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Reactivity of Ph_3PNLi towards P^{III} and P^{V} electrophiles

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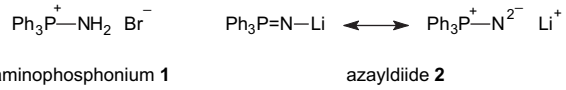
ABSTRACT

A study of the reactivity of $Ph_3P{=}NLi$ towards phosphorus electrophiles allowed us to develop a general method to isolate, or cleanly generate in situ, a broad family of polyphosphinimines displaying P=N–P bonds. A preliminary application of this methodology is presented here with the synthesis of various Schwesinger-type bases by a simple new procedure employing $Ph_3P{=}NLi$.

1. Introduction

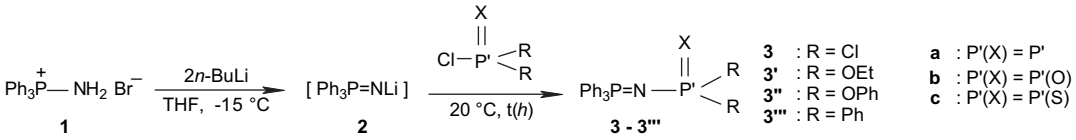
The lithium triphenylphosphonium azayldiide Ph_3PNLi (**2**) was first prepared by Schmidbaur and Jonas.[1] This reagent, which is isoelectronic with lithium phosphonium methyldiide Ph_3PCHLi,[2] can be easily obtained by double deprotonation of aminotriphenylphosphonium bromide **1** (Table 1).



aminophosphonium **1** azayldiide **2**

As part of our work on metallated ylides exhibiting high nucleophilicity,[3] we report here a study of the reactivity of Ph_3PNLi (**2**) towards various P^{III} and P^{V} phosphorus electrophiles. From this

Table 1
Monosubstitution of $P'(X)R_2Cl$ by $Ph_3P{=}NLi$



Entry	$-P'(X)R_2$	t (h)[a]	Product (%)[b]		^{31}P NMR (THF), δ (ppm)/J (Hz)		
					$\delta_{P=N}$ (doublet)	$\delta_{P'-R}$ (doublet)	$^2J_{PP'}$
1	$-P'Cl_2$	16	**3a**	94(70)	14.75	165.75	74.2
2	$-P'(O)Cl_2$	7	**3b**	90(75)	14.09	−8.68	14.2
3[c]	$-P'(S)Cl_2$	7	**3c**	93(85)	13.55	34.35	0
4	$-P'(OEt)_2$	12	**3′a**	83(72)	5.84	136.95	55.3
5	$-P'(O)(OEt)_2$	12	**3′b**	86(78)	11.55	0.97	33.6
6	$-P'(S)(OEt)_2$	12	**3′c**	83(73)	9.74	61.04	29.6
7	$-P'(O)(OPh)_2$	12	**3″b**	88(80)	13.00	−10.23	35.9
8	$-P'Ph_2$	0.5	**3‴a**	91(85)	16.81	40.43	103
9	$-P'(O)Ph_2$	0.5	**3‴b**	95(85)	14.43	13.95	1.8
10	$-P'(S)Ph_2$	0.5	**3‴c**	80(70)	15.01	43.23	0.9

One-pot synthesis of monophosphinimines **3**, **3′**, **3″** and **3‴**.

[a] In entries 2–10, the phosphorus electrophile is added over 1 min to $Ph_3P{=}NLi$ formed in situ and '*t*' is the reaction time. In entry 1, $Ph_3P{=}NLi$ is added to the phosphorus electrophile and '*t*' means the addition time.

[b] Yields are based on starting material $P'(X)ClR_2$ and were determined by ^{31}P NMR, with NMR parameters taking titration into account (Ph_3PO as external standard). Isolated yields are in brackets. In entries 1,4 and 8 the product is isolated as the oxide derivative after addition of hydrogen peroxide.

[c] Solvent: toluene. Reaction temperature: 110 °C.

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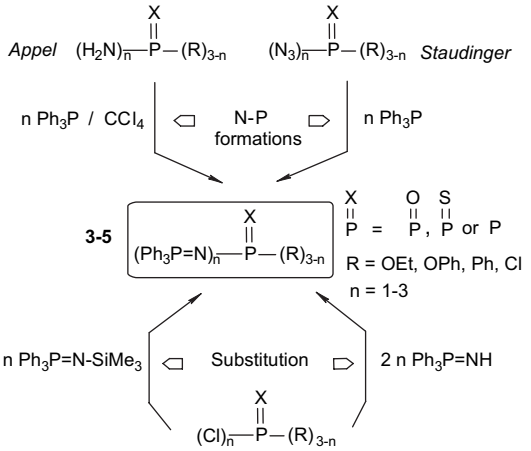
study, it appears that **2** is a convenient tool for the isolation, or in situ generation, of numerous polyphosphinimines containing a P═N–P skeleton (**3**–**5**). Such compounds have previously been prepared by two main methods: by direct condensation of nitrogen with phosphorus moieties; or through substitution reactions between phosphinimines and phosphorus electrophiles (Scheme 1). The main direct condensation method is the Staudinger reaction, which provides access to various mono- (n=1)[4] and diphosphinimines (n=2)[5] containing P═N–P bonds. However, a drawback to this approach is the need to handle potentially explosive azides.[5] The Appel reagent, although much less common, also provides access to several monophosphinimines,[6] while others are efficiently prepared using Kirsanov–Horner–Oediger[7] and Mitsunobu[8] reactions.



Scheme 1. Synthesis of polyphosphinimines with P═N–P skeletons.

