Versatile and Efficient Synthesis of a New Class of Aza-Based Phosphinic Amide Ligands *via* Unusual P–C Cleavage

by **Shih-Chung Tsai**, **Yaw-Shien Fu**, **Ju-Hsiou Liao**, and **Shuchun Joyce Yu***

Department of Chemistry and Biochemistry, National Chung Cheng University, Min-Hsiung, Chia-Yi, Taiwan 621
(phone: +886-5-242-8138; fax: +886-5-272-1040; e-mail: chejyy@ccu.edu.tw)

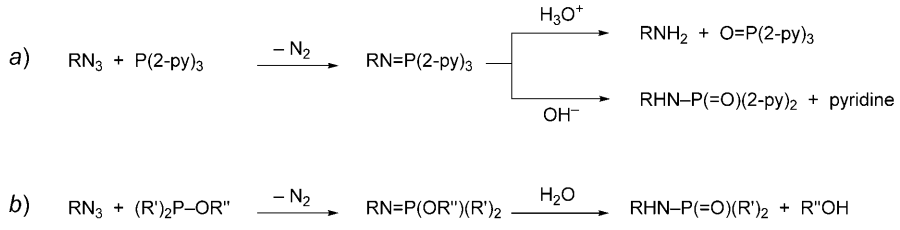
A new class of bidentate, aza-based phosphinic amide ligands of the type $RN(H)P(=O)(2\text{-py})_2$ (2-py = 2-pyridyl) was synthesized within minutes *via* a one-pot process including *Staudinger* reaction of an organic azide (RN_3) with 2-pyridylphosphines, followed by partial, unprecedented hydrolysis under loss of one aromatic substituent. The structure of the unusual-hydrolysis product $H_2C{=}CH(CH_2)_9N(H)P(=O)(2\text{-py})_2$ (**5a**) was characterized by IR, ^{1}H- and ^{31}P-NMR, as well as by X-ray crystal-structure analysis (*Figure*). The tetrahedral P-atom was found to be surrounded by a trigonal-pyramidal arrangement of the substituents. To gain insight into the formation of these novel phosphinic amides, a series of intermediate iminophosphoranes, $H_2C{=}CH(CH_2)_9N{=}P(Ar)_n(2\text{-py})_{3-n}$ ($n = 0$–3), compounds **1a**–**1f**, were synthesized, and their hydrolyses were studied. All tested compounds followed the classical hydrolysis route of P=N cleavage under *acidic* conditions. Sequential hydrolysis to **5a**–**5d** only occurred under either *basic* conditions or in wet MeCN as solvent. Notably, $H_2C{=}CH(CH_2)_9N{=}P(C_6H_5)(4\text{-MeO-2-py})_2$ (**1c**) was hydrolyzed at a much slower rate compared to its analogue **1b** lacking the MeO group. On the contrary, the halogenated compounds $H_2C{=}CH(CH_2)_9N{=}P(4\text{-X-}C_6H_4)_3$ (**1f**,**g**) (X = F, Cl) were hydrolyzed at a notably faster rate relative to the non-halogenated congener **1e** (X = H).

Introduction. – The *Staudinger* reaction, reported in 1919 and later [1], proceeds initially by the nucleophilic attack of, *e.g.*, triphenylphosphine (Ph_3P) on an azide, followed by elimination of N_2 to afford an iminophosphorane. Iminophosphoranes are valuable species since they undergo *Wittig*-type reactions with various functionalities [2]. In addition, hydrolysis of *Staudinger* products with H_2O, diluted acids, or ammonia allows for the generation of a free amine and triphenylphosphine oxide ($Ph_3P{=}O$) *via* P=N cleavage with high chemo- and stereoselectivity. Since the azido (N_3) group is fairly easy to incorporate into molecules, is relatively inert under most biological conditions, and can be selectively hydrolyzed, often without protection of distal functionalities, the *Staudinger* reaction has been frequently employed as one of the mildest and most-selective methods both in synthetic and biological chemistry to convert azides into amines (for reviews, see [3]; for recent examples, see [4]).

In continuation of our efforts to develop a new series of P- an/or N-containing ligands in coordination chemistry, we have recently reported the synthesis of a new class of aza-based bidentate ligands of the type $R(H)N{-}P(=O)(2\text{-py})_2$ by hydrolysis of *N*-substituted iminotris(2-pyridyl)phosphoranes ($(2\text{-py})_3P{=}NR$) after *Staudinger* reaction between RN_3 and $(2\text{-py})_3P$ (*Scheme 1*, *a*) [5]. We also found that the hydrolysis of $(2\text{-py})_3P{=}NR$ may proceed *via* two possible pathways to afford totally different products, depending on the reaction conditions. In acidic media, hydrolysis of the *Stau-*

dinger product generates the free amine (RNH_2) and $(2\text{-py})_3P{=}O$ *via* P=N cleavage, as expected. However, under *basic* conditions, the hydrolysis follows an unconventional pathway, producing an *N*-substituted phosphinic amide ($R(H)N{-}P(=O)(2\text{-py})_2$) plus one liberated pyridine.

Scheme 1



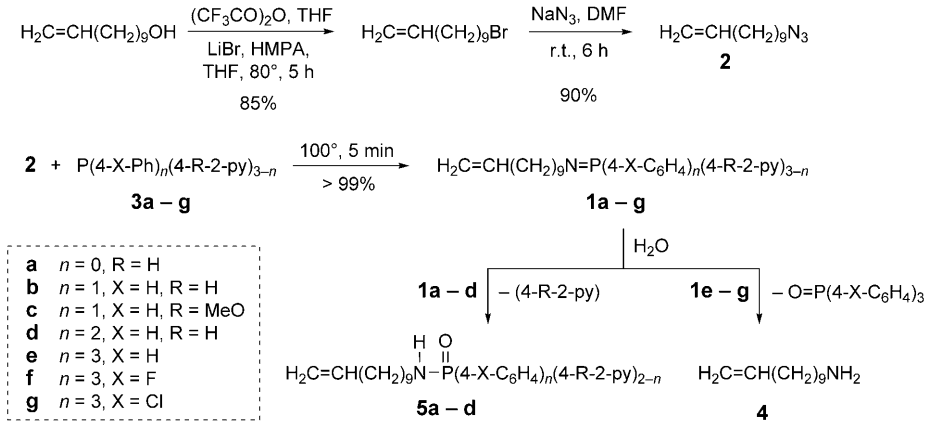
Usually, this type of *N*-substituted phosphinoyl amides are prepared by the cleavage of a chemically much more labile RO–P bond in the *Arbuzov* rearrangement (*Scheme 1*,*b*) [6], which is often used for phosphinyl protection of amino groups in peptide synthesis [7]. In contrast, the efficient formation of phosphinic amides in our study involves the cleavage of the relatively inert $P{-}C_{py}$ bond of the iminophosphoranes $P(2\text{-py})_3P{=}N{-}R$.

