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Reaction between triphenylphosphine and aromatic amines in the presence of diethyl azodicarboxylate: an efficient synthesis of aryliminophosphoranes under neutral and mild conditions

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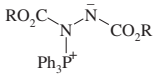
ABSTRACT

An efficient synthesis of aryliminophosphoranes is described. A mixture of an aromatic amine, diethyl azodicarboxylate and triphenylphosphine undergo a Mitsonobu type reaction at ambient temperature in dry dichloromethane to afford aryliminophosphoranes in excellent yields.

1. Introduction

In the course of his extensive investigations on azodicarboxylic esters and with a quest to discover novel 1,3-dipoles, Huisgen generated a zwitterion by the addition of triphenylphosphine to dimethyl azodicarboxylate.[1,2] In addition to establishing its structure, he also demonstrated the nucleophilic reactivity of this species by its reaction with dimethyl acetylenedicarboxylate, phenyl isocyanate and phenyl isothiocyanate.[1c] After this work, apart from its pivotal role in the Mitsunobu reaction[3] offering the most reliable and universally accepted synthetic protocol for the stereochemical inversion of a hydroxyl group, the chemistry of Huisgen zwitterion has received only scant attention. Kolasa and Miller's observation[4] of unexpected transformations in the attempted Mitsunobu reaction of hydroxy esters and the transformation of ketones to vinyl hydrazines under Mitsunobu conditions reported by Liu[5] et al. are noteworthy in this connection. Other synthetically useful reactions of the Huisgen zwitterion, include synthesis of oxadiazolines from α-ketoesters,[6] and protected hydrazones from salicylaldehydes.[7] Recent studies on the chemistry of this zwitterion have uncovered a number of interesting reactions, which include the formation of a monohydrazone from benzil via an unprecedented rearrangement,[8] formation of novel pyrazolopyridazines from dienones,[9] spirooxadiazolines from isatins[10] and pyrazoles from allenes.[11]



Huisgen zwitterion

Iminophosphoranes, compounds of general structure $R_3P{=}NR'$ with four-coordinate phosphorus and incorporating a formal phosphorus–nitrogen double bond, are reactive species, which take part in many valuable reactions in organic synthesis.[12–15] Iminophosphoranes were first reported by Staudinger and Meyer[16] in 1919 but virtually no additional chemistry was reported until the early 1960s. Much chemistry has been discovered in the last three decades with numerous applications to organic synthesis.[12–15,17] Several methods have been developed for the preparation of iminophosphoranes.[12–21]

As part of our studies on the development of efficient and facile methods for the preparation of interesting organic compounds from readily available building blocks,[22] we have reported new syntheses of aryliminophosphoranes.[23] Stable phosphorous ylides were obtained from the 1:1:1 addition reaction between triphenylphosphine, dimethyl acetylenedicarboxylate and some aromatic amines. These phosphoranes underwent an intramolecular reaction in boiling *p*-xylene or toluene to afford the corresponding aryliminophosphoranes. However, that reaction suffers from some

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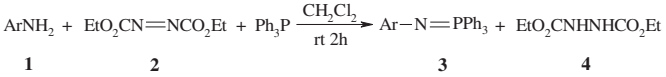
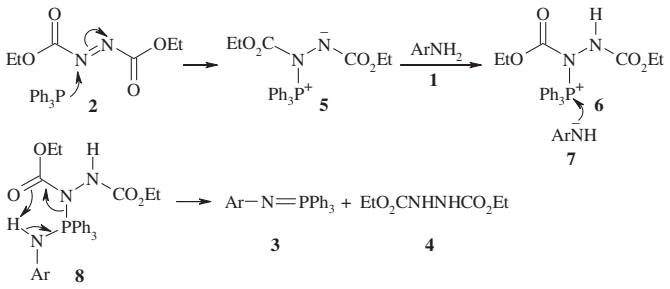
drawbacks such as long reaction times and high reaction temperatures.