The dominant substitution route has been the use of triphenylphosphinimine Ph_3PNH as nucleophile towards phosphorus electrophiles.[9] By this strategy many mono-, di- and some trisubstituted products have been synthesized. However, a major drawback of this reaction is the transylidation process by which 50% of the phosphorus reagent is lost.[10] Indeed, for each halide replaced, 2 equiv of Ph_3P═NH is consumed, one for the substitution and the other as hydrogen chloride scavenger. Several examples of *N*-substituted molecules have also been obtained from Ph_3P═$NSiMe_3$, the silylated analogue of the triphenylphosphinimine.[9b,11] This reagent has the advantage over Ph_3P═NH of avoiding transylidation but it turns out to be much less reactive. Finally, some *N*-monosubstituted compounds have also been synthesized from stabilized phosphorus ylides and azides[4d] by oxidation of preformed diphosphinimines (with sulfur,[11a,12] $PSCl_3$,[12] oxygen,[12] or SO_2[13]), by hydrolysis of phosphinimine-dihalogen phosphates[14] and from Grignard reagents and pentachloro-*N*-phosphoryl-monophosphinimine.[15]

2. Results and discussion

2.1. Monosubstitution reactions

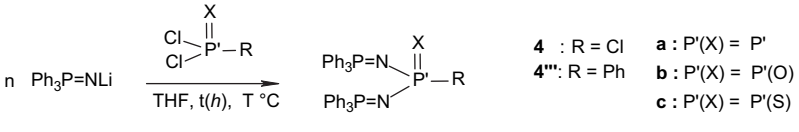
We first studied the monosubstitution of phosphorus electrophiles displaying three available substitution sites by Ph_3PNLi (Table 1, entries 1–3). The equimolar addition of $P'Cl_3$ to Ph_3PNLi led, as expected, to complex mixtures. However, monosubstituted product **3a** could be selectively and quantitatively formed via a slow inverse addition, so as to maintain an excess of $P'Cl_3$ in the reaction mixture (entry 1). It is worth noting that the less reactive Ph_3PNH also affords **3a**, but only in moderate yield (29%). With $P'(O)Cl_3$, it was not necessary to use inverse addition to successfully obtain the monosubstituted phosphinimine **3b** (entry 2). Finally, in the case of the less reactive $P'(S)Cl_3$, a higher temperature (110 °C in toluene) was required to prepare **3c**, probably due to the weaker polarization of the P═S bond (entry 3).

We then tested the reactivity of Ph_3PNLi towards phosphorus electrophiles having only one free substitution site (Table 1, entries 4–10). Thus corresponding monosubstituted products (**3′a**–**c**, **3″b**, **3‴a**–**c**) were prepared in situ in good yields from phenoxy and ethoxy groups (Table 1, entries 4–7) whatever be the nature of X (X=electron pair, O, S).[16] It is worth noting that the speed of the reaction was similar for both substituents (Table 1, entries 5 and 7, X=O), even though the phenoxy group is much more electron withdrawing than is ethoxy. Likewise, the markedly increased reactivity observed in the presence of the weakly withdrawing phenyl group was difficult to explain (comparison between entries 8–10 and 2–7). The corresponding products (**3‴a**–**c**) were obtained in excellent yield after reacting only for 0.5 h.

2.2. Disubstitution reactions

Next, we examined disubstitution of P^{III} and P^{IV} phosphorus electrophiles with three potential substitution sites by Ph_3PNLi (Table 2, entries 1–3). Firstly, we observed that Ph_3PNLi (2 equiv)

Table 2
Disubstitution of $P'(X)RCl_2$ by Ph_3P═NLi



2 **4** ; **4‴**

Entry	–P′(X)R	n	t (h)[a]/T (°C)	Product (%)[b]		^{31}P NMR (THF), δ (ppm)/J (Hz)		
						$\delta_{P=N}$	δ_{P-R}	$^2J_{PP'}$
1	–P′Cl	2	7/−78	**4a**	50[c] (42)	13.77 (d)	−3.62 (t)	16
2	–P′(O)Cl	3	48/65	**4b**	100 (80)	5.11 (d)	0.55 (t)	20
3	–P′(S)Cl	4	46/65	**4c**	45	16.98 (d)	−0.55 (t)	12.8
4	–P′Ph	2	0.2/−15	**4‴a**	85 (69)	16.23 (d)	−3.51 (t)	5.2
5	–P′(O)Ph	2	12/20	**4‴b**	65 (57)	4.85 (d)	2.28 (t)	4.7
6	–P′(S)Ph	5	300/65	**4‴c**	32	4.91 (d)	40.21 (t)	4.8

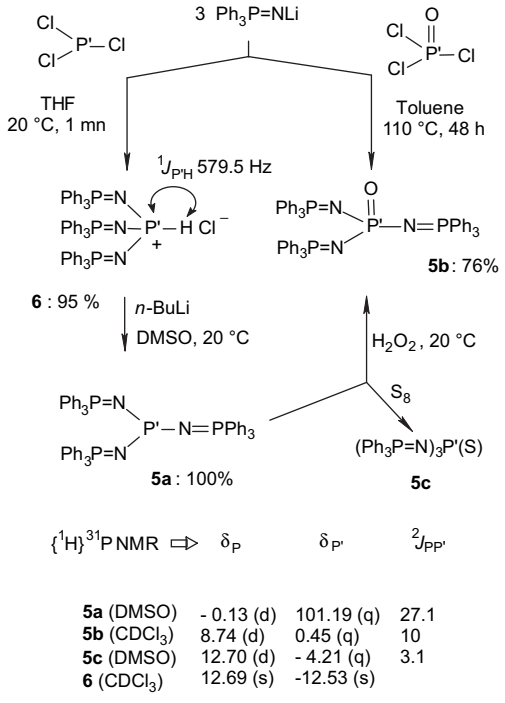
One-pot synthesis of diphosphinimines **4** and **4‴**.

[a] In entries 2,3 and 5,6, the phosphorus electrophile is added in 1 min to the in situ formed Ph_3P═NLi and '*t*' and '*T*' are, respectively, the reaction time and the temperature of reaction. In the entries 1 and 4, Ph_3P═NLi is added to the phosphorus electrophile and '*t*' and '*T*' mean, respectively, the addition time and the temperature of the mixture during this addition.

[b] Yields based on starting material $P'(X)RCl_2$ and determined by ^{31}P NMR, with NMR parameters taking titration into account (Ph_3PO as external standard). Isolated yields are in brackets. In entries 1 and 4, the product is isolated under the oxide form after addition of hydrogen peroxide.

