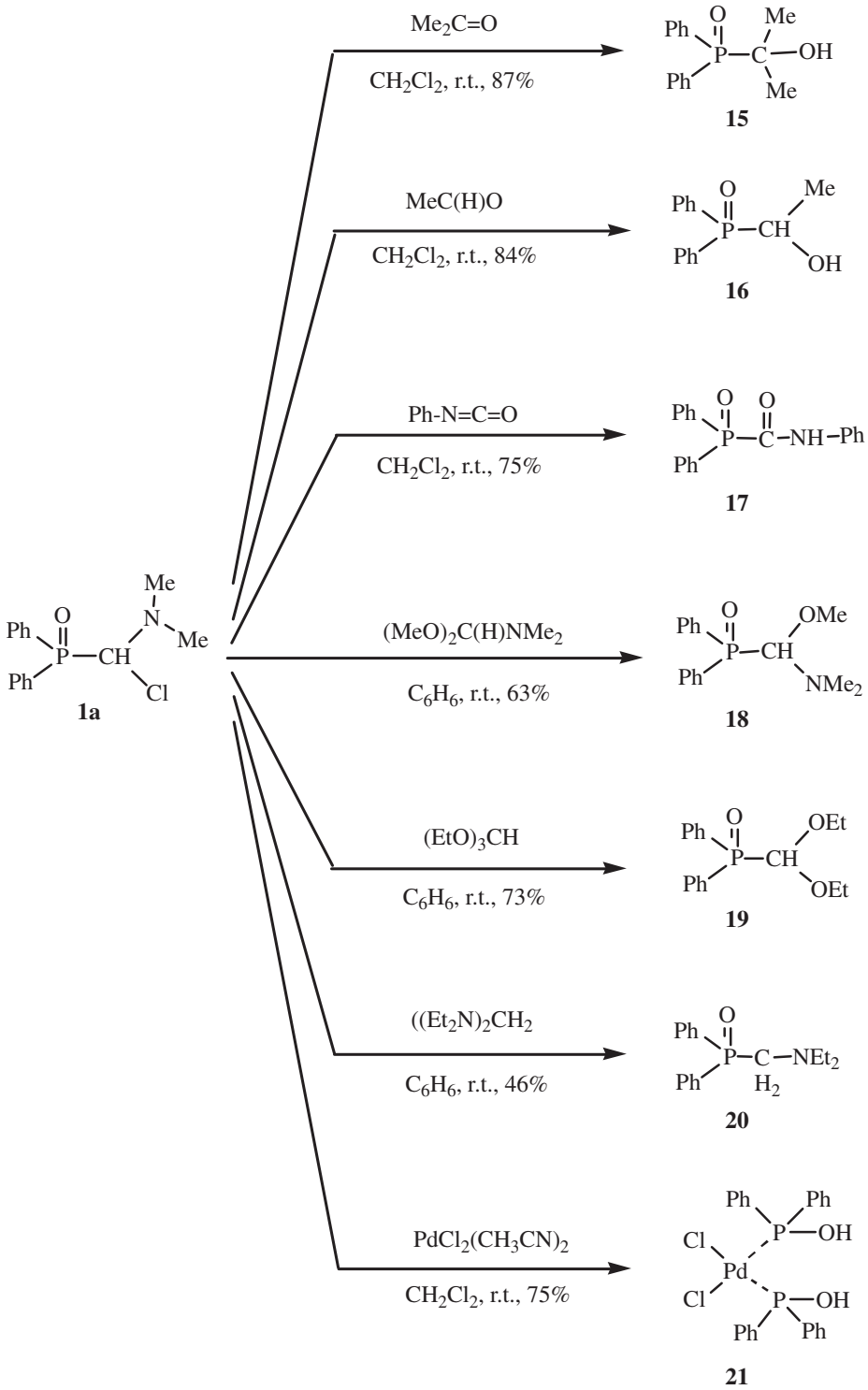
Experimental

^{1}H and ^{31}P NMR spectra were recorded on a Bruker Avance 300 spectrometer operating at 300.11 and 121.50 MHz with tetramethylsilane (TMS) as an internal standard, respectively. The ^{31}P and ^{1}H NMR spectra of individual compounds were obtained in $CDCl_3$, ^{31}P NMR spectra of reaction mixtures were recorded also in $CHCl_3$ using 85% H_3PO_4 as an external standard. ^{13}C NMR spectrum of compound **3** was recorded on a Bruker Avance 300 spectrometer operating at 75.47 MHz with tetramethylsilane (TMS) as an internal standard.

Syntheses of earlier published compounds **4**,[3k] **6**,[3k] **9**,[16] **12**,[17] **15**,[18] **16**,[19] **17**,[20] **19**,[3i] **20**,[21] and **21**[22] by reactions of compound **1a** with diethyl trimethylsilyl phosphite, diethyl phosphite, diphenylphosphine oxide, *N*,*N*-dimethylaniline, amines, water, alcohols, acetone, acetaldehyde, phenyl isocyanate, dimethylformamide dimethylacetal, triethyl orthoformate, bis(diethylamino)methane, and acetonitrile complex palladium(II) chloride (see Supporting Information).