There are some documented examples of metal- or strong-base-catalyzed P–C cleavages [8]. For instance, treatment of R_3P with an alkali metal results in the formation of R_2P^- [8]. In addition, the alkaline hydrolysis of R_4P^+, affording $R_3P{=}O$ and RH by nucleophilic substitution (or addition–elimination) at the tetracoordinated P center has been reported [9]. The hydrolyses of $R_3P{=}O$ and $R_3P{=}S$ involving P–C cleavage are also known to proceed in the presence of strong acids or strong bases [10]. Recently, fragmentation of one of the P–C–P bonds of a novel class of phosphazenes has been demonstrated [11]. Herein, we report the first example of a *base-catalyzed* P–C cleavage of simple iminophosphoranes.

Results and Discussion. – In the current study, a new class of bidentate aza-based ligands of type $CH_2{=}CH(CH_2)_9NHP(=O)(2\text{-py})_2$ were readily synthesized within a few minutes *via* one-pot reaction of an organic azide (RN_3) with $(2\text{-py})_3P$ under alkaline hydrolytic conditions (*Scheme 2*). In contrast to the conventional P=N cleavage upon hydrolysis of *Staudinger* products, the formation of *N*-substituted phosphinoyl amides proceeds *via* cleavage of the $P{-}C_{py}$ bond of simple iminophosphoranes $(2\text{-py})_3P{=}NR$. To gain insight into this 'unconventional' hydrolysis, a series of iminophosphorane intermediates, compounds **1a**–**1g**, were prepared from the azide **2** and compounds **3a**–**3g**, and isolated for further investigations. While acidic hydrolysis generated the expected primary amine **4** and the corresponding phosphine oxides, hydrolysis under *basic* conditions afforded the corresponding phosphinoyl amides (**5a**–**5d**) under loss of pyridine (*Scheme 2*).

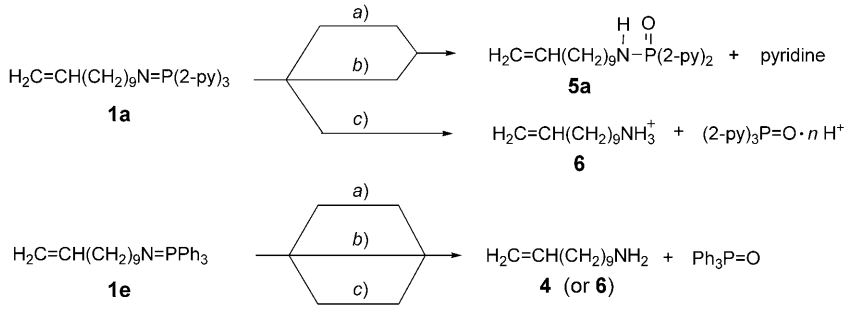
As stated earlier, acidic hydrolysis of **1a** generates $H_2C{=}CH(CH_2)_9NH_3^+$ (**6**) and $(2\text{-py})_3P{=}O\cdot(HCl)_n$ through the conventional path (*Scheme 3*). However, hydrolysis of **1a** in the presence of NaOH, or simply in wet MeCN, was found to proceed not only much

Scheme 2



faster, but also gave $H_2C{=}CH(CH_2)_9N(H)P(=O)(2\text{-py})_2$ (**5a**) and pyridine. For example, the hydrolysis of **1a** (46.3 mM) in MeCN in the presence of 20 equiv. of H_2O and 5 equiv. of HCl was complete within 5 min. However, hydrolysis under the same conditions, but in the presence of 1.2 equiv. of NaOH (instead of HCl) was finished in 30 s. Even in the absence of acid or base, hydrolysis in hydrous MeCN was also completed within 30 s.

Scheme 3

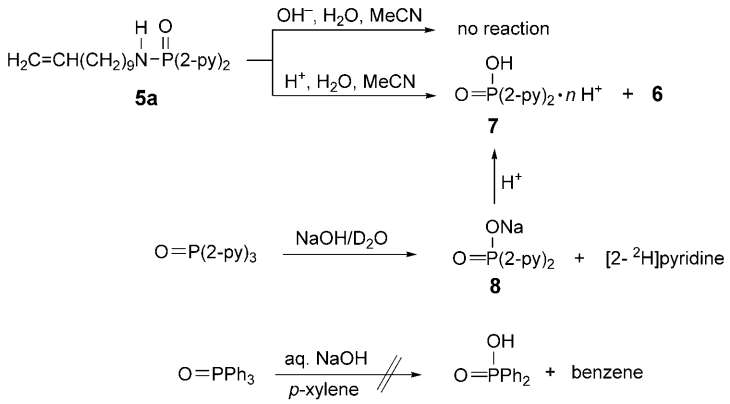


a) H_2O, MeCN. *b*) H_2O, OH^-, MeCN. *c*) H_2O, H^+, MeCN.

Interestingly, **5a** could be further hydrolyzed to **6** and $O{=}P(OH)(2\text{-py})_2{\cdot}n\ H^+$ (**7**) only in acidic media (*Scheme 4*). For comparison, $H_2C{=}CH(CH_2)_9N{=}PPh_3$ (**1e**) was also hydrolyzed. Here, 'conventional' hydrolysis under P=N cleavage occurred, affording exclusively $Ph_3P{=}O$ and **4** or **6**, depending on the reaction conditions (*Scheme 3*). This means that no hydrolytic $P{-}C_{Ph}$ cleavage occurred in **1e**. No significant rate differences were observed when the hydrolysis of **1e** was carried out in the presence of either HCl or NaOH. In a particular set of experiments, a 46.6 mM MeCN solution of **1e** was exposed to 12 equiv. of H_2O and hydrolyzed for 10 min, which gave 28% completion. The same reaction mixture, but in the presence of 1.2 equiv. of NaOH or 1.2 equiv.

of HCl, respectively, gave 26 and 25% completion after 10 min. Further, we found that, under pseudo-first-order conditions, the initial hydrolysis rate of **1e** was doubled when the amount of H_2O was doubled.

Scheme 4



The NMR and IR spectroscopic data of **5a** [$\delta(^1H)$ 4.45 (*m*, NH), $\delta(^{31}P)$ 14.5 (*s*, P=O); 3270 (N–H) and 1247 cm^{-1} (P=O)] were in agreement with the proposed structure, which was unequivocally proved by single-crystal X-ray analysis (*Figure*; see also *Table 3* in the *Exper. Part*). In the ORTEP drawing of **5a**, a tetrahedral P-atom with a trigonal-pyramidal arrangement of the substituents around the P center can be seen, with N–P and P–O bond lengths of 1.63 and 1.48 Å, respectively, two 2-pyridyl residues having a bond angle py–P–py of 106.25°.