[c] Byproduct **6** (30%; trisubstitution) is also obtained.

was very reactive towards P′Cl_3, which at very low temperature rapidly formed the double substitution product **4a** together with the trisubstituted phosphonium salt **6** (Table 2, entry 1 and Scheme 2). With 2 equiv of Ph_3PNLi, P′(O)Cl_3 or P′(S)Cl_3 only yielded the already described monophosphinimines **3b** and **3c** at 20 °C but the synthesis of double substitution products **4b** and **4c** was feasible at 65 °C by employing an excess of the azayldiide **2** (Table 2, entries 2 and 3).



Scheme 2. Trisubstitution of P′Cl_3 by Ph_3PNLi.

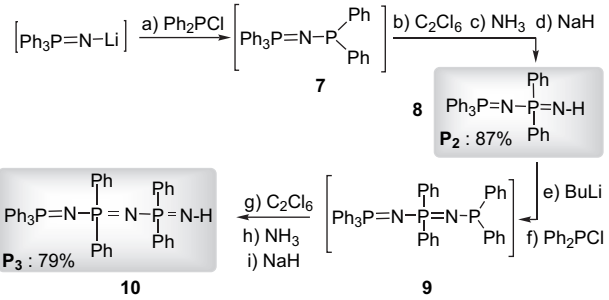
With the phosphorus electrophile P′$PhCl_2$, which has only two possible substitution sites, the almost quantitative formation of the diphosphinimine **4‴a** (entry 4) was observed in presence of Ph_3PNLi (2 equiv). Disubstitution (**4‴b**) was also performed from this reagent and the corresponding oxide, while with the sulfur analogue the double substitution product **4‴c** was more difficult to obtain (Table 2, entries 5 and 6).

2.3. Trisubstitution reactions

When 3 equiv of Ph_3PNLi was brought into reaction with 1 equiv of P′Cl_3, the expected trisubstituted phosphine **5a** was not observed by ^{31}P NMR (Scheme 2). Instead, the corresponding phosphonium chloride **6** was instantaneously obtained as a white precipitate. We could, however, quantitatively generate **5a** via the deprotonation of **6** with *n*-BuLi. Due to its sensitivity, this phosphine could not be isolated but it was trapped by oxidation with H_2O_2 to the trisubstituted phosphine oxide **5b** (76%). Note that the latter could also be obtained from P′(O)Cl_3 in the presence of 3 equiv of Ph_3PNLi while the sulfur analogue **5c** was accessible by the reaction of sulfur with **5a**. The formation of the phosphonium salt **6** is probably due to deprotonation of the THF solvent by **5a**, which behaves as a very strong base, thanks to its electron-donating substituents ($Ph_3P{=}N-$). It is already known that the phosphine **5a** is a stronger base than $Ph_3P{=}NH$ (pK_a (H_2O) of 20.6 for the pair $Ph_3PNH_2^+Br^-/Ph_3P{=}NH$).[9f] Our results show that **5a** is also more basic than the azayldiide Ph_3PNLi (pK_a (H_2O) of 28.1 for the pair $Ph_3P{=}NH/Ph_3P{=}NLi$). Indeed, with regard to the formation of **6** from Ph_3PNLi (Scheme 2), the protonation process that takes place in THF is quantitative after 1 min at 20 °C. By comparison, only 24% of Ph_3PNLi is protonated in Ph_3PNH after 24 h in THF at 65 °C. The very strong basicity of **5a** places it among the strong non-ionic nitrogen and phosphorous bases, namely Schwesinger's[17] and Verkade's[18] bases (pK_a (MeCN) values of 26–47[17c,d,18e]). While **5a** is similar to the former by its phosphazene type PNP skeleton, it actually resembles the second by its protonation mode, which takes place at the phosphorus atom.

2.4. Applications to the synthesis of strong non-ionic bases

We have developed a simple new way to synthesize Schwesinger-type bases using Ph_3PNLi. Preliminary results of this approach were recently published and two pertinant examples of linear bases obtained with our new approach are shown in Scheme 3.[19]



Scheme 3. Examples of the reactivity of Ph_3PNLi towards phosphorus electrophiles: application to the syntheses of P_2 and P_3 Schwesinger-type bases.

A P_2-type-Schwesinger base can thus be obtained by reaction of Ph_3PNLi with chlorodiphenylphosphine followed by addition first of hexachloroethane and subsequently gaseous ammonia. The last step is the deprotonation of the resulting aminophosphonium ion. The product P_2 (**8**) can itself be deprotonated and react further with Ph_2PCl by a similar route to give the P_3 base (**10**). The same sequences can also be performed with primary amines instead of ammonia. Note that branched P_4-type bases are accessible by direct functionalization of the trisubstituted compound **5a**.[19]

3. Conclusion

The work reported here has significantly extended applications of the phosphonium azayldiide $Ph_3P{=}NLi$. Indeed, we have developed a general method to easily isolate, or cleanly generate in situ, a broad family of polyphosphinimines. Our method is particularly significant in comparison to the traditional methodology by avoiding two major inconveniences: the use of hazardous compound or the loss of half of the phosphorus as an HCl scavenger. Thus we have developed an original and general procedure for the synthesis of P_{2-4}-Schwesinger-type bases. Work is currently in progress to generalize this new method and develop other applications for $Ph_3P{=}NLi$, particularly in the field of transition metal catalyzed arylation of nucleophiles.[20]

4. Experimental

4.1. General

The experiments were performed under dry nitrogen, using Schlenk techniques. Electrophiles were purchased from Aldrich and distilled before use. Tetrahydrofuran was dried and distilled according to the usual procedures. Solutions of *n*-BuLi in hexane were purchased from Aldrich and titrated according to the usual methods. Melting points were determined with a Wild Leitz 350 apparatus and are uncorrected. ^1H, ^{31}P and ^{13}C NMR were recorded on a Bruker AC-200 spectrometer (respectively, at 200.132 MHz,

81.0 MHz and 50.323 MHz). IR spectra were obtained with a Perkin–Elmer 377 instrument. Mass spectra were measured with a JEOL SX 102 spectrometer using FAB techniques with GT (glycerol/thioglycerol) matrix.