2. Results and discussion

We report here an efficient synthetic route to aryliminophosphoranes using triphenylphosphine, diethyl azodicarboxylate (DEAD) and aromatic amines. Thus, a mixture of an aromatic amine **1**, DEAD **2** and triphenylphosphine undergo a smooth Mitsonobu type reaction at ambient temperature in dry dichloromethane to afford aryliminophosphoranes **3a**–**p** in 85–98% yields (Scheme 1, Fig. 1). All the reactions went to completion within a few hours. ^{1}H NMR spectroscopic analysis of the reaction mixtures clearly indicated formation of the corresponding aryliminophosphoranes **3**. Any product other than **3** and diethyl 1,2-hydrazindicarboxylate **4** could not be detected by NMR spectroscopy.



Scheme 1.



Scheme 2.

aromatic amines, diethyl azodicarboxylate and triphenylphosphine at ambient temperature. This reaction offers significant advantages for the synthesis of iminophosphoranes from aromatic amines. Simply available starting materials, excellent yields of the products, mild reaction conditions and short reaction times are the main advantages of this method. The reactions have been performed under neutral conditions and the substances have been mixed without any activation or modification. The procedure described here may be an acceptable method for the preparation of aryliminophosphoranes with variable functionalities.

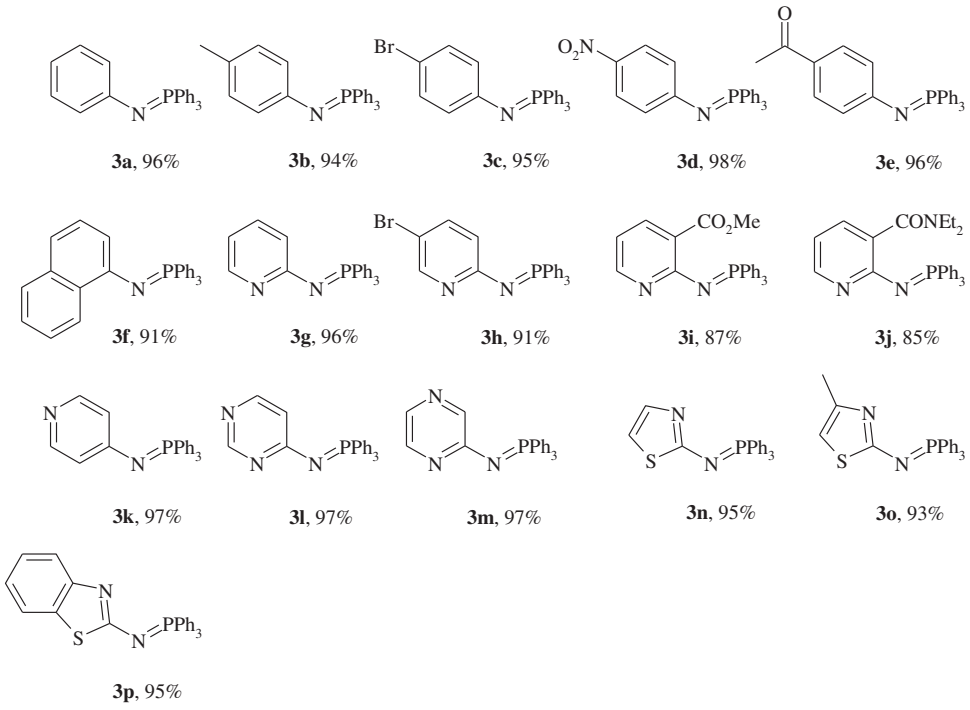


Fig. 1. Aryliminophosphoranes **3a**–**p**.

The following mechanistic postulate may be invoked to rationalise formation of the iminiphosphoranes. Initially zwitterion **5**[1–3,24–27] generated from nucleophilic attack of triphenylphosphine upon diethyl azodicarboxylate **2** is protonated by the amine **1**. Next, nucleophilic addition of the conjugate base of the NH-acid **7** on the phosphonium ion **6** give the adduct intermediate **8**, which will be readily fragmentated under the reaction conditions to afford the isolated iminiphosphorane **3** by removal of diethyl 1,2-hydrazindicarboxylate **4** (Scheme 2).