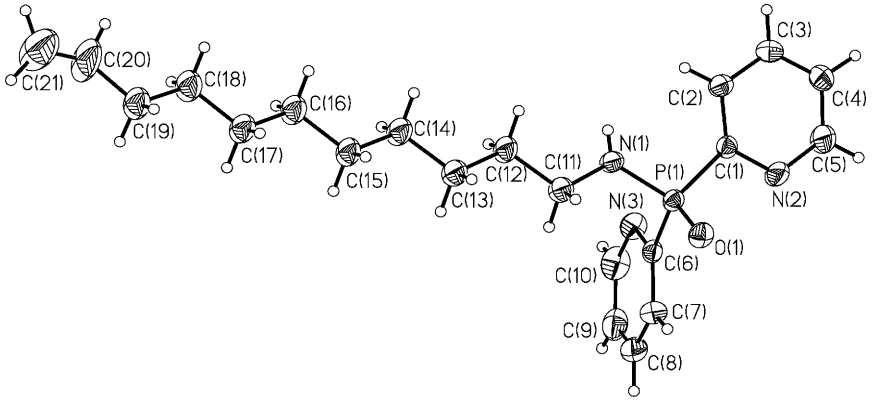


Figure. *X-Ray crystal structure of* $H_2C=CH(CH_2)_9N(H)P(=O)(2\text{-}py)_2$ (**5a**). ORTEP Representation with thermal ellipsoids at the 50%-probability level. Selected bond distances [Å] and angles [°]: P–O(1), 1.482(4); P–N(1), 1.627(3); P–C(6), 1.807(3); P–C(1), 1.811(3); O(1)–P–N(1), 115.03(15); O(1)–P–C(6), 108.54(15); O(1)–P–C(1), 113.19(14); N(1)–P–C(6), 107.74(16); N(1)–P–C(1), 105.62(15); C(1)–P–C(6), 106.25(15).

It has been reported that the conventional hydrolysis of both $(R')_3P{=}N{-}R$ and R_4P^+ proceeds under inversion of configuration at the P centers[1]). The stereochemistry involved in both cases possibly results from initial protonation of the basic phosphinimine N-atom, followed by an S_N2 type backside attack of either H_2O or OH^-, with both RNH and the nucleophile residing in the axial positions of the trigonal-bipyramidal transition state or intermediate. It is reasonable to postulate that, in basic environment, an additional pathway is open for the hydrolysis of, *e.g.*, **1a**, in which there is a 2-pyridyl (2-py) group instead of the RNH group, the OH^- being in axial positions. Most likely, the transition state or intermediate of this new pathway is stabilized by the higher electron-acceptor quality of the 2-py groups under basic conditions. Similar suggestions have been made by *Uchida* and *Kozawa* [10b] in studying the ligand coupling/exchange reactions in the hydrolysis of R_4P^+ and $R_3P{=}O$.

We reasoned that, if the hydrolysis of **1a** proceeds via $P{-}C_{py}$ cleavage in basic environment, a similar behavior might also be observed for the structurally related but much simpler phosphine oxide $(2\text{-py})_3P{=}O$, which was synthesized by oxidation of $(2\text{-py})_3P$ with 30% H_2O_2 in acetone. As can be seen from *Scheme 4*, $(2\text{-py})_3P{=}O$ did not undergo hydrolysis in H_2O or wet MeCN; and in acidic media, only protonation was observed. However, $P{-}C_{py}$ cleavage of $(2\text{-py})_3P{=}O$ was clearly noticed in $NaOH/D_2O$, which gave $(2\text{-py})_3P(=O)ONa$ (**8**) and [2-^{2}H]pyridine.

Note that $(2\text{-py})_3P{=}O$ is a weaker base in comparison to **1a**. The pH of a saturated (53 mM) aqueous solution of $(2\text{-py})_3P{=}O$ was found to be 7.7. An additional base seemed to be required for $(2\text{-py})_3P{=}O$ to undergo hydrolytic $P{-}C_{py}$ cleavage. It has been reported that, at elevated temperature and under basic conditions, ligand coupling in $(2\text{-py})_2(Ph)P$ may occur to provide bipyridine [10a]. Cleavage of $P{-}C_{py}$ bonds due to ligand exchange/coupling reactions has also been reported for $(2\text{-py})_3P{=}O$ at reflux in aqueous HCl [10b]. However, so far, no pyridyl coupling has been noticed for $(2\text{-py})_3P{=}O$ under our experimental conditions. In addition, $Ph_3P{=}O$ was found to be unreactive toward hydrolysis in the presence of either strong bases or strong acids at temperatures of 25–190°.

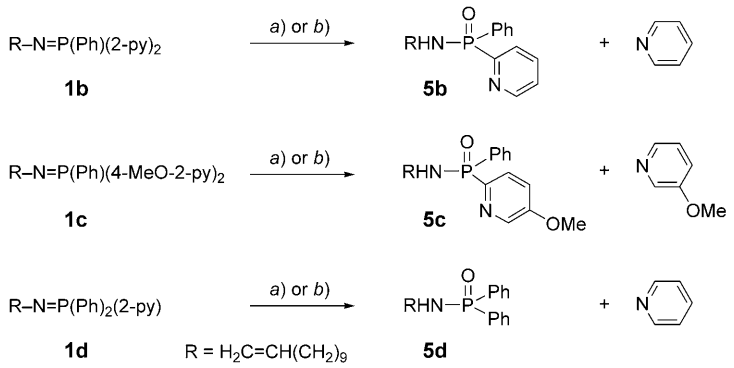
Two mixed phenyl/pyridyl phosphorane intermediates, $H_2C{=}CH(CH_2)_9N{=}P(Ph)_n(2\text{-py})_{3-n}$, compounds **1b** ($n=1$) and **1d** ($n=2$), were synthesized and studied as model compounds. Under basic conditions or in wet MeCN, the two phosphoranes were found to be hydrolyzed *via* the unconventional route, affording **5b** and **5d**, respectively (*Scheme 5*). In contrast, acidic hydrolyses of **1b**,**d** gave the conventional product **6** (not shown). These results clearly indicate that the 2-pyridyl moiety is a decisive factor in the observed unconventional P–C cleavages.

Furthermore, when compared to the non-substituted pyridyl phosphoranes **1a**,**b**,**d**, compound $H_2C{=}CH(CH_2)_9N{=}P(Ph)(4\text{-MeO-2-py})_2$ (**1c**), which carries an electron-donating MeO substituent in *para* position, was hydrolyzed at a much slower rate to afford $H_2C{=}CH(CH_2)_9N(H)P(=O)(Ph)(4\text{-MeO-2-py})$ (**5c**) and 4-methoxypyridine (see *Scheme 4* and *Table 1*). On the contrary, the *halogenated* phosphoranes $H_2C{=}CH(CH_2)_9N{=}P(4\text{-X-}C_6H_4)_3$ (X = F, Cl), *i.e.*, compounds **1f** (X = F) and **1g** (X = Cl),

---

[1]) For hydrolysis of *Staudinger* products under basic conditions, see [12a]; under acidic conditions, see [12b,c]. For alkaline hydrolysis of phosphonium salts, see [8c][12a][13].

Scheme 5



a) H_2O, MeCN. *b*) H_2O, OH^-, MeCN.

Table 1. *Hydrolysis of Compounds* **1a**–**d** *as a Function of Reaction Time.* Conditions: 0.38 mmol of substrate, hydrous MeCN (2 ml), r.t.

Time [s]	Conversion [%][a])			
	1a	**1b**	**1c**	**1d**
30	100	65	8.8	53
60	100	70	9.3	65
90	100	81	9.6	71

[a]) Determined by ^{1}H-NMR integration.