4.2. Preparation of lithium triphenylphosphonium azayldiide (2)[21]

In a two necked round-bottomed flask we placed aminophosphonium bromide **1** (1.5 g, 4.19 mmol) in THF (50 mL). The white suspension was cooled to −15 °C and 5.2 mL of *n*-butyllithium (8.38 mmol, 1.6 M in hexanes) was added dropwise (5 min) at this temperature. The reaction mixture was stirred for half an hour and then allowed to warm up at 25 °C. After 1 h at this temperature, a homogenous and colourless solution of azayldiide **2** was obtained (4.20 mmol, 100%, based on ^{31}P NMR (THF)); δ=−4.9 (s), −7.5 (s).

4.3. Synthesis of monosubstitution products (Table 1)

4.3.1. *N*-Dichlorophosphino-triphenylphosphinimine (**3a**)[4i,k,11c,d,22] and *N*-dichlorophosphinyl-triphenylphosphinimine (**3b**)[4j,9d]

To a solution of freshly distilled P′Cl$_3$ (366 μL, 4.20 mmol) in THF (5 mL) was added dropwise Ph$_3$P=NLi (**2**, 4.20 mmol) in THF (50 mL) at −15 °C for 16 h. To the resulting mixture was added hydrogen peroxide (30 wt %, 0.48 mL, 4.20 mmol). The resulting mixture was concentrated under reduced pressure. The residue was recrystallized from EtOH and gave after filtration the oxidized form **3b** of the phosphinimine **3a**, as a white solid. Compound **3a**. Yield 94% (determined by ^{31}P NMR). ^{31}P NMR (THF) δ=14.75 (d, $^2J_{P'P}$=74.2 Hz, *P*=N), 165.75 (d, $^2J_{P'P}$=74.2 Hz, *P*′–Cl). Compound **3b**. Isolated yield 70%. Mp (EtOH) 189 °C (lit.[9d] 183–184 °C). MS [EI]: *m*/*z*=394 [M]. IR (KBr) 3070 (w), 1440 (s), 1320 (vs, P=N), 1310 (vs), 1275 (vs), 1225 (vs, P=O), 1120 (s), 1005 (m), 750 (vs), 730 (vs), 695 (vs), 550 (vs), 535 (vs), 515 (vs). ^{1}H NMR (CDCl$_3$) δ=7.53–7.79 (m, 15H, C$_6H_5$). ^{13}C NMR (CDCl$_3$) δ=127.13 (dd, $^1J_{PC}$=107.6 Hz, $^3J_{P'C}$=4.5 Hz, *ipso*-*C*), 129.00 (d, $^3J_{PC}$=13.3 Hz, *m*-*C*), 132.70 (d, $^2J_{PC}$=11.3 Hz, *o*-*C*), 133.20 (d, $^4J_{PC}$=2.9 Hz, *p*-*C*). ^{31}P NMR (CDCl$_3$) δ=−7.14 (d, $^2J_{PP'}$=14.3 Hz, P′), 14.39 (d, $^2J_{PP'}$=14.3 Hz, P). ^{31}P NMR (THF) δ=−8.68 (d, $^2J_{PP'}$=14.2 Hz, P′), 14.09 (d, $^2J_{PP'}$=14.2 Hz, P). $C_{18}H_{15}Cl_2NOP_2$ (394.18) calcd C, 54.85; H, 3.84; N, 3.55. Found: C, 54.80; H, 3.80; N, 3.60.

4.3.2. Monophosphinimines (**3b**, **3c**, **3′a–c**, **3″b**, **3‴a–c**)

General procedure. To a solution of Ph$_3$P=NLi (**2**, 4.20 mmol) in THF (50 mL), prepared as described above, was added dropwise at 25 °C, 1 equiv of a freshly distilled phosphorus electrophile (4.2 mmol). After stirring at a temperature and for a time indicated in Table 1, the resulting mixture was neutralized by acetic acid (480 μL, 8.38 mmol), concentrated under diminished pressure and methylene chloride (100 mL) was added. The mixture was washed three times with 40-mL portions of H$_2$O. The combined aqueous fraction was extracted three times with 40-mL portions of methylene chloride. The combined organic fraction was dried (Na$_2$SO$_4$), filtered, and concentrated under reduced pressure.

4.3.3. *N*-Dichlorophosphinyl-triphenylphosphinimine (**3b**)[4j,9d]

The residue was recrystallized from EtOH to give **3b** (see description below). Yield 75%.

4.3.4. *N*-Dichlorothiophosphinyl-triphenylphosphinimine (**3c**)[4j]

The residue was recrystallized from EtOH to give **3c** as a white solid. Yield 48% (at 20 °C in THF) and 85% (at 110 °C in toluene). Mp 168 °C (lit.[4j] 172 °C). MS [EI]: *m*/*z*=410 [M]. IR (KBr) 3040 (w), 1482 (m), 1384 (vs), 1303 (s, P=N), 1115 (vs), 1070 (s), 996 (s), 743 (s), 723 (vs), 691 (vs, P=S), 689 (vs), 642 (vs), 534 (vs), 476 (m). ^{1}H NMR (CDCl$_3$) δ=7.56–7.82 (m, 15H, C$_6H_5$). ^{13}C NMR (CDCl$_3$) δ=126.45 (dd, $^1J_{PC}$=106.9 Hz, $^3J_{P'C}$=4.8 Hz, *ipso*-*C*), 128.78 (d, $^3J_{PC}$=13.2 Hz, *m*-*C*), 132.59 (d, $^2J_{PC}$=11.3 Hz, *o*-*C*), 133.43 (d, $^4J_{PC}$=3.0 Hz, *p*-*C*). ^{31}P NMR (CDCl$_3$) δ=14.75 (d, $^2J_{PP'}$=1.7 Hz, P), 35.73 (d, $^2J_{PP'}$=1.7 Hz, P′). ^{31}P NMR (THF) δ=13.55 (s, P), 34.35 (s, P′). $C_{18}H_{15}Cl_2NP_2S$ (410.24) calcd C, 52.70; H, 3.69; N, 3.41. Found: C, 52.50; H, 3.80; N, 3.50.

4.3.5. *N*-Diethoxyphosphino-triphenylphosphinimine (**3′a**)

Yield 83%. ^{31}P NMR (THF) δ=5.84 (d, $^2J_{PP'}$=55.3 Hz, P), 136.95 (d, $^2J_{PP'}$=55.3 Hz, P′).