3. Conclusion

In summary, we have developed an efficient synthesis of aryliminophosphoranes from a Mitsunobu type reaction between

4. Experimental

4.1. General

Diethyl azodicarboxylate, aromatic amines and triphenylphosphine were obtained from Merck (Germany) and Fluka (Buchs, Switzerland) and were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus. ^{1}H and ^{13}C NMR spectra were measured ($CDCl_3$ solution with TMS as an internal standard) with a Brucker DRX-500 AVANCE spectrometer at 500.1 and 125.8 MHz, respectively.

4.2. General procedure for the preparation of compound 3a–p, exemplified with 3a

To a magnetically stirred solution of triphenylphosphine (0.524 g, 2 mmol) and aniline (0.186 g, 2 mmol) in dry dichloromethane (2 mL) was added dropwise a solution of diethyl azodicarboxylate (40% in toluene, 1.045 g, 2.4 mmol) in dry dichloromethane (1 mL) at ambient temperature over 10 min. The reaction mixture was stirred at ambient temperature for 2 h and then was diluted with diethyl ether (10 mL). The organic phase was washed with saturated aq $NaHCO_3$ (2×5 mL). The organic layer was dried with Na_2SO_4, filtered and evaporated. The residue was crystallised from 1:1 *n*-hexane/EtOAc.

*4.2.1. N-Phenyltriphenyliminophosphorane (**3a**).* White solid, mp 132–133 °C (133–134 °C),[28] yield: 0.678 g, 96%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.74 (6H, dd, $^3J_{HH}$=7.7 Hz and $^3J_{PH}$=12.0 Hz, $6CH_{ortho}$), 7.49 (3H, dt, $^3J_{HH}$=7.7 Hz and $^5J_{PH}$=1.5 Hz, $3CH_{para}$), 7.42 (6H, td, $^3J_{HH}$=7.7 Hz and $^4J_{PH}$=2.9 Hz, $6CH_{meta}$), 7.00 (2H, dd, J=7.2 Hz and J=8.0 Hz, 2CH), 6.80 (2H, d, J=8.0 Hz, 2CH), 6.64 (1H, t, J=7.2 Hz, CH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 151.1 (d, $^2J_{PC}$=2.1 Hz, C–N=P), 132.6 (d, $^2J_{PC}$=9.6 Hz, CH_{ortho}), 131.6 (d, $^4J_{PC}$=2.6 Hz, CH_{para}), 131.2 (d, $^1J_{PC}$=98.9 Hz, C_{ipso}), 128.6 (CH), 128.6 (d, $^3J_{PC}$=12.2 Hz, CH_{meta}), 123.5 (d, $^3J_{PC}$=17.5 Hz, CH), 117.3 (CH).

*4.2.2. N-(4-Methylphenyl)triphenyliminophosphorane (**3b**).* White solid, mp 138 °C (136–137 °C),[28] yield: 0.690 g, 94%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.73 (6H, dd, $^3J_{HH}$=7.9 Hz and $^3J_{PH}$=11.7 Hz, $6CH_{ortho}$), 7.43 (3H, dt, $^3J_{HH}$=7.9 Hz and $^5J_{PH}$=1.3 Hz, $3CH_{para}$), 7.36 (6H, dt, $^3J_{HH}$=7.9 Hz and $^4J_{PH}$=2.9 Hz, $6CH_{meta}$), 6.80 (2H, d, J=8.0 Hz, 2CH), 6.73 (2H, d, J=8.0 Hz, 2CH), 2.15 (3H, s, CH_3). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 148.3 (d, $^2J_{PC}$=2.6 Hz, C–N=P), 132.5 (d, $^2J_{PC}$=9.6 Hz, CH_{ortho}), 131.5 (d, $^4J_{PC}$=2.5 Hz, CH_{para}), 131.2 (d, $^1J_{PC}$=98.6 Hz, C_{ipso}), 129.2 (CH), 128.5 (d, $^3J_{PC}$=11.9 Hz, CH_{meta}), 126.2 (*C*–CH_3), 123.2 (d, $^3J_{PC}$=17.4 Hz, CH), 20.5 (CH_3).