Chloro(dimethylamino)(diphenylphosphinoyl)methane (1a).[10] Dimethylformamide (0.53 mL, 0.5 g, 7 mmol) was dissolved in 3 mL of toluene at ambient temperature. Phenylphosphonic dichloride $PhP(O)Cl_2$ (0.03 g, 0.15 mmol) was added in inert gas atmosphere with stirring; after 20 min, 0.4 mL (0.5 g, 2.3 mmol) of chlorodiphenylphosphine (Ph_2PCl) was added. After 3 h, the reaction mixture became red-brown and precipitation of analytically pure compound **1a** began, which completed after 18 h. The resulting precipitate was separated by filtration, washed with toluene (3 × 5 mL) and dried in vacuum[24] to give 0.61 g (91%) of compound **1a** as colorless needle-like crystals, mp 92–94 °C dec.[9] The compound is highly hygroscopic. ^{31}P NMR (121.50 MHz, $CDCl_3$, 25 °C, 85% H_3PO_4): δ 22.80 (d, $^2J_{P,H} = 11$ Hz). ^{1}H NMR (300.11 MHz, $CDCl_3$, 25 °C, TMS): δ 8.00–7.93 (m, 4H, *o*-H, Ph), 7.89 (d, $^2J_{P,H} = 11$ Hz, 1H, P–C–H), 7.56–7.49 (m, 6H, *m*- and *p*-H, Ph), 3.08 (s, 6H, $N(CH_3)_2$). Found: C, 61.44; H, 5.79; N, 4.68; P, 10.40%. Calcd for $C_{15}H_{17}ClNOP$ (293.74): C, 61.34; H, 5.83; N, 4.77; P, 10.55%.

(Dimethoxyphosphinoyl)(dimethylamino)(diphenylphosphinoyl)methane (5). Dimethyl phosphite (1.5 mL, 2.25 g, 20 mmol) was added to a solution of 0.3 g (1 mmol) of compound **1a** in 1.5 mL of CH_2Cl_2 with stirring. The mixture was allowed to stand for 18 h at 20 °C, diluted with 10 mL of CH_2Cl_2, and washed with water (4 × 5 mL). The organic layer was separated and dried with K_2CO_3. The drying agent was separated by filtration, washed with CH_2Cl_2 (2 × 5 mL), and the filtrate was concentrated to about 1 mL. The concentrate was diluted with 8 mL of hexane and the resultant precipitate was reprecipitated twice from $CHCl_3$–hexane to give 0.31 g (84%) of compound **5** as colorless needles, mp 134–135 °C; ^{31}P{^{1}H} NMR (121.50 MHz, $CDCl_3$, 25 °C, 85% H_3PO_4): δ 26.36 (d, $^2J_{P,P} = 36$ Hz, 1P, $Ph_2P(O)$–), 23.75 (d, $^2J_{P,P} = 36$ Hz, 1P, $(CH_3O)_2P(O)$–); ^{1}H NMR (300.11 MHz, $CDCl_3$, 25 °C, TMS): δ 7.98–7.84 (m, 4H, *o*-H, Ph), 7.50–7.43 (m, 6H, *m*- and *p*-H, Ph), 3.91 (dd, $^2J_{P,H} = 22.5$ Hz, $^2J_{P,H} = 16.9$ Hz, 1H, P–C–H), 3.79 (d, $^3J_{P,H} = 9$ Hz, 3H, CH_3–O), 3.56 (d, $^3J_{P,H} = 9$ Hz, 3H, CH_3–O), 2.50 (d, $^4J_{P,H} = 2.4$ Hz, 6H, $N(CH_3)_2$). ^{13}C NMR



Scheme 7. The reactions of compound **1a** with electrophilic substrates.

(75.47 MHz, $CDCl_3$, 25 °C, TMS): δ 133.31 (d, $^1J_{P,C} = 4.6$ Hz, P–C, Ph), 132.95 (d, $^1J_{P,C} = 3.4$ Hz, P–C, Ph), 131.69 (dd, $^2J_{P,C} = 36.5$ Hz, $^4J_{P,C} = 8.9$ Hz, *o*-C, Ph), 131.87 (s, *p*-C, Ph), 128.19 (d, $^3J_{P,C} = 11.8$ Hz, *m*-C, Ph), 64.68 (dd, $^2J_{P,C} = 124.4$ Hz, $^2J_{P,C} = 77.3$ Hz, P–C–H), 52.80 (s, CH_3–O), 51.89 (s, CH_3–O), 44.42 (s, $N(CH_3)_2$). Found: C, 55.53; H, 6.19; N, 3.70; P, 16.56%. Calcd for $C_{17}H_{23}NO_4P_2$ (367.30): C, 55.59; H, 6.31; N, 3.81; P, 16.86%.