Table 2. *Hydrolysis of Compounds* **1e**–**g** *as a Function of Reaction Time.* Conditions: 0.38 mmol of substrate, (D_6)DMSO (2 ml) containing 1 equiv. of H_2O, r.t.

Time [min]	Conversion [%][a])		
	1e (X = H)	**1f** (X = F)	**1g** (X = Cl)
15	11	28	26
25	15	33	32
40	20	47	35

[a]) Determined by ^{1}H-NMR integration.

underwent hydrolysis to **4** significantly faster when compared to the parent compound **1e** (X = H) (*Table 2*).

These results demonstrate that both basicity and electronic effects are major determinants for the observed unusual $P-C_{py}$ cleavages. Similar results have been found for the alkaline hydrolysis of Ar_4P^+: aryl (Ar) groups with electron-withdrawing substituents are more easily displaced due to the preferential loss of a more stable Ar^- anion [8c]. Therefore, by carefully adjusting the electronic effects, one might be able to design

a mixed phenyl/pyridyl system with electron-withdrawing substituents on the phenyl ring and electron-donating substituents on the pyridyl ring to engage competition between both hydrolytic P=N *vs.* P–C cleavage.

Conclusions. – A new class of phosphinic-amide ligands can be readily synthesized in a one-pot process of *Staudinger* reactions of organic azides and 2-pyridylphosphines, followed by sequential hydrolysis. This novel methodology not only provides the simplest way to construct phosphinic amides, but also demonstrates a new route for base-induced P–C cleavage. Our results may also be helpful for researchers in the area of synthetic and biological chemistry dealing with amine or amide syntheses and phosphorus chemistry.

This work was supported by the *National Science Council of Taiwan* (NSC-93-2113-M-194-004). The authors thank Prof. *Wei-Ping Hu* for helpful discussions.

Experimental Part

General. 2,2′,2″-Phosphanetriyltripyridine ($(2\text{-py})_3P$; **3a**) was synthesized by modification of a reported procedure [14]. Compounds $(Ph)_2(2\text{-py})P$ (**3d**), Ph_3P (**3e**), $(4\text{-F-}C_6H_4)_3P$ (**3f**), and $(4\text{-Cl-}C_6H_4)_3P$ (**3g**) are commercially available and used without further purification. IR Spectra: in cm^{-1}. NMR Spectra: recorded at 27°; chemical shifts δ and coupling constants J in ppm and Hz, resp. Mass spectra: in m/z (rel. %).

11-Bromoundec-1-ene. To a soln. of $H_2C{=}CH(CH_2)_9OH$ (10 g, 58.8 mmol) in THF (20 ml) was added $(CF_3CO)_2O$ (14.85 g, 70.56 mmol). The mixture was stirred for 20 min at r.t., and the excess $(CF_3CO)_2O$ was removed under vacuum to give a light-yellow soln. LiBr (5.2 g, 60 mmol) in THF (40 ml) and HMPA (30 ml) were added, and the mixture was stirred for 5 h at 70°. The salt was filtered off, and the filtrate was extracted with hexane (6×30 ml). The extract was dried to afford the title compound: 11.6 g (85%). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.25–1.40 (br. *s*, 12 H); 1.34–1.44 (*m*, 2 H); 2.01–2.07 (*m*, 2 H); 3.25 (*t*, J = 3.4, 2 H); 4.92–5.02 (*m*, 2 H); 5.78–5.85 (*m*, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$, 27°): 28.2; 28.7; 28.9; 29.1; 29.4; 32.8; 33.8; 33.8; 114.1; 139.1.

11-Azidoundec-1-ene (**2**). *11-Bromoundec-1-ene* (2.0 g, 8.62 mmol) was added to a soln. of NaN_3 (0.672 g, 10.34 mmol) in DMF (20 ml). The mixture was stirred for 6 h at r.t. The NaBr was filtered off, the filtrate was extracted with hexane (6×15 ml), and the extract was dried: 1.55 g (92%). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.29–1.44 (br. *s*, 12 H); 1.56–1.61 (*m*, 2 H); 2.01–2.66 (*m*, 2 H); 3.40 (*t*, J = 3.5, 2 H); 4.91–5.01 (*m*, 2 H); 5.77–5.84 (*m*, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.7; 28.8; 28.9; 29.0; 29.3, 29.4; 33.7; 51.4; 114.1; 139.1. Anal. calc. for $C_{11}H_{21}N_3$ (195.31): C 67.65, H 10.84, N 26.51; found: C 67.54, H 10.67, N 26.60.

*2-(*P,P-*Dipyridin-2-yl*-N-*undec-10-en-1-ylphosphorimidoyl)pyridine* (**1a**). Compound **2** (0.2 g, 1.02 mmol) and $(2\text{-py})_3P$ (**3a**; 0.27 g, 1.02 mmol) were placed in a 20-ml reaction vial, and the mixture was stirred for 5 min at 100° (immediate gas evolution). Yield: 0.43 g (99%). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.17–1.35 (br. *s*, 12 H); 1.48–1.54 (*m*, 2 H); 1.94–2.00 (*m*, 2 H); 3.22–3.30 (*m*, 2 H); 4.84–4.94 (*m*, 2 H); 5.70–5.77 (*m*, 1 H); 7.23–7.26 (*m*, py); 7.68–7.44 (*m*, py); 8.01–8.67 (*m*, py); 8.65 (*d*, J = 2.3, py). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.8; 28.4; 28.5; 28.6; 28.9; 29.1; 29.1; 33.3; 113.6; 124.2 (^3J(P,C) = 3); 128.4 (^2J(P,C) = 19); 135.2 (^3J(P,C) = 9); 138.6; 149.5 (^2J(P,C) = 18); 155.0 (^1J(P,C) = 122). ^{31}P-NMR (160 MHz, $CDCl_3$): –1.0. EI-MS: 432 (25, ($[M+H]^+$, $C_{26}H_{34}N_4P^+$).

2,2′-(Phenylphosphanediyl)dipyridine (**3b**). To a soln. of BuLi (45 ml of a 1.6M soln. in hexane; 63 mmol) in Et_2O (70 ml) was added 2-bromopyridine (10 g, 63 mmol) in Et_2O (25 ml) at –90°, and the dark-red soln. was stirred at this temp. for 4 h. Then, a soln. of Cl_2PPh (4.3 ml, 32 mmol) in Et_2O (40 ml) was added dropwise, and the mixture was stirred at –90° for another 2 h. The mixture was finally extracted with 2M aq. H_2SO_4 (80 ml), and then neutralized with sat. aq. NaOH soln. The precipitate was collected and washed first with H_2O (3×30 ml) and then with petroleum ether (3×15 ml). Recrys-

tallization of the crude from acetone gave the product: 4.6 g (56%). ^{1}H-NMR (400 MHz, $CHCl_3$): 7.09–7.17 (*m*, py); 7.30–7.31 (*m*, py); 7.43–7.45 (*m*, Ph); 7.48–7.49 (*m*, Ph); 8.62 (*d*, py). ^{13}C-NMR (100 MHz, $CHCl_3$): 122.0; 127.9 (^1J(P,C) = 18); 128.3 (^2J(P,C) = 8); 129.1; 134.5 (^1J(P,C) = 20); 134.73 (^2J(P,C) = 10); 135.3; 149.8 (^2J(P,C) = 12); 162.5. ^{31}P-NMR (160 MHz, $CHCl_3$): −2.4.