*4.2.3. N-(4-Bromophenyl)triphenyliminophosphorane (**3c**).* White solid, mp 126–127 °C (126–127 °C),[28] yield: 0.821 g, 95%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.72 (6H, dd, $^3J_{HH}$=7.7 Hz and $^3J_{PH}$=11.6 Hz, $6CH_{ortho}$), 7.49 (3H, dt, $^3J_{HH}$=7.7 Hz and $^5J_{PH}$=1.3 Hz, $3CH_{para}$), 7.42 (6H, dt, $^3J_{HH}$=7.7 Hz and $^4J_{PH}$=3.0 Hz, $6CH_{meta}$), 7.05 (2H, d, J=8.2 Hz, 2CH), 6.65 (2H, d, J=8.2 Hz, 2CH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 150.5 (d, $^2J_{PC}$=1.9 Hz, C–N=P), 132.5 (d, $^2J_{PC}$=9.6 Hz, CH_{ortho}), 131.8 (d, $^4J_{PC}$=1.8 Hz, CH_{para}), 131.3 (CH), 130.6 (d, $^1J_{PC}$=99.4 Hz, C_{ipso}), 128.6 (d, $^3J_{PC}$=12.1 Hz, CH_{meta}), 124.9 (d, $^3J_{PC}$=17.6 Hz, CH), 109.3 (C–Br).

*4.2.4. N-(4-Nitrophenyl)triphenyliminophosphorane (**3d**).* Pale yellow solid, mp 156–158 °C (158–159 °C),[28] yield: 0.780 g, 98%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.90 (2H, d, J=9.2 Hz, 2CH), 7.73 (6H, dd, $^3J_{HH}$=7.6 Hz and $^3J_{PH}$=12.2 Hz, $6CH_{ortho}$), 7.57 (3H, dt, $^3J_{HH}$=7.6 Hz and $^5J_{PH}$=1.4 Hz, $3CH_{para}$), 7.48 (6H, td, $^3J_{HH}$=7.6 Hz and $^4J_{PH}$=3.0 Hz, $6CH_{meta}$), 6.68 (2H, d, J=9.2 Hz, 2CH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 160.1 (d, $^2J_{PC}$=2.5 Hz, C–N=P), 138.0 (C), 132.6 (d, $^2J_{PC}$=9.7 Hz, CH_{ortho}), 132.1 (d, $^4J_{PC}$=2.9 Hz, CH_{para}), 129.1 (d, $^1J_{PC}$=100.0 Hz, C_{ipso}), 128.8 (d, $^3J_{PC}$=12.1 Hz, CH_{meta}), 125.5 (CH), 122.2 (d, $^3J_{PC}$=19.0 Hz, CH).

*4.2.5. N-(4-Acetylphenyl)triphenyliminophosphorane (**3e**).* White solid, mp 130–131 °C (127–130 °C),[23a] yield: 0.759 g, 96%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.69 (2H, d, J=8.7 Hz, 2CH), 7.65 (6H, dd, $^3J_{HH}$=7.6 Hz and $^3J_{PH}$=12.2 Hz, $6CH_{ortho}$), 7.55 (3H, dt, $^3J_{HH}$=7.6 Hz and $^5J_{PH}$=1.4 Hz, $3CH_{para}$), 7.47 (6H, dt, $^3J_{HH}$=7.6 Hz and $^4J_{PH}$=3.0 Hz, $6CH_{meta}$), 6.76 (2H, d, $^3J_{HH}$=8.7 Hz, 2CH), 2.45 (3H, s, CH_3). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 196.6 (C=O), 157.7 (d, $^2J_{PC}$=2.4 Hz, C–N=P), 132.6 (d, $^2J_{PC}$=9.7 Hz, CH_{ortho}), 132.1 (d, $^4J_{PC}$=2.9 Hz, CH_{para}), 130.0 (d, $^1J_{PC}$=99.8 Hz, C_{ipso}), 129.9 (d, $^4J_{PC}$=1.6 Hz, CH), 128.8 (d, $^3J_{PC}$=12.2 Hz, CH_{meta}), 126.8 (C), 122.6 (d, $^3J_{PC}$=18.9 Hz, CH), 26.0 (CH_3).

