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# Heterocycles from Phosphonium-Iodonium Ylides. Photochemical Synthesis of $\lambda^5$ -Phosphinolines

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A photochemical reaction of mixed phosphonium-iodonium vlides with acetvlenes vielding  $\lambda^5$ phosphinolines, a rare class of phosphorus heterocycles hardly accessible by other methods, was found. The yields of  $\lambda^5$ -phosphinolines vary from 35% to 80%. The structures of two phosphinolines were established by single-crystal X-ray diffraction. The X-ray diffraction and NMR spectra data indicate the superposition of vlidic and aromatic structures for phosphinolines.

### Introduction

The unusual and diverse reactivity of hypervalent iodine compounds<sup>1</sup> and, in particular, iodonium ylides<sup>2,3</sup> was extensively investigated. These compounds became syntheti-

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cally useful reagents in organic synthesis. Moreover, their synthetic applications have been widely reviewed.<sup>4</sup>

Special interest requires the mixed phosphoniumiodonium ylides of type 1. They can easily be prepared by the reaction of carbonyl-stabilized phosphonium ylides  $Ph_3P=CHR$  (R = COOC<sub>2</sub>H<sub>5</sub>, COAr) with derivatives of iodine(III) as ArIHal<sub>2</sub>, ArIO, and ArI(OAc)<sub>2</sub>.<sup>5</sup> Mixed ylides are well described by resonance structures (1a-d) (Scheme 1). In the case of ylide 1 we have shown that it prevails in the Z-configuration (1d) in the solid state<sup>5a,6</sup> and undergoes Z/E isomerization in solution<sup>6</sup>

The significant contribution of the resonance structure 1d with separated charges on the P, I, and O atoms rationalizes

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SCHEME 2. Interaction between Ylides 1, 2, and Triple Bond Compounds



the reactivity of the ylide. Indeed, we have shown that ylide **1** can be used as the O-nucleophile in alkylation, acylation, and silylation due to a negative charge on the O-carbonyl atom.<sup>6</sup> Mixed ylides such as **1** contain the excellent leaving phenyliodonium group and thus a nucleophilic substitution reaction with halogen anions and S-nucleophiles occurs.<sup>5b,7</sup> The presence of the phosphonium group in ylidic molecules has allowed us to perform one-pot reactions of the nucleophilic substitution and the Wittig reaction.<sup>5b,7</sup>

Recently we have suggested that mixed ylides of type (1) have the possibility to react as 1,3 dipoles and, hence, undergo [3+2]-cycloaddition reactions<sup>8</sup> (Scheme 2).

The experimental verification of this hypothesis has led us to a series of interesting results. The reaction of mixed ylide 1 with dimethyl acetylenedicarboxylate (DMAD) in acetonitrile resulted to our surprise not in the furan 3a (X = Y =C), but led to oxazole **3b** (X- $R^2 = N$ ; Y = C); in other words, the solvent acetonitrile acts as a reagent in this process. It should be noted that no reaction was observed in the absence of DMAD. Thus, the interesting catalysis of one dipolarophilic reaction by another dipolarophile has been observed.<sup>8</sup> We have shown that the process of the thermal pseudocycloaddition of the ylides 1 and 2 in the presence of DMAD can be applied to some other aliphatic nitriles to yield a rare class of phosphonium-substituted oxazoles.<sup>9</sup> Moreover, we have serendipitously discovered that under UV irradiation conditions (Hg lamp) this cycloaddition leads to oxazoles with good yields in the absence of DMAD and may be considered as a general process for mixed ylides such as 1 and 2 and various nitriles.<sup>10</sup> These results encouraged us to investigate the reaction of mixed ylides 1 and 2 with alkynes under UV irradiation.