Reaction of Chloro(dimethylamino)(diphenylphosphinoyl)methane (1a) with Itself. A solution of 3.4 g (11.6 mmol) of compound **1a** in 10 mL of $CHCl_3$ freshly distilled over P_2O_5 was kept at 5 °C for 18 h. Then, benzyloxytrimethylsilane (1.04 g, 6 mmol) was added at 20 °C with stirring. A slight exotherm was observed. The mixture was kept at 5 °C for an additional 18 h, diluted with 30 mL of CH_2Cl_2, and washed with 5 mL of H_2O. The organic layer was separated

and dried with $MgSO_4$. The drying agent was separated by filtration, washed with CH_2Cl_2 (4 × 5 mL), and the filtrate was concentrated to about 5 mL. The concentrate was diluted with 40 mL of hexane and cooled to −10 °C. After 18 h, the resulting precipitate was separated by filtration, washed with hexane (4 × 5 mL) cooled to 0 °C, and reprecipitated twice from $CHCl_3$–hexane to give 2.25 g (85%) of compound **6**. The filtrate after separation of compound **6** was concentrated in vacuum of 12 Torr at 20 °C. The residue was distilled using a collar adapter to give 0.89 g of a mixture of benzyl chloride (**13**) and DMF (**14**). ^{1}H NMR of the mixture (300.11 MHz, $CDCl_3$, 25 °C, TMS): δ 8.03 (s, 0.3H, DMF), 7.41 (m, 5H, Ph, benzyl chloride), 4.62 (s, 2H, CH_2, benzyl chloride), 2.94 (s, 0.9H, N–CH_3, DMF), 2.89 (s, 0.9H, N–CH_3, DMF). The mixture was dissolved in 10 mL of CH_2Cl_2 and washed with water (4 × 5 mL). The organic layer was separated and dried with $MgSO_4$. The drying agent was separated by filtration, washed with CH_2Cl_2 (4 × 5 mL), and the filtrate was concentrated. The residue was distilled using a collar adapter to give 0.76 g (52%) of benzyl chloride (**13**). ^{1}H NMR (300.11 MHz, $CDCl_3$, 25 °C, TMS): δ 7.39 (m, 5H, Ph), 4.62 (s, 2H, CH_2).

(Dimethylamino)(diphenylphosphinoyl)methoxymethane (18). Dimethylformamide dimethylacetal (0.41 g, 3.4 mmol) was added to a suspension of 0.5 g (1.7 mmol) of compound **1a** in 5 mL of benzene with stirring. The mixture was stirred at 20 °C for 24 h (Within this period, compound **1a** dissolved completely and then a white solid precipitated). The mixture was diluted with 10 mL of CH_2Cl_2 and washed with water (4 × 5 mL). The organic layer was separated and dried with K_2CO_3. The drying agent was separated by filtration, washed with CH_2Cl_2 (2 × 5 mL), and the filtrate was concentrated to about 2 mL. The concentrate was diluted with 8 mL of hexane. The resulting precipitate was reprecipitated twice from CH_2Cl_2–hexane to give 0.31 g (63%) of compound **18** as colorless needles, mp 78–81 °C. ^{31}P{^{1}H} NMR (121.50 MHz, $CDCl_3$, 25 °C, 85% H_3PO_4): δ 24.06 (s). ^{1}H NMR (300.11 MHz, $CDCl_3$, 25 °C, TMS): δ 8.00–7.94 (m, 2H, *o*-H, Ph), 7.88–7.81 (m, 2H, *o*-H, Ph), 7.50–7.40 (m, 6H, *m*-, *p*-H, Ph), 5.55 (d, $^2J_{P,H}$ = 1 Hz, 1H, P–C–H), 3.38 (s, 3H, CH_3–O), 2.53 (d, $^4J_{P,H}$ = 1.3 Hz, 6H, N(CH_3)$_2$).[25] Found: C, 66.47; H, 6.97; N, 4.36; P, 11.05%. Calcd for $C_{16}H_{20}NO_2P$ (289.30): C, 66.42; H, 6.97; N, 4.84; P, 10.71%.

Supporting Information

Syntheses of compounds **4**, **6**, **9**, **12**, **15**, **16**, **17**, **19**, **20**, and **21**; NMR spectra of new compounds: (dimethoxyphosphinoyl)(dimethylamino)(diphenylphosphinoyl)methane (**5**) and (dimethylamino)(diphenylphosphinoyl)methoxymethane (**18**). This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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24 Purification of **1a** by recrystallization or reprecipitation failed because of decomposition of the compound. Therefore the preparation of analytically pure **1a** was carried out in DMF–toluene (1:6) where **1a** presumably may be reprecipitated were it stable.

25 We cannot provide ^{13}C NMR spectrum of (dimethylamino)(diphenylphosphinoyl)methoxymethane (**18**) because it, like compound **1a**, undergoes decomposition when dissolved in $CHCl_3$ to give (dimethylamino)bis(diphenylphosphinoyl)methane (**6**).