*4.2.6. N-1-Naphthyltriphenyliminophosphorane (**3f**).* White solid, mp 112 °C (110–112 °C),[23a] yield: 0.734 g, 91%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 8.91 (1H, d, J=8.1 Hz, CH), 7.83 (6H, dd, $^3J_{HH}$=8.0 Hz and $^3J_{PH}$=11.9 Hz, $6CH_{ortho}$), 7.71 (1H, d, J=7.8 Hz, CH), 7.49 (4H, m, $3CH_{para}$ and CH), 7.42 (7H, m, $6CH_{meta}$ and CH), 7.13 (1H, d, J=8.1 Hz, CH), 6.99 (1H, t, J=7.8 Hz, CH), 6.43 (1H, d, J=7.4 Hz, CH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 148.0 (C–N=P), 135.1 (d, $^4J_{PC}$=2.6 Hz, C), 132.6 (d, $^2J_{PC}$=9.6 Hz, CH_{ortho}), 132.0 (d, $^3J_{PC}$=22.1 Hz, C), 131.7 (d, $^4J_{PC}$=2.6 Hz, CH_{para}), 131.2 (d, $^1J_{PC}$=99.6 Hz, C_{ipso}), 128.6 (d, $^3J_{PC}$=12.2 Hz, CH_{meta}), 127.4, 126.2, 125.5, 125.4, 123.7, and 116.7 (6CH), 114.1 (d, $^3J_{PC}$=10.6 Hz, CH).

*4.2.7. N-(2-Pyridyl)triphenyliminophosphorane (**3g**).* White solid, mp 147–148 °C (146–148 °C),[23a] yield: 0.680 g, 96%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.89 (6H, dd, $^3J_{HH}$=7.6 Hz and $^3J_{PH}$=12.2 Hz, $6CH_{ortho}$), 7.86 (1H, d, $^3J_{HH}$=7.0 Hz, CH), 7.50 (3H, dt, $^3J_{HH}$=7.6 Hz and $^5J_{PH}$=1.4 Hz, $3CH_{para}$), 7.43 (6H, dt, $^3J_{HH}$=7.6 and $^4J_{PH}$=3.0 Hz, $6CH_{meta}$), 7.39 (1H, dt, $^3J_{HH}$=7.1 Hz and $^4J_{HH}$=1.1 Hz, CH), 7.01(1H, d, J=8.3 Hz, CH), 6.92 (1H, dt, J=8.4, 0.8 Hz, CH), 6.47 (1H, dd, J=7.0 Hz and J=5.1 Hz, CH), 6.44 (1H, ddd, J=6.1, 5.0, 1.1 Hz, CH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 163.6 (d, $^2J_{PC}$=6.3 Hz, C–N=P), 147.0 (CH), 136.5 (d, $^4J_{PC}$=4.5 Hz, CH), 133.1 (d, $^2J_{PC}$=9.6 Hz, CH_{ortho}), 131.4 (d, $^4J_{PC}$=2.6 Hz, CH_{para}), 130.3 (d, $^1J_{PC}$=99.6 Hz, C_{ipso}), 128.8 (d, $^3J_{PC}$=12.0 Hz, CH_{meta}), 117.2 (d, $^3J_{PC}$=24.0 Hz, CH), 112.5 (CH).