4.3.6. *N*-Diethoxyphosphoryl-triphenylphosphinimine (**3′b**)[4g,9b,23]

The residue was purified by chromatography on a silica gel column. Gradient elution with 0–5% methanol in methylene chloride afforded **3′b** as a yellow oil. Yield 78%. MS [FAB$^+$]: *m*/*z*=414 [M+H$^+$]. IR (KBr) 3050 (w), 1435 (s), 1290 (s, P=N), 1205 (s, P=O), 1180 (s), 1120 (vs), 995 (w), 955 (s), 720 (vs). ^{1}H NMR (CDCl$_3$) δ=1.14 (t, $^3J_{HH}$=7.1 Hz, 6H, C*H*$_3$), 3.91 (m, 4H, C*H*$_2$), 7.40–7.79 (m, 15H, C$_6H_5$). ^{13}C NMR (CDCl$_3$) δ=16.22 (d, $^3J_{P'C}$=7.7 Hz, *C*H$_3$), 61.40 (d, $^2J_{P'C}$=6.1 Hz, *C*H$_2$), 128.48 (d, $^3J_{PC}$=12.8 Hz, *m*-*C*), 130.33 (dd, $^1J_{PC}$=106.1 Hz, $^3J_{P'C}$=4.0, *ipso*-*C*), 132.10 (d, $^4J_{PC}$=2.9 Hz, *p*-*C*), 132.64 (d, $^2J_{PC}$=10.8 Hz, *o*-*C*). ^{31}P NMR (CDCl$_3$) δ=3.69 (d, $^2J_{PP'}$=31.1 Hz, P′), 13.49 (d, $^2J_{PP'}$=31.1 Hz, P). ^{31}P NMR (THF) δ=0.97 (d, $^2J_{PP'}$=33.6 Hz, P′), 11.55 (d, $^2J_{PP'}$=33.6 Hz, P). $C_{22}H_{25}NO_3P_2$ (413.40) calcd C, 63.92; H, 6.10; N, 3.39. Found: C, 64.00; H, 6.20; N, 3.40.

4.3.7. *N*-Diethoxythiophosphoryl-triphenylphosphinimine (**3′c**)[4e,g,6,24]

The residue was recrystallized from CH$_2$Cl$_2$ to give **3′c** as a white solid. Yield 73%. Mp 116–118 °C (lit.[4e] 139–141 °C). MS [FAB$^+$]: *m*/*z*=430 [M+H$^+$]. IR (KBr) 3040 (w), 1430 (s), 1220 (s, P=N), 1110 (s), 1055 (s), 1030 (vs), 950 (vs), 790 (vs, P=S), 775 (vs), 540 (vs), 530 (vs). ^{1}H NMR (CDCl$_3$) δ=1.17 (t, $^3J_{HH}$=7.1 Hz, 6H, C*H*$_3$), 3.97 (q, 4H, C*H*$_2$), 7.45–7.82 (m, 15H, C$_6H_5$). ^{13}C NMR (CDCl$_3$) δ=16.50 (d, $^3J_{P'C}$=8.5 Hz, *C*H$_3$), 61.95 (d, $^2J_{P'C}$=6.2 Hz, *C*H$_2$), 128.42 (d, $^3J_{PC}$=12.9 Hz, *m*-*C*), 129.64 (dd, $^1J_{PC}$=102.7 Hz, $^3J_{P'C}$=3.7 Hz, *ipso*-*C*), 132.20 (d, $^4J_{PC}$=2.9 Hz, *p*-*C*), 132.89 (d, $^2J_{PC}$=10.8 Hz, *o*-*C*). ^{31}P NMR (CDCl$_3$) δ=12.25 (d, $^2J_{PP'}$=28.0 Hz, P), 60.59 (d, $^2J_{PP'}$=28.0 Hz, P′). ^{31}P NMR (THF) δ=9.74 (d, $^2J_{PP'}$=29.6 Hz, P), 61.04 (d, $^2J_{PP'}$=29.6 Hz, P′). $C_{22}H_{25}NO_2P_2S$ (429.46) calcd C, 61.53; H, 5.87; N, 3.26. Found: C, 61.60; H, 5.90; N, 3.50.

4.3.8. *N*-Diphenoxyphosphoryl-triphenylphosphinimine (**3″b**)[4j,6,9d,23,25]

The residue was recrystallized from EtOAc to give **3″b** as a white solid. Yield 80%. Mp (ethyl acetate) 141 °C (lit.[6] 139 °C). MS [EI]: *m*/*z*=509 [M]. IR (KBr) 3040 (w), 1580 (m), 1480 (s), 1425 (m), 1320 (vs, P=N), 1300 (vs), 1190 (vs, P=O), 1110 (vs), 995 (w), 910 (vs), 890, 770 (vs), 715 (s), 685 (vs). ^{1}H NMR (CDCl$_3$) δ=7.00–7.24 (m, 10H, C$_6H_5$), 7.36–7.46 (m, 6H, C$_6H_5$), 7.50–7.70 (m, 9H, C$_6H_5$). ^{13}C NMR (CDCl$_3$) δ=120.50 (d, $^4J_{P'C}$=5.1 Hz, *m*-*C*′), 123.40 (s, *p*-*C*′), 128.44 (d, $^3J_{PC}$=13.0 Hz, *m*-*C*), 128.95 (d, $^4J_{PC}$=2.9 Hz, *p*-*C*), 129.24 (dd, $^1J_{PC}$=106.9 Hz, $^3J_{P'C}$=4.0 Hz, *ipso*-*C*), 132.20 (s, *o*-*C*′), 132.38 (d, $^2J_{PC}$=11.1 Hz, *o*-*C*), 152.29 (d, $^2J_{P'C}$=7.7 Hz, *ipso*-*C*′). ^{31}P NMR (CDCl$_3$) δ=−6.84 (d, $^2J_{PP'}$=33.7 Hz, P′), 14.72 (d, $^2J_{PP'}$=33.7 Hz, P). ^{31}P NMR (THF) δ=−10.23 (d, $^2J_{PP'}$=35.9 Hz, P′), 13.00 (d, $^2J_{PP'}$=35.9 Hz, P). $C_{30}H_{25}NO_3P_2$ (509.49) calcd C, 70.73; H, 4.95; N, 2.75. Found: C, 70.50; H, 5.00; N, 2.80.