### **Results and Discussion**

Attempts to perform the photochemical reactions of different ylides with arylalkynes containing electronwithdrawing groups in the phenyl ring afforded complex mixtures (in the <sup>31</sup>P NMR spectrum at least eight signals were found) whereas the desired furans of type **3** were not isolated. However, the reaction of the ylide **2** with 4-methoxyphenylacetylene (**4a**) under UV irradiation afforded the mixture of two isolated compounds (see Scheme 3). One of them is the furan **5** in 30% yield. Spectroscopic evidence showed that the second product was [4-(4-methoxyphenyl)-1,1-diphenyl-1 $\lambda^5$ phosphinolin-2-yl](phenyl)methanone (**6**), which was obtained in 45% yield (see Scheme 3). Thus this photochemical reaction led to the serendipitous discovery of novel pathways to  $\lambda^5$ -phosphinolines.

In the literature the first synthesis of 1,1-diphenyl- $\lambda^5$ phosphinoline by the intermolecular alkylation of the phosphonium salt o-MeO(CH<sub>2</sub>CH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>P<sup>+</sup>(Ph<sub>2</sub>)CH<sub>2</sub>RX<sup>-</sup> (R = H,  $C_6H_5$ ) with subsequent treatment with NaNH<sub>2</sub> or t-BuOK was reported in 1963.<sup>11</sup> This method was applied for the synthesis of 1,1-dibenzyl- $\lambda^5$ -phosphinoline.<sup>12</sup> In 1996 the preparation of the  $\lambda^5$ -phosphinoline by the [2+2] cycloaddition of the four-membered  $\lambda^5$ -phosphete to DMAD was described.<sup>13</sup> Since then no new methods for the synthesis of  $\lambda^5$ -phosphinolines were published. At the same time the question whether the six-membered  $\lambda^5$ -phosphinines are aromatic or ylidic is under discussion in the literature.<sup>14,15</sup> On the basis of geometric, energetic, and magnetic criteria it was concluded that the structure of these compounds represents a hybrid of zwitterions (ylidic) and a "Hueckel" aromatic system.<sup>14,15</sup> The reactivity of  $\lambda^5$ -phosphinolines was poorly studied. The development of a novel synthesis of  $\lambda^5$ phosphinolines provides an excellent opportunity to investigate this class of phosphorus heterocycles.

Considering the principal novelty of our synthetic approach to such rare P-heterocyclic systems, we decided to study the scope and limitations of the reaction shown in Scheme 3 by using the ylides 1 and 2 and various alkynes (4a to 4h). The general results obtained are summarized in Table 1.

The resulting  $\lambda^5$ - phosphinolines were isolated for all processes in 35–80% yields. Moreover in all the cases of **4b** to **4h** the corresponding furan was not observed. The regioselectivity of the process looks straightforward: for monosubstituted acetylenes observed so far the bulky substituent (R<sup>2</sup>) prefers a position removed from the substituent R<sup>1</sup>-CO.

To rationalize our results we assume that the irradiation causes an elimination of phenyliodide to generate an intermediate **A** with a carbocationic center at the carbon atom adjacent to the  $Ph_3P$  moiety. The following attack by the nucleophilic alkyne via the transition state  $B^{\ddagger}$  with subsequent cyclization to the intermediate C results in the formation of the phosphinoline (see Scheme 4).

To find out the nature of the proposed intermediate A we have heated a solution of 1 in degassed methylene chloride under argon atmosphere. After workup we isolated iodobenzene (100%) and the product 21 (85%) (Scheme 5). Triphenylphosphinoxide (15%) was isolated as the minor product. Irradiation of 1 in the presence of styrene yielded the same products as obtained by thermolysis.