*4.2.8. N-(5-Bromo-2-pyridyl)triphenyliminophosphorane (**3h**).* White solid, mp 167–168 °C (165–167 °C),[23a] yield: 0.788 g, 91%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.80 (1H, d, $^4J_{HH}$=2.1 Hz, CH), 7.78 (6H, dd, $^3J_{HH}$=8.0 Hz and $^3J_{PH}$=12.0 Hz, $6CH_{ortho}$), 7.44 (3H, t, $^3J_{HH}$=7.5 Hz, $3CH_{para}$), 7.38 (6H, td, $^3J_{HH}$=8.0 Hz and $^4J_{PH}$=2.3 Hz, $6CH_{meta}$), 7.34 (1H, dd, $^3J_{HH}$=8.7 Hz and $^4J_{HH}$=2.1 Hz, CH), 6.82 (1H, d, J=8.7 Hz, CH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 162.4 (d, $^2J_{PC}$=6.5 Hz, C–N=P), 147.4 (CH), 138.9 (d, $^4J_{PC}$=4.5 Hz, CH), 133.0 (d, $^2J_{PC}$=9.7 Hz, CH_{ortho}), 131.6 (d, $^4J_{PC}$=2.6 Hz, CH_{para}), 129.8 (d, $^1J_{PC}$=99.9 Hz, C_{ipso}), 128.3 (d, $^3J_{PC}$=12.0 Hz, CH_{meta}), 119.0 (d, $^3J_{PC}$=24.0 Hz, CH), 107.2 (C–Br).

*4.2.9. N-(3-Methoxycarbonyl-2-pyridyl)triphenyliminophosphorane (**3i**).* Pale yellow solid, mp 175–176 °C (173–176 °C),[29] yield: 0.717 g, 87%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 8.01–7.97 (2H, m, 2CH), 7.87 (6H, dd, $^3J_{HH}$=7.9 Hz and $^3J_{PH}$=11.7 Hz, $6CH_{ortho}$), 7.51 (3H, dt, $^3J_{HH}$=7.8 Hz and $^5J_{PH}$=1.3 Hz, $3CH_{para}$), 7.39 (6H, td, $^3J_{HH}$=7.6 Hz and $^4J_{PH}$=2.7 Hz, $6CH_{meta}$), 6.39 (1H, dd, J=7.7, 4.6 Hz, CH), 3.92 (3H, s, OCH_3). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 169.0 (C=O), 162.7 (d, $^2J_{PC}$=6.8 Hz, C–N=P), 151.1 (CH), 140.6 (d, $^4J_{PC}$=3.1 Hz, CH), 133.7 (d, $^2J_{PC}$=9.7 Hz, CH_{ortho}), 131.8 (d, $^4J_{PC}$=2.8 Hz, CH_{para}), 130.6 (d, $^1J_{PC}$=100.4 Hz, C_{ipso}), 128.6 (d, $^3J_{PC}$=10.2 Hz, CH_{meta}), 117.4 (d, $^3J_{PC}$=21.5 Hz, C), 112.1 (CH), 52.0 (OCH_3).

*4.2.10. N-(3-Diethylaminocarbonyl-2-pyridyl)triphenyliminophosphorane (**3j**).* Pale yellow solid, mp 168–169 °C (169–170 °C),[29] yield: 0.771 g, 85%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.89 (1H, dd, J=5.2, 2.0 Hz, CH), 7.82 (6H, dd, $^3J_{HH}$=7.8 Hz and $^3J_{PH}$=12.0 Hz, $6CH_{ortho}$), 7.55 (1H, d, J=7.2 Hz, CH), 7.51 (3H, td, $^3J_{HH}$=7.2 Hz and $^5J_{PH}$=1.6 Hz, $3CH_{para}$), 7.34 (6H, td, $^3J_{HH}$=7.7 Hz and $^4J_{PH}$=2.8 Hz, $6CH_{meta}$), 6.43 (1H, dd, J=7.0, 5.1 Hz, CH), 3.95 and 3.35 [4H, 2q, J=7.1 Hz, $N(CH_2CH_3)_2$], 1.33 and 1.07 [3H, 2t, J=7.1 Hz, $N(CH_2CH_3)_2$]. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 171.2 (C=O), 159.6 (d, $^2J_{PC}$=6.2 Hz, C–N=P), 147.8 (CH), 135.0 (d, $^4J_{PC}$=3.6 Hz, CH), 133.4 (d, $^2J_{PC}$=9.7 Hz, CH_{ortho}), 131.8 (d, $^4J_{PC}$=2.7 Hz, CH_{para}), 130.9 (d, $^1J_{PC}$=100.2 Hz, C_{ipso}), 128.5 (d, $^3J_{PC}$=12.1 Hz, CH_{meta}), 126.4 (d, $^3J_{PC}$=24.0 Hz, C), 111.9 (CH), 42.5 and 38.7 [$N(CH_2CH_3)_2$], 14.5 and 13.3 [$N(CH_2CH_3)_2$].