*2-(*P-*Phenyl*-P-*pyridin-2-yl*-N-*undec-10-en-1-ylphosphorimidoyl)pyridine* (**1b**). Compounds **2** (75 mg, 0.38 mmol) and **3b** (0.1 g, 0.38 mmol) were placed in a 20-ml reaction vial, and the mixture was stirred at 100° (immediate gas evolution). Yield: 0.13 g (99%). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.12–1.25 (br. *s*, 12 H); 1.44–1.49 (*m*, 2 H); 1.88–1.92 (*m*, 2 H); 3.10–3.18 (*m*, 2 H); 4.79–4.89 (*m*, 2 H); 5.63–5.72 (*m*, 1 H); 7.17–7.26 (*m*, py); 7.31–7.35 (*m*, Ph); 7.61–7.62 (*m*, py); 7.82–7.90 (*m*, Ph, py); 8.59 (*d*, *J* = 2.1, py). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.5; 27.1; 28.6; 28.7; 28.6; 28.9; 29.2; 29.4; 33.6; 113.9; 124.4 (^3J(P,C) = 3); 127.9 (^1J(P,C) = 11); 128.3 (^2J(P,C) = 20); 131.1; 132.9 (^2J(P,C) = 7); 135.2 (^3J(P,C) = 9); 138.9; 149.8 (^2J(P,C) = 18); 156.0 (^1J(P,C) = 122). ^{31}P-NMR (160 MHz, $CDCl_3$): 3.1. FAB-MS: 432 (25, $[M+H]^+$, $C_{27}H_{35}N_3P^+$).

2,2′-(Phenylphosphanediyl)bis(4-methoxypyridine) (**3c**). To a soln. of BuLi (29 mmol; 1.6M soln. in hexane) in Et_2O (50 ml) was added a soln. of 2-bromo-4-methoxypyridine (5 g, 29 mmol) in Et_2O (25 ml). The resulting dark-red soln. was stirred at −90° for 4 h. A soln. of Cl_2PPh (2.59 g, 15 mmol) in Et_2O (30 ml) was added dropwise, and the mixture was stirred at −90° for another 2 h. The mixture was finally extracted with 2M aq. H_2SO_4 (50 ml), neutralized with sat. aq. NaOH soln., and re-extracted with $CHCl_3$ (4 × 50 ml). The $CHCl_3$ extract was dried to give the product. Yield: 4.35 g (65%). ^{1}H-NMR (400 MHz, $CHCl_3$): 3.9 (*s*, 3 H); 6.71 (*d*, *J* = 4.18); 7.26–7.34 (*m*, Ph); 7.48–7.49 (*m*, py); 8.05 (*d*, *J* = 3.22). ^{13}C-NMR (100 MHz, $CHCl_3$): 3.5; 123.8 (^2J(P,C) = 12); 128.6 (^2J(P,C) = 6); 128.8; 132.8 (^2J(P,C) = 19); 143.4 (^2J(P,C) = 17); 151.2 (^1J(P,C) = 29); 164.7. ^{31}P-NMR (160 MHz, $CHCl_3$): −21.4. EI-MS: 324 (100, $[M+H]^+$, $C_{18}H_{18}N_2O_2P^+$).

*4-Methoxy-2-[*P-*(4-methoxypyridin-2-yl)*-P-*phenyl*-N-*undec-10-en-1-ylphosphorimidoyl]pyridine* (**1c**). A mixture of **2** (75 mg, 0.38 mmol) and **3c** (0.12 g, 0.38 mmol) in a 20-ml reaction vial was stirred for 5 min at 100° (immediate gas evolution). Yield: 0.14 g (99%). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.12–1.26 (br. *s*, 12 H); 1.46–1.48 (*m*, 2 H); 1.88–1.94 (*m*, 2 H); 2.94–3.02 (*m*, 2 H); 3.84 (*s*, 2 MeO); 4.78–4.89 (*m*, 2 H); 5.58–5.71 (*m*, 1 H); 6.70 (*d*, py); 7.34–7.36 (*m*, Ph); 7.51–7.54 (*m*, Ph); 7.71–7.37 (*m*, py); 8.22 (*d*, *J* = 2, py). ^{13}C-NMR (100 MHz, $CDCl_3$): 27.1; 28.7; 28.9; 29.2; 29.3; 29.4; 33.6; 35.5; 45.2; 53.5; 110.9 (^2J(P,C) = 10); 113.9; 128.3 (^1J(P,C) = 12); 132.0 (^2J(P,C) = 9); 139.0; 141.8; 151.6 (^1J(P,C) = 15); 165.8. ^{31}P-NMR (160 MHz, $CDCl_3$): 4.9. EI-MS: 492 (51, $[M+H]^+$, $C_{29}H_{39}N_3O_2P^+$).

*2-(*P,P-*Diphenyl*-N-*undec-10-en-1-ylphosphorimidoyl)pyridine* (**1d**). A mixture of **2** (75 mg, 0.38 mmol) and $(Ph)_2$(2-py)P (**3d**; 0.1 g, 0.38 mmol) in a 20-ml reaction vial was stirred at 100° for 5 min (immediate gas evolution). Yield: 0.13 g (99%). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.20–1.33 (br. *s*, 12 H); 1.53–1.60 (*m*, 2 H); 1.97–2.03 (*m*, 2 H); 3.08–3.17 (*m*, 2 H); 4.88–4.98 (*m*, 2 H); 5.74–5.81 (*m*, 1 H); 7.25–7.26 (*m*, py); 7.35–7.45 (*m*, Ph); 7.70–7.75 (*m*, Ph); 8.18 (*t*, *J* = 3.0, py); 8.67 (*d*, *J* = 2.1, py). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.6; 28.8; 28.9; 29.0; 29.1; 33.7; 114.0; 124.5 (^3J(P,C) = 3); 128.0 (^1J(P,C) = 11); 128.2 (^2J(P,C) = 12); 131.0; 131.5; 132.6; 135.7 (^3J(P,C) = 9); 139.1; 149.8 (^2J(P,C) = 18); 156.6 (^1J(P,C) = 127). ^{31}P-NMR (160 MHz, $CDCl_3$): 6.9. FAB-MS: 431 (34, $[M+H]^+$, $C_{28}H_{37}N_2P^+$).