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		starting material				
ylide		alkyne			products	
no.	$\mathbb{R}^1$	$\mathbf{R}^2$	R <sup>3</sup>	no.	no.	yields, %
2	Ph	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	Н	4a	6	45 <sup><i>a</i></sup>
1	$OC_2H_5$	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	Н	4a	7	65
2	Ph	Ph	Н	4b	8	50
1	$OC_2H_5$	Ph	Η	4b	9	75
2	Ph	C <sub>8</sub> H <sub>17</sub>	Н	4c	10	50
1	$OC_2H_5$	C <sub>8</sub> H <sub>17</sub>	Н	4c	11	50
2	Ph	Ph <sub>2</sub> CH	Ph	4d	12	50
1	$OC_2H_5$	Ph <sub>2</sub> CH	Ph	4d	13	45
2	Ph	$(CH_2)_4C \equiv CH$	Н	4e	14	60
1	$OC_2H_5$	(CH <sub>2</sub> ) <sub>4</sub> C≡CH	Н	4e	15	40
2	Ph	PhC≡C	Ph	<b>4</b> f	16	35
2	Ph	cycloC <sub>3</sub> H <sub>5</sub>	Н	4g	17	65
1	$OC_2H_5$	cycloC <sub>3</sub> H <sub>5</sub>	Н	4g	18	65
2	Ph	$R_2 + R_3 = (CH_2)_6$ 4h		4h	19	80
1	OC <sub>2</sub> H <sub>5</sub>	$R_{2} + R_{2} = (CH_{2})$	)6	4h	20	$60^{b}$

<sup>*a*</sup>Furan **5** (30%) only was isolated from this reaction. <sup>*b*</sup>The corresponding  $\lambda^5$ -phosphinoline is labile and we could not isolate it in pure form.

No cyclopropane derivative was isolated. These experiments reveal no evidence for a carbenic nature of intermediate **A**.

Our X-ray results reveal a nearly planar phosphorin ring for 8. The six-membered ring of 19 (Chart 1), however, shows a strongly flattened screw (intermediate between half-chair and twist boat) conformation with nearly flat fragments C1-C2-C4-C26 and C4-C26-C21-P (see also the Supporting Information). This geometry was reproduced by the RICON program<sup>16</sup> showing the following ZP puckering parameters:<sup>17</sup> total puckering amplitude  $s = 0.220, \theta =$ 63.2°,  $\Psi 2 = 31.4^\circ$ , and  $\sigma = 1.0$  (the respective torsional angles are equal to  $1.9^{\circ}$  and  $1.0^{\circ}$ ). The six-membered rings in 8 and **19** show a considerable bond alternation: a long  $(1.78 \text{ \AA})$ bond for the P-C21 bond as compared to P-C1 (1.74 Å, 1.73 Å) and shorter C-C bonds C21-C26 (1.41 Å) and C4-C2 (1.35 Å, 1.36 Å) as compared to C4-C26 (1.46 Å) (see Supporting Information). These X-ray diffraction data point to an ylidic character of the phosphorin rings in 8 and **19**. In agreement with these views are the <sup>13</sup>C NMR spectra

of the phosphinolines, especially in the benzoyl-substituted ones. The <sup>13</sup>C NMR signal of C1 is observed at  $\delta$  73 (<sup>1</sup> $J_{CP}$  = 100–105 Hz) whereas for an aromatic environment it is expected at  $\delta$  125–140. The above-mentioned bond alternance is contrasted by the results reported for 1,1-dimethyl-2,4,6-triphenylphosphorin **22**.<sup>18</sup> In this compound the P–C2, P–C6 bonds amount to 1.74 Å, whereas the C–C bond lengths within the six-membered ring vary between 1.38 and 1.40 Å, only. These values agree quite well with the results of calculations on 1,1-dimethylphosphorin<sup>14</sup> for which calculated NICS values support a nonaromatic character.

The disubstituted acetylene 1,1,3-triphenylpropyne **4d** reacts with ylide **2** yielding the mixture of two regioisomers of phosphinoline **12** (Scheme 6); attempts to separate both were unsuccessful. However, the mixture of isomers could be identified by their NMR spectra. In the <sup>13</sup>C NMR spectra the signals of both isomers are observed (two doublets of quaternary C-atom at  $\delta$  113 (<sup>1</sup> $J_{CP}$ = 85.1 Hz) and 115 (<sup>1</sup> $J_{CP}$ = 85.9 Hz)).