*4.2.11. N-(4-Pyridyl)triphenyliminophosphorane (**3k**).* White solid, mp 155–157 °C (154–155 °C),[30] yield: 0.687 g, 97%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 8.09 (2H, d, J=5.2 Hz, 2CH), 7.72 (6H, dd, $^3J_{HH}$=7.6 Hz and $^3J_{PH}$=11.9 Hz, $6CH_{ortho}$), 7.61 (3H, td, $^3J_{HH}$=7.3 Hz and $^5J_{PH}$=1.8 Hz, $3CH_{para}$), 7.47 (6H, td, $^3J_{HH}$=7.5 Hz and $^4J_{PH}$=3.0 Hz, $6CH_{meta}$), 6.57 (2H, d, J=5.2 Hz, 2CH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 158.8 (d, $^2J_{PC}$=2.4 Hz, C–N=P), 148.8 (CH), 132.4 (d, $^2J_{PC}$=9.7 Hz, CH_{ortho}), 131.9 (d, $^4J_{PC}$=2.4 Hz, CH_{para}), 129.4 (d, $^1J_{PC}$=99.9 Hz, C_{ipso}), 128.3 (d, $^3J_{PC}$=12.1 Hz, CH_{meta}), 117.8 (d, $^3J_{PC}$=19.2 Hz, CH).

*4.2.12. N-(3-Pyrimidyl)triphenyliminophosphorane (**3l**).* White solid, mp 119–121 °C (118–120 °C),[31] yield: 0.689 g, 97%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 8.16 (1H, d, J=1.0 Hz, CH), 7.98 (1H, dd, J=5.6, 1.2 Hz, CH), 7.79 (6H, dd, $^3J_{HH}$=7.8 Hz and $^3J_{PH}$=12.0 Hz, $6CH_{ortho}$), 7.52 (3H, dt, $^3J_{HH}$=7.6 Hz and $^5J_{PH}$=1.7 Hz, $3CH_{para}$), 7.44 (6H, td, $^3J_{HH}$=7.8 Hz and $^4J_{PH}$=2.7 Hz, $6CH_{meta}$), 6.83 (1H, d, J=5.6 Hz, CH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 168.2 (d, $^2J_{PC}$=6.4 Hz, C–N=P), 156.8 (CH), 153.4 (d, ^4J_P=4.4 Hz, CH), 132.9 (d, $^2J_{PC}$=9.9 Hz, CH_{ortho}), 131.8 (d, $^4J_{PC}$=2.5 Hz, CH_{para}), 128.8 (d, $^1J_{PC}$=100.2 Hz, C_{ipso}), 128.3 (d, $^3J_{PC}$=12.1 Hz, CH_{meta}), 114.4 (d, $^3J_{PC}$=24.5 Hz, CH).

*4.2.13. N-(2-Pyrazyl)triphenyliminophosphorane (**3m**).* White solid, mp 177–178 °C (180.5–182 °C),[29] yield: 0.689 g, 97%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 8.10 (1H, d, J=4.6 Hz, CH), 7.81 (6H, dd, $^3J_{HH}$=7.8 Hz and $^3J_{PH}$=11.9 Hz, $6CH_{ortho}$), 7.70 (1H, d, J=1.2 Hz, CH), 7.66 (1H, dd, J=4.6, 1.2 Hz, CH), 7.53 (3H, dt, $^3J_{HH}$=7.6 Hz and $^5J_{PH}$=1.8 Hz, $3CH_{para}$), 7.42 (6H, td, $^3J_{HH}$=7.6 Hz and $^4J_{PH}$=2.7 Hz, $6CH_{meta}$). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 160.2 (d, $^2J_{PC}$=6.7 Hz, C–N=P), 142.0 (d, $^3J_{PC}$=25.5 Hz, CH), 141.1 (CH), 133.3 (d, $^2J_{PC}$=9.6 Hz, CH_{ortho}), 132.2 (CH), 131.8 (d, $^4J_{PC}$=2.6 Hz, CH_{para}), 129.6 (d, $^1J_{PC}$=99.1 Hz, C_{ipso}), 128.8 (d, $^3J_{PC}$=12.0 Hz, CH_{meta}).