4.3.9. *N*-Diphenylphosphino-triphenylphosphinimine (**3‴a**)[9c,11a,19,26]

Yield 91%. ^{31}P NMR (THF) δ=16.81 (d, $^2J_{PP'}$=103 Hz, P), 40.43 (d, $^2J_{PP'}$=103 Hz, P′).

4.3.10. *N*-Diphenylphosphinyl-triphenylphosphinimine (**3‴b**)[4b,c,8,15b,23,27]

The residue was recrystallized from *i*-PrOH/H$_2$O to give **3‴b** as a white solid. Yield 85%. Mp 150 °C. MS [FAB$^+$]: *m*/*z*=478 [M+H$^+$].

IR (KBr) 3400 (s), 3040 (m), 1435 (s), 1300 (vs, P═N), 1170 (vs, P═O), 1110 (vs), 1000 (m), 720 (vs), 690 (vs), 550 (vs), 540, (vs). ^{1}H NMR ($CDCl_3$) δ=7.27–7.48 (m, 15H, C_6H_5), 7.63–7.79 (m, 10H, C_6H_5). ^{13}C NMR ($CDCl_3$) δ=127.70 (d, $^{3}J_{P'C}$=12.7 Hz, *m*-*C*′), 128.52 (d, $^{3}J_{PC}$=12.8 Hz, *m*-*C*), 129.87 (d, $^{4}J_{P'C}$=2.7 Hz, *p*-*C*′), 130.14 (dd, $^{1}J_{PC}$=105.5 Hz, $^{3}J_{P'C}$=3.1 Hz, *ipso*-*C*), 131.10 (d, $^{2}J_{P'C}$=9.9 Hz, *o*-*C*′), 132.04 (d, $^{4}J_{PC}$=2.9 Hz, *p*-*C*), 132.46 (d, $^{2}J_{PC}$=11.0 Hz, *o*-*C*), 138.50 (dd, $^{1}J_{P'C}$=134.2 Hz, $^{3}J_{PC}$=5.6 Hz, *ipso*-*C*′). ^{31}P NMR ($CDCl_3$) δ=15.01 (d, $^{2}J_{PP'}$=1.8 Hz, P′), 16.40 (d, $^{2}J_{PP'}$=1.8 Hz, P). ^{31}P NMR (THF) δ=13.95 (d, $^{2}J_{PP'}$=1.8 Hz, P′), 14.43 (d, $^{2}J_{PP'}$=1.8 Hz, P). $C_{30}H_{25}NOP_2$ (477.49) calcd C, 75.46; H, 5.28; N, 2.93. Found: C, 75.50; H, 5.40; N, 3.00.

4.3.11. *N*-Diphenylthiophosphinyl-triphenylphosphinimine (**3‴c**)[4a,6,9c,11a,12,23,28]

The residue was recrystallized from EtOH to give **3‴c** as a white solid. Yield 70%. Mp 180 °C (lit.[11a] 173–175 °C). MS [FAB$^+$]: *m*/*z*=494 [M+H$^+$]. IR (KBr) 3020 (s), 1430 (s), 1240 (vs, P═N), 1110 (s), 1000 (m), 790 (s, P═S), 540 (s). ^{1}H NMR ($CDCl_3$) δ=7.21–7.55 (m, 15H, C_6H_5), 7.68–8.01 (m, 10H, C_6H_5). ^{13}C NMR ($CDCl_3$) δ=127.68 (d, $^{3}J_{P'C}$=12.9 Hz, *m*-*C*′), 128.48 (d, $^{3}J_{PC}$=12.8 Hz, *m*-*C*), 129.64 (d, $^{4}J_{P'C}$=2.9 Hz, *p*-*C*′), 130.11 (dd, $^{1}J_{PC}$=78.9 Hz, $^{3}J_{P'C}$=3.2 Hz, *ipso*-*C*), 130.75 (d, $^{2}J_{P'C}$=11.2 Hz, *o*-*C*′), 132.11 (d, $^{4}J_{PC}$=2.9 Hz, *p*-*C*), 132.88 (d, $^{2}J_{PC}$=10.8 Hz, *o*-*C*), 141.33 (dd, $^{1}J_{P'C}$=108.0 Hz, $^{3}J_{PC}$=5.8 Hz, *ipso*-*C*′). ^{31}P NMR ($CDCl_3$) δ=18.77 (d, $^{2}J_{PP'}$=0.9 Hz, P), 39.88 (d, $^{2}J_{PP'}$=0.9 Hz, P′). ^{31}P NMR (THF) δ=15.01 (d, $^{2}J_{PP'}$=0.9 Hz, P), 43.23 (d, $^{2}J_{PP'}$=0.9 Hz, P′). $C_{30}H_{25}NOP_2$ (493.55) calcd C, 73.01; H, 5.11; N, 2.84. Found: C, 73.20; H, 5.10; N, 2.80.

4.4. Synthesis of disubstitution products (Table 2)

4.4.1. Diphosphinimines (**4a** and **4‴**)

General procedure. To a solution of freshly distilled phosphorus electrophile (4.20 mmol) in THF (5 mL) was added dropwise Ph_3P═NLi (**2**) (2.38 g, 8.40 mmol), prepared as described above in THF (100 mL). The temperatures and addition times are indicated in Table 2. After addition, hydrogen peroxide (30 wt %) (0.95 mL, 8.40 mmol) was added to the resulting mixture and let stir 1 h at 20 °C. The resulting mixture was neutralized by acetic acid (480 μL, 8.4 mmol), concentrated under reduced pressure and methylene chloride (100 mL) was added. The mixture was washed three times with 40-mL portions of H_2O and the combined aqueous fraction was extracted three times with 40-mL portions of methylene chloride. The combined organic fraction was dried (Na_2SO_4), filtered, and concentrated under diminished pressure.