The reaction of diphenylbutadiyne **4f** with ylide **2** yielded only one phosphinoline **16a** (Scheme 7); the NMR data of this product have allowed us to define exactly the positions of the substituents (the doublet of acetylene carbon at  $\delta$  92.69 with  ${}^{3}J_{PC} = 16.9$  Hz).

Phosphinolines (6, 8, 10, 12, 14, 17, and 19) of the benzoylsubstituted series are stable compounds, while phosphinolines of the carboethoxy-substituted series are labile ones. Only one phospholine 16a (Scheme 7) was isolated. The other possible isomer 16b was not detected.

The structure of all phosphinolines was confirmed by their NMR spectroscopic data. In the <sup>31</sup>P NMR spectrum the signals of the phosphinolines are observed in a wide area of  $\delta 2$ –13 depending on the substituents of the C=C fragment. In the <sup>1</sup>H NMR spectra of the benzoyl-substituted phosphinolines, synthesized from terminal acetylenes, the doublet of the vinylic proton is observed at  $\delta 7.0-7.15$  (<sup>3</sup>*J*<sub>PH</sub> = 31–32 Hz).

A comparison of the NMR spectra of the benzoylsubstituted phosphinoline (6, 8, 10, 12, 14, 16, 17, and 19) with those of the carboethoxy-substituted phosphinolines (7, 9, 11, 15, 18) shows for the latter systems strongly broadened lines with low intensity of the signals for the protons of the ylidic fragment. This fact complicated their interpretation. The same appearance of spectra was observed for the mixed ylide 1. The broadness of the signals in the NMR spectra we attribute to a dynamic equilibrium between two geometric isomers of the phosphinolines shown in Scheme 8.

In the <sup>13</sup>C NMR spectra of the carboethoxy-substituted phosphinolines (7, 9, 11, 15, and 18) the signal for the ylidic C-atom was not observed, even at higher temperature (30-40 °C). The same effect was found for the ylide 1.

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SCHEME 4. Proposed Mechanism for the Photochemical Formation of Phosphinolines



## SCHEME 5. Thermolysis of 1



CHART 1. Formulas of 8 and 19



SCHEME 6. The Reaction of Ylide 2 with 1,1,3-Triphenylpropyne 4d



# SCHEME 7. Synthesis of $\lambda^5$ -Phosphinoline 16a from Diphenylbutadiyne 4f and Ylide 2



In the <sup>31</sup>P NMR spectrum at -50 °C the signal of carboethoxy-substituted phosphinoline **9** is observed as the superposition of two signals. And in the <sup>13</sup>C NMR spectrum of this phosphinoline the signal of the ylidic C-atom represents two doublets at  $\delta$  55.81 and 57.26 (<sup>1</sup> $J_{CP} = 109.5$  Hz, <sup>1</sup> $J_{CP} = 110$  Hz). This fact indicates the presence of a dynamic

SCHEME 8. A Dynamic Equilibrium between Two Geometric Isomers of Carboethoxy-Substituted Phosphinolines



equilibrium between two geometric isomers of the phosphinoline.

The reaction of ylide 1 with 1,1,3-triphenylpropyne leads to the mixture of two regioisomers of phosphinoline 13 (see Scheme 9), and each of them can be in a dynamic equilibrium between two geometric isomers. One of the regioisomers, 13a, has been isolated by chromatographic separation. NMR spectra of this isomer are highly resolved: in the <sup>1</sup>H NMR spectrum the signals of the ethoxy group represent a triplet at  $\delta$  0.5 (CH<sub>3</sub>) and a quadruplet at  $\delta$  3.25 (OCH<sub>2</sub>), in the <sup>13</sup>C NMR spectrum the signal of the ylidic C atom is observed at  $\delta$  53 (<sup>1</sup>J<sub>CP</sub> = 110 Hz).

### Conclusion

Our investigations of the chemistry of the phosphonium– iodonium ylides 1 and 2 suggest that the irradiation of these species with UV light generates a highly electrophilic intermediate. In the presence of nucleophilic alkynes this intermediate can be trapped by cycloaddition to yield  $\lambda^5$ -phosphinolines. This reaction provides a novel access to these heterocycles. Our structure investigations of the resulting products reveal a nearly planar phosphinoline ring.