Triphenyl(undec-10-en-1-ylimino)-λ^5-phosphane (**1e**). A mixture of **2** (0.2 g, 1.02 mmol) and Ph_3P (**3e**; 0.27 g, 1.03 mmol) in a 20-ml reaction vial was stirred for 5 min at 100° (immediate gas evolution). Yield: 0.43 g (99%). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.22–1.36 (br. *s*, 12 H); 1.55–1.59 (*m*, 2 H); 2.01–2.06 (*m*, 2 H); 3.04–3.13 (*m*, 2 H); 4.92–4.97 (*m*, 2 H); 5.78–5.82 (*m*, 1 H); 7.27–7.52 (br. *s*, Ph); 7.63–7.69 (*m*, Ph). ^{13}C-NMR (100 MHz, $CDCl_3$): 28.9; 29.1; 29.4; 29.5; 29.5; 33.7; 114.0; 128.2 (^1J(P,C) = 11); 131.9 (^2J(P,C) = 10); 132.5 (^2J(P,C) = 9); 139.2. ^{31}P-NMR (160 MHz, $CDCl_3$): 10.9. FAB-MS: 430 (100, $[M+H]^+$, $C_{29}H_{37}NP^+$).

Tris(4-fluorophenyl)(undec-10-en-1-ylimino)-λ^5-phosphane (**1f**). A mixture of **2** (75 mg, 0.38 mmol) and (4-F-C_6H_4)$_3$P (**3f**; 0.12 g, 0.38 mmol) in a 20-ml reaction vial was stirred at 100° for 5 min (immediate gas evolution). Yield: 0.14 g (99%). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.18–1.32 (br. *s*, 12 H); 1.49–1.52 (*m*, 2 H); 1.97–1.99 (*m*, 2 H); 2.96–3.04 (*m*, 2 H); 4.85–4.95 (*m*, 2 H); 5.75–5.76 (*m*, 1 H); 7.07–7.12 (*m*, C_6H_4); 7.55–7.61 (*m*, C_6H_4). ^{13}C-NMR (100 MHz, $CDCl_3$): 27.3; 28.8; 29.0; 29.35; 29.43; 29.5; 33.7; 35.5; 45.3; 114.0; 115.5; 115.7; 115.8; 115.9; 127.0 (^3J(P,C) = 3); 127.5 (^1J(F,C) = 99); 128.0 (^3J(P,C) = 3); 134.5; 134.6 (^2J(P,C) = 9); 134.7 (^2J(P,C) = 9); 139.1; 164.7 (^1J(P,C) = 253). ^{31}P-NMR (160 MHz, $CDCl_3$): 7.3. EI-MS: 484 (53, $[M+H]^+$, $C_{26}H_{34}F_3NP^+$).

Tris(4-chlorophenyl)(undec-10-en-1-ylimino)-λ⁵-phosphane (**1g**). A mixture of **2** (75 mg, 0.38 mmol) and (4-Cl-C_6H_4)$_3$P (**3g**; 0.14 g, 0.38 mmol) in a 20-ml reaction vial was stirred for 5 min at 100° (immediate gas evolution). Yield: 0.20 g (99%). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.18–1.33 (br. *s*, 12 H); 1.48–1.52 (*m*, 2 H); 1.96–2.02 (*m*, 2 H); 2.95–3.04 (*m*, 2 H); 4.87–4.97 (*m*, 2 H); 5.76–5.77 (*m*, 1 H); 7.38–7.44 (*m*, C_6H_4); 7.50–7.57 (*m*, C_6H_4). ^{13}C-NMR (100 MHz, $CDCl_3$): 27.2; 28.8; 29.0; 29.4; 29.4; 29.5; 33.7; 35.4; 45.2; 114.0; 128.8 (^1J(P,C) = 12); 133.2 (^1J(Cl,C) = 11); 133.6; 138.0; 138.6 (^3J(P,C) = 3). ^{31}P-NMR (160 MHz, $CDCl_3$): 7.5. EI-MS: 532 (47, $[M+H]^+$, $C_{26}H_{34}Cl_3NP$).

P,P-*Dipyridin-2-yl*-N-*undec-10-en-1-ylphosphinic Amide* (**5a**). *Method A*. To a soln. of **1a** (0.4 g, 0.93 mmol) in MeCN (8 ml) was added H_2O (2 ml), the mixture was stirred for 30 min at r.t., and then concentrated and dried under vacuum. Yield: 0.33 g (95%).

Method B. To a soln. of **1a** (0.4 g, 0.93 mmol) in MeCN (8 ml) was added 0.6M aq. NaOH soln. (2 ml), and the mixture was stirred for 30 min at r.t. All volatiles were removed, and the residue was extracted with $CHCl_3$ (3×15 ml). The org. layer was separated and dried. Yield: 0.30 g (87%).

Data of **5a**. Light-yellow solid. IR (nujol): 3270 (NH), 1247 (P=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.20–1.35 (br. *s*, 12 H); 1.48–1.54 (*m*, 2 H); 1.97–2.02 (*m*, 2 H); 2.94–3.01 (*m*, 2 H); 4.44–4.47 (*m*, 1 H); 4.88–4.98 (*m*, 2 H); 5.74–5.81 (*m*, 1 H); 7.31–7.34 (*m*, py); 7.74–7.77 (*m*, py); 8.05–8.07 (*m*, py); 8.72 (*d*, *J* = 2.22, py). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.6; 28.8; 29.0; 29.1; 29.30; 29.33; 32.0; 32.1; 33.7; 39.8; 114.0; 125.3 (^3J(P,C) = 3); 128.2 (^2J(P,C) = 22); 136.03 (^3J(P,C) = 10); 139.1; 150.1 (^2J(P,C) = 19.2); 155.3 (^1J(P,C) = 154). ^{31}P-NMR (160 MHz, $CDCl_3$): 14.5. Anal. calc. for $C_{21}H_{30}N_3OP$ (371.21): C 67.90, H 8.14, N 11.31; found: C 67.95, H 8.16, N 11.34. X-Ray crystal structure: see below.

P-*Phenyl*-P-*pyridin-2-yl*-N-*undec-10-en-1-ylphosphinic Amide* (**5b**). To a soln. of **1b** (0.13 g, 0.38 mmol) in MeCN (4 ml) was added H_2O (1 ml), the mixture was stirred for 30 min at r.t., and then concentrated and dried under vacuum. Yield: 0.12 g (87%). Light-yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.21–1.33 (br. *s*, 12 H); 1.50–1.55 (*m*, 2 H); 1.98–2.03 (*m*, 2 H); 2.90–2.98 (*m*, 2 H); 3.83–3.85 (*m*, 1 H); 4.89–4.98 (*m*, 2 H); 5.75–5.82 (*m*, 1 H); 7.33–7.42 (*m*, py); 7.43–7.35 (*m*, Ph); 7.72–7.73 (*m*, py); 7.92–7.97 (*m*, Ph, py); 8.71 (*d*, *J* = 2.2, py). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.7; 28.9; 29.0; 29.1; 29.3; 29.7; 32.0; 32.1; 33.7; 40.1; 114.0; 125.1 (^3J(P,C) = 3); 127.9 (^1J(P,C) = 22); 128.3 (^2J(P,C) = 13); 131.3; 131.8 (^2J(P,C) = 3); 132.6 (^2J(P,C) = 20); 136.1 (^3J(P,C) = 10); 139.1; 149.7 (^2J(P,C) = 19); 156.3 (^1J(P,C) = 153). ^{31}P-NMR (160 MHz, $CDCl_3$): 18.2. Anal. calc. for $C_{22}H_{31}N_2OP$: C 71.35, H 8.37, N 7.56; found: C 71.12, H 8.40, N 7.48.