4.4.2. *N*,*N*′-(Chlorophosphinediyl)bis-triphenylphosphinimine (**4a**)

Yield 50% (determined by ^{31}P NMR). ^{31}P NMR (THF) δ=−3.62 (t, $^{2}J_{PP'}$=16 Hz, P′), 13.77 (d, $^{2}J_{PP'}$=16 Hz, P).

4.4.3. *N*,*N*′-(Chlorophosphorediyl)bi-triphenylphosphinimine (**4b**)[9d]

The residue was purified by chromatography on silica. Gradient elution with 0–5% methanol in methylene chloride afforded the oxidized form **4b** of the diphosphinimine **4a** as an off-white solid. Compound **4b**. Yield 42%. Mp 90 °C ($CHCl_3$/hexane). MS [FAB$^+$]: *m*/*z*=599 [M−Cl]. IR (KBr) 3040 (w), 1465 (s), 1240 (vs, P═N), 1142 (s, P═O), 1025 (w). ^{1}H NMR ($CDCl_3$) δ=7.26–7.61 (m, 30H, C_6H_5). ^{13}C NMR ($CDCl_3$) δ=128.26 (d, $^{3}J_{PC}$=12.7 Hz, *m*-*C*), 131.11 (dd, $^{1}J_{PC}$=101.8 Hz, $^{3}J_{P'C}$=3.7 Hz, *ipso*-*C*), 131.67 (d, $^{4}J_{PC}$=2.6 Hz, *p*-*C*), 132.70 (d, $^{2}J_{PC}$=10.8 Hz, *m*-*C*). ^{31}P NMR ($CDCl_3$) δ=1.71 (t, $^{2}J_{PP'}$=17.9 Hz, P′), 5.81 (d, $^{2}J_{PP'}$=17.9 Hz, P). ^{31}P NMR (THF) δ=0.55 (t, $^{2}J_{PP'}$=20 Hz, P′), 5.11 (d, $^{2}J_{PP'}$=20 Hz, P). $C_{36}H_{30}ClN_2OP_3$ (635.03) calcd C, 68.09; H, 4.76; N, 4.41. Found: C, 68.3; H, 4.9; N, 4.5.

4.4.4. *N*,*N*′-(Phenylphosphinediyl)bis-triphenylphosphinimine (**4‴a**)[9b]

Yield 85% (determined by ^{31}P NMR). ^{31}P NMR (THF) δ=−3.51 (t, $^{2}J_{PP'}$=5.2 Hz, P′), 16.23 (d, $^{2}J_{PP'}$=5.2 Hz, P).

4.4.5. *N*,*N*′-(Phenylphosphorediyl)bis-triphenylphosphinimine (**4‴b**)[9b]

The residue was purified by chromatography on silica. Gradient elution with 0–5% methanol in methylene chloride afforded the oxidized form **4‴b** of the diphosphinimine **4‴a** as an off-white solid. Compound **4‴b**. Yield 69%. Mp (*i*-PrOH/H_2O) 190 °C (lit.[9b] 171–172 °C). MS [FAB$^+$]: *m*/*z*=677 [M+H$^+$]. IR (KBr) 3040 (s) 1430 (vs), 1230 (vs, P═N), 1205 (vs, P═O), 1110 (vs), 995 (m), 715 (vs), 535 (vs). ^{1}H NMR ($CDCl_3$) δ=7.20–7.48 (m, 30H, C_6H_5P), 7.59–7.73 (m, 5H, C_6H_5P′). ^{13}C NMR ($CDCl_3$) δ=126.57 (d, $^{3}J_{P'C}$=13.7 Hz, *m*-*C*′), 127.57 (d, $^{4}J_{P'C}$=2.9 Hz, *p*-*C*′), 127.73 (d, $^{3}J_{PC}$=12.7 Hz, *m*-*C*), 129.86 (d, $^{2}J_{P'C}$=9.3 Hz, *o*-*C*′), 130.98 (d, $^{4}J_{PC}$=2.7 Hz, *p*-*C*), 131.12 (dd, $^{1}J_{PC}$=104.7 Hz, $^{3}J_{P'C}$=3.4 Hz, *ipso*-*C*), 132.31 (d, $^{2}J_{PC}$=10.7 Hz, *o*-*C*), 142.11 (td, $^{1}J_{P'C}$=142.1 Hz, $^{3}J_{PC}$=4.7 Hz, *ipso*-*C*′). ^{31}P NMR ($CDCl_3$) δ=4.77 (t, $^{2}J_{PP'}$=6.4 Hz, P′), 5.34 (d, $^{2}J_{PP'}$=6.4 Hz, P). ^{31}P NMR (THF) δ=2.28 (t, $^{2}J_{PP'}$=4.7 Hz, P′), 4.85 (d, $^{2}J_{PP'}$=4.7 Hz, P). $C_{42}H_{35}N_2OP_3$ (676.68) calcd C, 74.55; H, 5.21; N, 4.14. Found: C, 74.8; H, 5.1; N, 4.1.

4.4.6. Diphosphinimines (**4b**, **4c** and **4‴b**, **4‴c**)

General procedure. To a solution of *n* equiv (see Table 2) of Ph_3P═NLi (*n*×4.2 mmol) in THF (*n*×50 mL) prepared as described above was added dropwise at 20 °C a freshly distilled phosphorus electrophile (4.2 mmol). After stirring at a temperature and for the time indicated in Table 2, the resulting mixture was neutralized by acetic acid (2 n×240 μL, 2 n×4.2 mmol), concentrated under reduced pressure and methylene chloride (100 mL) was added. The mixture was then washed three times with 40-mL portions of H_2O and the combined aqueous fraction was extracted three times with 40-mL portions of methylene chloride. The combined organic fraction was dried (Na_2SO_4), filtered, and concentrated under reduced pressure.

4.4.7. *N*,*N*′-(Chlorophosphorediyl)bis-triphenylphosphinimine (**4b**)[9d]

Isolated yield 80% (see the purification and description and ^{31}P NMR in Section 4.1).

4.4.8. *N*,*N*′-(Chlorothionophosphorediyl)bis-triphenylphosphinimine (**4c**)

Yield 45% (determined by ^{31}P NMR). ^{31}P NMR (THF) δ=−0.55 (t, $^{2}J_{PP'}$=12.8 Hz, P′), 16.98 (d, $^{2}J_{PP'}$=12.8 Hz, P).