#### **Experimental Section**

**General.** The <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> and CD<sub>2</sub>Cl<sub>2</sub> with Me<sub>4</sub>Si as the internal standard. The IR spectra were measured in CCl<sub>4</sub>. The mass spectra were obtained on a quadrupole mass spectrometer (EI, 70 eV, direct inlet). The progress of the reactions and the purity after chromatographic separation were monitored by TLC on Silica gel 60 plates. Chromatographic separation was carried out on columns with Silica gel 60.

Cyclooctyne was prepared by bromination of cyclooctene followed by two dehydrobrominations with *t*-BuOK and LDA.<sup>19</sup>

General Procedure for the Reaction of Ylides with Alkynes. The alkyne was added to a solution of ylides 1 and 2 (0.3 g) in

<sup>(19)</sup> Brandsma, L.; Verkruijsse, H. D. Synthesis 1978, 290.

### SCHEME 9. The Reaction of Ylide 1 with 1,1,3-Triphenylpropyne 4d



anhydrous dichloromethane. The reactions were irradiated in a quartz flask with a mercury light (366 nm) source in argon atmosphere. The course of the reaction was monitored by TLC. After the end of the reaction the mixtures were concentrated in vacuo. The residue was dissolved in a minimum of  $CH_2Cl_2$  and chromatographed on silica gel. To elute the residual alkynes and PhI benzene were used; the corresponding phosphinoline was eluted by using a  $CH_2Cl_2/MeOH$  mixture in a ratio of 200:1.

**Preparation of Phenyl(1,1,4-triphenyl-1**λ<sup>5</sup>-phosphinolin-2-yl)methanone **8**. Starting material: 0.1 mL (0.9 mmol) of **4b**. Product: 0.11 g (50%) of **8** as yellow crystals. Mp: 259– 260 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>), δ: 7.07 (d, <sup>3</sup>*J*<sub>PH</sub> = 31,5 Hz, 1H, CH), 7.12 (m, 1H, arom.), 7.25 (m, 1H, arom.), 7.35–7.45 (m, 10H, arom), 7.51–7.65 (m, 8H, arom.), 7.84–7.90 (m, 4H, arom.). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>), δ: 73.73 (d, <sup>1</sup>*J*<sub>CP</sub> = 100.5 Hz, C1), 110.78 (d, <sup>1</sup>*J*<sub>CP</sub> = 85.8 Hz, arom.), 116.85 (d, *J*<sub>CP</sub> = 10.0 Hz, CHCPh), 124.00 (d, <sup>2</sup>*J*<sub>CP</sub>=11.5 Hz, arom.), 125.43 (d, <sup>3</sup>*J*<sub>CP</sub> = 7.6 Hz, arom.), 125.93 (s, arom.), 127.04 (d, <sup>1</sup>*J*<sub>CP</sub> = 93.5 Hz, arom.), 127.88 (s, arom.), 128.30 (s, arom.), 128.55 (d, <sup>3</sup>*J*<sub>CP</sub> = 13.0 Hz, arom.), 128.67 (s, arom.), 129.43 (s, arom.), 129.93 (s, arom.), 131.47 (s, arom.), 131.78 (d, <sup>4</sup>*J*<sub>CP</sub> = 3.1 Hz, arom.), 133.19 (s, CH), 133.31 (d, <sup>2</sup>*J*<sub>CP</sub> = 10.7 Hz, arom.), 133.46 (s, arom.), 142.75 (s, arom.), 189.39 (d, *J*<sub>CP</sub> = 6.1 Hz, CO). <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ 2.94 s. IR, ν/cm<sup>-1</sup>: 1580 (C=O), 1520 (C=C), 720–750, 1470 (Ar). Anal. Calcd for C<sub>34</sub>H<sub>25</sub>OP: C, 85.00; H, 5.21. Found: C, 85.24; H, 5.07.