P-*(4-Methoxypyridin-2-yl)*-P-*phenyl*-N-*undec-10-en-1-ylphosphinic Amide* (**5c**). To a soln. of **1c** (0.18 g, 0.38 mmol) in MeCN (4 ml) was added H_2O (1 ml), the mixture was stirred at r.t. for 30 min, and then concentrated and dried under vacuum. The resulting light-yellow solid was washed with hexane (3×30 ml) and hot H_2O (5×20 ml), and finally dried. Yield: 0.028 g (20%). Light-yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.25–1.32 (br. *s*, 12 H); 1.67–1.71 (*m*, 2 H); 2.04–2.08 (*m*, 2 H); 7.94–7.96 (*m*, 2 H); 3.97 (*s*, MeO); 4.03–4.04 (*m*, 1 H); 5.75–5.90 (*m*, 1 H); 6.80 (*d*, *J* = 3.4, 2 H); 7.45–7.52 (*m*, arom. H); 7.84–7.89 (*m*, arom. H); 8.04–8.06 (*m*, 1 H); 8.64 (*d*, *J* = 4.0, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.7; 28.9; 29.0; 29.2; 29.4; 29.5; 32.1; 33.8; 40.9; 54.1; 114.1; 128.7 (^1J(P,C) = 12); 131.9 (^2J(P,C) = 10); 132.1; 139.2; 142.6; 166.1. ^{31}P-NMR (160 MHz, $CDCl_3$): 22.2.

P,P-*Diphenyl*-N-*undec-10-en-1-ylphosphinic Amide* (**5d**). To a soln. of **1d** (0.13 g, 0.38 mmol) in MeCN (4 ml) was added H_2O (1 ml), the mixture was stirred for 30 min at r.t., and then concentrated and dried under vacuum. Yield: 0.13 g (95%). Light-yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.22–1.35 (br. *s*, 12 H); 1.51–1.56 (*m*, 2 H); 1.98–2.03 (*m*, 2 H); 2.86–2.94 (*m*, 2 H); 4.89–4.99 (*m*, 2 H); 5.75–5.82 (*m*, 1 H); 7.39–7.48 (*m*, Ph); 7.86–7.90 (*m*, Ph). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.6; 28.8; 29.0; 29.1; 29.27; 29.33; 32.0; 32.1; 33.7; 40.7; 114.0; 128.4 (^1J(P,C) = 13); 131.7 (^2J(P,C) = 3); 131.9; 132.1; 133.2; 139.1. ^{31}P-NMR (160 MHz, $CDCl_3$): 23.8. Anal. calc. for $C_{23}H_{32}NOP$: C 74.79, H 8.67, N 3.79; found: C 74.51, H 8.64, N 3.80).

Undec-10-en-1-amine (**4**). *Method A*. To a soln. of **1a** (0.4 g, 0.93 mmol) in MeCN (8 ml) was added 1.8M aq. HCl (2 ml), and the mixture was stirred for 30 min at r.t. All volatiles were removed, the residue was extracted with $CHCl_3$ (4×5 ml), and the org. layer was separated, concentrated, and dried. Yield: 0.147 g (78%).

Method B. To a soln. of **1e** (0.4 g, 0.93 mmol) in MeCN (8 ml) was added 1.8M aq. HCl (2 ml), and the mixture was stirred for 30 min at r.t. All volatiles were removed, the residue was extracted with $CHCl_3$ (4×15 ml), and the org. layer was separated, concentrated, and dried. Yield: 0.147 g (82%).

Method C. To a soln. of **5a** (0.2 g, 0.54 mmol) in MeCN (8 ml) was added aq. 1.8M HCl (2 ml). The mixture was stirred for 1 h at r.t. All volatiles were removed, and the residue was extracted with $CHCl_3$ (4×15 ml), concentrated, and dried. Yield: 0.083 g (76%).

Data of **5a**. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.29–1.44 (br. *s*, 12 H); 1.83–1.99 (*m*, 2 H); 2.04–2.06 (*m*, 2 H); 4.91–5.01 (*m*, 2 H); 5.75–5.86 (*m*, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.8; 28.7; 29.2; 29.3; 29.7; 33.3; 33.4; 42.5; 113.8; 138.8.

Undec-10-en-1-aminium (**6**). *Method A*. To a soln. of **1e** (0.4 g, 0.93 mmol) in MeCN (8 ml) was added H_2O (2 ml). The soln. was stirred for 30 min at r.t. All volatiles were removed. The residue was extracted with hexane (4×15 ml), and the org. extract was dried. Yield: 0.13 g (83%).

Method B. To a soln. of **1e** (0.4 g, 0.93 mmol) in MeCN (8 ml) was added 0.6M aq. NaOH soln. (2 ml). The mixture was stirred for 30 min at r.t. All volatiles were removed, and the residue was extracted with hexane (4×15 ml). The org. extract was concentrated and dried. Yield: 0.122 g (78%).

Data of **6**. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.29–1.38 (br. *s*, 16 H); 1.75–1.77 (*m*, 2 H); 2.00–2.05 (*m*, 2 H); 2.68 (*t*, J=3.5, 2 H); 4.91–5.00 (*m*, 2 H); 5.76–5.83 (*m*, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.8; 28.9; 29.1; 29.4; 29.5; 33.4; 33.7; 42.0; 114.0; 139.2.

Sodium Dipyridin-2-ylphosphinate (**8**). To a soln. of $(2\text{-py})_3P{=}O$ (0.2 g, 0.73 mmol) in D_2O (1 ml) and (D_6)DMSO (2 ml) was added NaOH (59 mg, 1.47 mmol). The soln. was stirred for 6 h at r.t. All volatiles were removed, and the residue was extracted with MeOH (3×15 ml), concentrated, and dried. Yield: 0.15 g (95%). Colorless solid. ^{1}H-NMR (400 MHz, D_2O): 7.38–7.41 (*m*, py); 7.85–7.88 (*m*, py); 7.93–7.95 (*m*, py); 8.44–8.45 (*m*, py). ^{13}C-NMR (100 MHz, D_2O): 125.9; 127.5 (^2J(P,C)=16); 137.5 (^3J(P,C)=8); 149.9 (^2J(P,C)=15); 158.63 (^1J(P,C)=128). ^{31}P-NMR (160 MHz, D_2O): 16.8. FAB-MS: 221 (82, $C_{10}H_8DN_2O_2P^+$).

Dipyridin-2-ylphosphinic Acid (**7**). Compound **8** (0.1 g, 4.16 mmol) was added to a 1.8M aq. HCl soln. (2 ml). The mixture was stirred for 30 min at r.t., and concentrated under vacuum. Colorless solid. IR (nujol): 2725, 2663 (P–OH), 1302 (P=O). ^{1}H-NMR (400 MHz, D_2O): 8.19–8.22 (*m*, py); 8.43–8.47 (*m*, py); 8.67–8.71 (*m*, py); 8.91–8.92 (*m*, py). ^{13}C-NMR (100 MHz, D_2O): 130.5; 132.15 (^2J(P,C)=9); 144.0 (^3J(P,C)=5); 148.2 (^2J(P,C)=6); 149.1 (^1J(P,C)=111). ^{31}P-NMR (160 MHz, D_2O): −2.7.