4.4.9. *N*,*N*′-(Phenylphosphorediyl)bis-triphenylphosphinimine (**4‴b**)[9b]

The residue was purified by chromatography on silica. Gradient elution with 0–5% methanol in methylene chloride afforded **4‴b** as an off-white solid. Isolated yield 57% (see the description in Section 4.1).

4.4.10. *N*,*N*′-(Phenylthionophosphorediyl)bis-triphenylphosphinimine (**4‴c**)[9c]

Yield 32% (determined by ^{31}P NMR). ^{31}P NMR (THF) δ=4.91 (d, $^{2}J_{PP'}$=4.8 Hz, P), 40.21 (t, $^{2}J_{PP'}$=4.8 Hz, P′).

4.5. Synthesis of trisubstitution products (Scheme 2)

4.5.1. *N*,*N*′,*N*″-(Phosphoretriyl)tris-triphenylphosphinimine (**5b**)[9b]

To a suspension of Ph_3P═NLi (1.19 g, 4.2 mmol) in toluene (50 mL) prepared as described above was added dropwise at room temperature, via a syringe, freshly distilled phosphorus oxychloride (130 μL, 1.40 mmol). After stirring at 110 °C for 48 h, the resulting mixture was neutralized by acetic acid (240 μL, 4.2 mmol), concentrated under reduced pressure and methylene chloride (100 mL) was added. The mixture was washed three times with 40-mL portions of H_2O and the combined aqueous fraction was extracted three times with 40-mL portions of methylene chloride.

The combined organic fraction was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica. Gradient elution with 0–5% methanol in methylene chloride afforded **5b** as an off-white solid. Yield 30%. Mp (dioxane) 190–191 °C (lit.[9b] 193 °C). MS [FAB$^+$]: m/z=876 [M+H$^+$]. IR (KBr) 3060 (m), 1435 (vs), 1230 (vs, P═N), 1190 (s), 1115 (vs, P═O), 720 (vs), 540 (vs). ^{1}H NMR ($CDCl_3$) δ=7.17–7.47 (m, 45H, C_6H_5). ^{13}C NMR ($CDCl_3$) δ=128.30 (d, $^3J_{PC}$=12.7 Hz, *m*-*C*), 130.35 (dd, $^1J_{PC}$=105.5 Hz, $^3J_{P'C}$=4.3 Hz, *ipso*-*C*), 131.64 (d, $^4J_{PC}$=2.6 Hz, *p*-*C*), 132.80 (d, $^2J_{PC}$=11.2 Hz, *o*-*C*). ^{31}P NMR ($CDCl_3$) δ=0.45 (q, $^2J_{PP'}$= 10.0 Hz, P′), 8.74 (d, $^2J_{PP'}$=10.0 Hz, P). $C_{54}H_{45}N_3OP_4$ (875.88) calcd C, 74.05; H, 5.18; N, 4.80. Found: C, 69.41; H, 5.06; N, 4.44.

4.5.2. *N,N′,N″-(Phosphinetriyl)tris-triphenylphosphinimine hydrochloride (**6**)*[9b,f]

To a suspension of Ph_3P═NLi (1.19 g, 4.2 mmol) in THF (50 mL) prepared as described above was added dropwise at room temperature, via a syringe, freshly distilled phosphorus trichloride (122 μL, 1.40 mmol). After stirring at room temperature for 30 min, a white precipitate was filtered off and washed with THF to give **6** as an off-white solid. Yield 95%. Mp 52–53 °C (lit.[9f] 49–50 °C). MS [FAB$^+$]: m/z=859 [M−Cl]. IR (KBr) 3025 (m), 1455 (m), 1235 (s, P═N), 1140 (m), 720 (w), 565 (s). ^{1}H NMR ($CDCl_3$) δ=7.46 (dd, $^1J_{PH}$=579.5 Hz, $^3J_{P'H}$=5.5 Hz, 1H), 7.29–7.55 (m, 45H, C_6H_5P). ^{13}C NMR ($CDCl_3$) δ=128.69 (d, $^3J_{PC}$=12.7 Hz, *m*-*C*), 129.27 (dd, $^1J_{PC}$=105.1 Hz, $^3J_{P'C}$=3.9 Hz, *ipso*-*C*), 132.29 (d, $^2J_{PC}$=10.8 Hz, *o*-*C*), 132.47 (d, $^4J_{PC}$=2.2 Hz, *p*-*C*). {^{1}H}^{31}P NMR ($CDCl_3$) δ=−12.53 (s, P′), 12.69 (s, P). ^{31}P NMR ($CDCl_3$) δ=−12.53 (d, $^1J_{P'H}$=579.5 Hz, P′), 12.69 (s, P).

4.5.3. *N,N′,N″-(Phosphinetriyl)tris-triphenylphosphinimine (**5a**)*[11] *and N,N′,N″-(thionophosphoretriyl) tris-triphenylphosphinimine (**5c**)*[29]

To a solution of *N,N′,N″*-(phosphinetriyl)tris-triphenylphosphinimine hydrochloride **6** (0.45 g, 0.5 mmol) in DMSO (10 mL) was added dropwise at room temperature *n*-butyllithium in hexanes (313 μL, 0.5 mmol). After stirring at room temperature for 30 min, an in situ ^{31}P NMR spectra showed the quantitative formation of *N,N′,N″*-(phosphinetriyl)tris-triphenylphosphinimine **5a**. ^{31}P NMR (DMSO) δ=−0.13 (br d, $^2J_{pp'}$=27.1 Hz, P), 101.19 (br q, $^2J_{pp'}$=27.1 Hz, P′). To the resulting mixture was added sulfur (32 mg, 1.0 mmol). After stirring at room temperature, an in situ ^{31}P NMR spectra showed the formation of **6** (12%), **5b** (52%) and **5c** (*N,N′,N″*-(thionophosphoretriyl)tris-triphenylphosphinimine); yield 24%; ^{31}P NMR (DMSO) δ=−4.21 (q, $^2J_{PP'}$=3.1 Hz, P′), 12.70 (d, $^2J_{PP'}$=3.1 Hz, P).

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