*4.2.14. N-(1,3-Thiazol-2-yl)triphenyliminophosphorane (**3n**).* Pale orange needles, mp 140 °C (139–141 °C),[23b] yield: 0.684 g, 95%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.86 (6H, dd, $^3J_{HH}$=7.7 Hz and $^3J_{PH}$=12.3 Hz, $6CH_{ortho}$), 7.58 (3H, t, $^3J_{HH}$=7.2 Hz, $3CH_{para}$), 7.50 (6H, dt, $^4J_{PH}$=2.3 Hz and $^3J_{HH}$=7.5 Hz, $6CH_{meta}$), 7.01 (1H, d, $^3J_{HH}$=3.8 Hz, CH), 6.43 (1H, dd, $^5J_{PH}$=3.6 Hz and $^3J_{HH}$=3.8 Hz, CH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 173.9 (C–N=P), 138.3 (CH), 133.1 (d, $^2J_{PC}$=9.9 Hz, CH_{ortho}), 132.2 (d, $^4J_{PC}$=2.5 Hz, CH_{para}), 128.8 (d, $^1J_{PC}$=101.1 Hz, C_{ipso}), 128.7 (d, $^3J_{PC}$=12.3 Hz, CH_{meta}), 108.8 (CH).

*4.2.15. N-(4-Methyl-1,3-thiazol-2-yl)triphenyliminophosphorane (**3o**).* Pale orange needles, mp 159–160 °C (157–159 °C),[23b] yield: 0.696 g, 93%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.86 (6H, dd, $^3J_{HH}$=7.6 Hz and $^3J_{PH}$=12.3 Hz, $6CH_{ortho}$), 7.56 (3H, t, $^3J_{HH}$=6.8 Hz, $3CH_{para}$), 7.47 (6H, dt, $^4J_{PH}$=2.6 Hz and $^3J_{HH}$=7.5 Hz, $6CH_{meta}$), 5.95 (1H, s, CH), 2.16 (3H, s, CH_3). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 171.6 (C–N=P), 148.0 (CH_3–C), 133.2 (d, $^2J_{PC}$=10.1 Hz, CH_{ortho}), 132.2 (d, $^4J_{PC}$=2.6 Hz, CH_{para}), 128.6 (d, $^1J_{PC}$=101.4 Hz, C_{ipso}), 128.6 (d, $^3J_{PC}$=12.3 Hz, CH_{meta}), 102.8 (CH), 17.7 (CH_3).

*4.2.16. N-(1,3-Benzothiazol-2-yl)triphenyliminophosphorane (**3p**).* Pale yellow solid, mp 148–149 °C (138–144 °C),[23b] yield: 0.780 g, 95%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.94 (6H, dd, $^3J_{HH}$=8.1 Hz and $^3J_{PH}$=12.4 Hz, $6CH_{ortho}$), 7.61 (3H, t, $^3J_{HH}$=7.4 Hz, $3CH_{para}$), 7.55–7.50 (7H, m, CH and $6CH_{meta}$), 7.48 (1H, d, J=8.0 Hz, CH), 7.23 (1H, t, J=7.5 Hz, CH), 7.05 (1H, t, J=7.5 Hz, CH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 171.4 (C–N=P), 152.8 and 134.0 (2C), 133.3 (d, $^2J_{PC}$=10.3 Hz, CH_{ortho}), 132.5 (CH_{para}), 128.7 (d, $^3J_{PC}$=12.5 Hz, CH_{meta}), 128.2 (d, $^1J_{PC}$=101.5 Hz, C_{ipso}), 124.8, 120.9, 120.4, and 118.7 (4CH).

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