Table 3. *X-Ray Crystal Data and Details of Structure Refinement for* **5a**

Formula		$C_{21}H_{30}N_3OP$
M_r [g/mol]		371.45
Temperature [K]		298(2)
Radiation (λ [nm])		MoK_α (0.7107)
Crystal system		monoclinic
Space group		$P\,2_1/c$
Lattice parameters:	a [Å]	23.423(4)
	b [Å]	8.421(2)
	c [Å]	10.943(2)
	α [°]	90.0
	β [°]	101.99(1)
	γ [°]	90.0
Z		4
V [Å^3]		2111.4(7)
ρ_{calc} [Mg/m^3]		1.169
θ Range [°]		3.56–50.04
Reflections collected		4948
Independent reflections		3709 (R(int)=0.0307)
Final R indices ($I>2\sigma(I)$)		$R1$=0.0606, $wR2$=0.1193
Largest difference peak and hole		0.544, −0.911 e/Å^3

X-Ray Crystal Structure of P,P-*Dipyridin-2-yl*-N-*undec-10-en-1-ylphosphinic Amide* (**5a**). General X-ray-operation procedures (SHELXS97 and SHELXL97) used are described in [15]. Selected crystallographic data and data-collection parameters are summarized in *Table 3*. A suitable, colorless crystal (*ca.* $0.32 \times 0.22 \times 0.16$ mm) was grown at r.t. from a MeCN soln. Diffraction data were recorded at ambient temperature on a *Bruker-P4* diffractometer using graphite-monochromated MoK_α radiation. Unit-cell dimensions were determined from 25 well-centered reflections, with 2θ values near 25°.

REFERENCES

[1] H. Staudinger, J. Meyer, *Helv. Chim. Acta* **1919**, *2*, 635; H. Staudinger, E. Hauser, *Helv. Chim. Acta* **1921**, *4*, 861.

[2] H. Schmidbaur, G. Jonas, *Chem. Ber.* **1967**, *100*, 1120; N. Wiberg, G. Schwenk, K. H. Schmid, *Chem. Ber.* **1972**, *105*, 1209; R. A. Shaw, B. W. Fitzsimmons, B. C. Smith, *Chem. Rev.* **1962**, *62*, 247; E. W. Abel, S. A. Mucklejohn, *Phosphorus Sulfur* **1981**, *9*, 235.

[3] E. F. V. Scriven, K. Turnbull, *Chem. Rev.* **1988**, *88*, 297; Y. G. Gololobov, L. F. Kasukhin, *Tetrahedron* **1992**, *48*, 1353; S. Gilbertson, *Chemtracts* **2001**, *14*, 524.

[4] E. Saxon, C. R. Bertozzi, *Science* **2000**, *287*, 2007; K. L. Kiick, E. Saxon, D. A. Tirrell, C. R. Bertozzi, *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 19; E. Saxon, S. J. Luchansky, H. C. Hang, C. Yu, S. C. Lee, C. R. Bertozzi, *J. Am. Chem. Soc.* **2002**, *124*, 14893; C. C. Wang, T. S. Seo, Z. Li, H. Ruparel, J. Ju, *Bioconjugate Chem.* **2003**, *14*, 697.

[5] Y.-S. Fu, S. J. Yu, *Angew. Chem., Int. Ed.* **2001**, *40*, 437.

[6] V. A. Gilyarov, E. I. Matrosov, F. I. Bel'skii, M. I. Kabachnik, *Zh. Obshch. Khim.* **1980**, *50*, 44; M. N. Dimukhametov, I. A. Nuretdinov, *Zh. Obshch. Khim.* **1985**, *55*, 2483; T. A. Mastryukova, N. V. Mashchenko, I. L. Odinets, P. V. Petrovskii, M. I. Kabachnik, *Zh. Obshch. Khim.* **1988**, *58*, 1967; B. A. Arbuzov, E. N. Dianova, *Izv. Akad. Nauk. SSSR. Ser. Khim.* **1983**, 418.

[7] C. Shin, Y. Yonezawa, K. Watanabe, J. Yoshimura, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3811.

[8] a) R. F. Hudson, in 'Structure and Mechanism in Organophosphorus Chemistry', Academic Press, New York, 1965, pp. 233–245; b) B. J. Walker, in 'Organophosphorus Chemistry', Penguin, Harmondsworth, 1972, Vol. 5, pp. 83–111; c) D. J. H. Smith, in 'Comprehensive Organic Chemistry', Eds. D. H. R. Barton, W. D. Ollis, Pergamon Press, Oxford, 1979, Vol. 2, pp. 1127–1187.

[9] H. J. Cristau, F. Plenat, in 'The Chemistry of Organophosphorus Compounds', Eds. R. F. Hartley, S. Patai, John Wiley & Sons, New York, 1994, Vol. 3. pp. 111–137.

[10] a) G. R. Newkome, D. C. Hager, *J. Am. Chem. Soc.* **1978**, *100*, 5567; b) Y. Uchida, H. Kozawa, *Tetrahedron Lett.* **1989**, *30*, 6365; c) R. S. Edmundson, in 'The Chemistry of Organophosphorus Compounds', Eds. R. F. Hartley, S. Patai, John Wiley & Sons, New York, 1992, Vol. 2, pp. 380–381.

[11] M. Alajarín, C. López-Leonardo, P. Llamas-Lorente, *Tetrahedron Lett.* **2001**, *42*, 1041.

[12] a) L. Horner, H. Winkler, *Tetrahedron Lett.* **1964**, 175; b) N. G. Andersen, P. D. Ramsden, D. Che, M. Parvez, B. Keay, *Org. Lett.* **1999**, *1*, 2009; c) N. G. Andersen, P. D. Ramsden, D. Che, M. Parvez, B. Keay, *J. Org. Chem.* **2001**, *66*, 7478.

[13] K. F. Kumli, W. E. McEwen, C. A. Vander Werf, *J. Am. Chem. Soc.* **1959**, *81*, 3805; M. Zanger, C. A. Vander Werf, W. E. McEwen, *J. Am. Chem. Soc.* **1959**, *81*, 3807; W. E. McEwen, *Top. Phosphourus Chem.* **1965**, *2*, 1.

[14] W. C. Davies, F. G. Mann, *J. Chem. Soc.* **1944**, 276; F. G. Mann, J. Watson, *J. Org. Chem.* **1948**, *13*, 502; K. Kurtev, D. Ribola, R. A. Jones, D. J. Cole-Hamilton, G. Wilkinson, *J. Chem. Soc., Dalton. Trans.* **1980**, 55.

[15] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467; G. M. Sheldrick, 'SHELXS97 and SHELXL97: Program for the Refinement of Crystal Structures', University of Göttingen, Germany, 1997.

Received August 23, 2006