**Preparation of (4-Cyclopropyl-1,1-diphenyl-1**λ<sup>5</sup>-phosphinolin-2-yl)(phenyl)methanone 17. Starting material: 100 mg (1.35 mmol) of 4g. Product: 0.130 g (65%) of 17 as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 0.45, 0.82 (both m, 2H, CH<sub>2</sub>), 1.73 (t, 1H, CH), 7.14 (d, <sup>3</sup>*J*<sub>PH</sub> = 32,1 Hz, 1H, CH), 7.15 (m, 1H, arom.), 7.41–7.57 (m, 11H, arom.), 7.65–7.67 (m, 2H, arom.), 7.81–7.86 (m, 4H, arom.), 8.01–8.04 (m, 1H, arom.). <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ: 6.08 (s, CH<sub>2</sub>), 14.64 (s, CH), 73.00 (d, <sup>1</sup>*J*<sub>CP</sub> = 100.4 Hz, arom.), 111.52 (d, <sup>1</sup>*J*<sub>CP</sub> = 85.1 Hz, arom.), 113.70 (d, <sup>3</sup>*J*<sub>CP</sub> = 9.6 Hz, CH=C), 123.67 (d, <sup>2</sup>*J*<sub>CP</sub> = 12.1 Hz, arom.), 124.01 (d, <sup>2</sup>*J*<sub>CP</sub> = 8.0 Hz, arom.), 127.07 (d, <sup>1</sup>*J*<sub>CP</sub> = 94.0 Hz, arom.), 129.27 (s, arom.), 130.43 (d, <sup>3</sup>*J*<sub>CP</sub> = 7.2 Hz, CH), 131.44 (d, <sup>4</sup>*J*<sub>CP</sub> = 2.4 Hz, arom.), 131.54 (s, arom.), 133.18 (d, <sup>3</sup>*J*<sub>CP</sub> = 7.3 Hz, arom.), 132.25 (d, <sup>2</sup>*J*<sub>CP</sub> = 10.4 Hz, arom.), 140.57 (d, <sup>2</sup>*J*<sub>CP</sub> = 9.6 Hz, arom.), 142.72 (d, <sup>3</sup>*J*<sub>CP</sub> = 4.9 Hz, arom.), 188.68 (d, *J*<sub>CP</sub> = 5.7 Hz, CO). <sup>31</sup>P NMR (CDCl<sub>3</sub>), δ: 2.84 s. IR,  $\nu/\text{cm}^{-1}$ : 1580 (C=O), 1525 (C=C), 770, 1440 (Ar). MS, m/z: 444 [M]<sup>+</sup>, 339 [M – PhCO]<sup>+</sup>. HRMS calcd for C<sub>31</sub>H<sub>25</sub>OP (M<sup>+</sup>) m/z 444.1643, found 444.1684.

**Preparation of (5,5-Diphenyl-7,8,9,10,11,12-hexahydro-5**λ<sup>5</sup>**cycloocta**[*c*]**phosphinolin-6-yl**)(**phenyl**)**methanone 19.** Starting material: 0.1 mL of **4h**. Product: 0.175 g (80%) of **19** as a red oil. This oil was dissolved in a minimum of CH<sub>2</sub>Cl<sub>2</sub> and subsequent addition of diethyl ether, hexane, and cyclohexane to this solution resulted in crystallization of phosphinoline **19** as red crystals. Mp: 179–180 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 0.92–1.04 (m, 4H, 2CH<sub>2</sub>), 1.18–1.34 (m, 4H, 2CH<sub>2</sub>), 2.41, 2.82 (both t, 2H, 2CH<sub>2</sub>), 6.97–7.00 (m, 2H, arom), 7.20–7.38 (m, 10H, arom.), 7.60–7.68 (m, 7H, arom.). <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ: 26.25, 26.39, 26.87, 29.63, 31.49 (all s, CH<sub>2</sub>), 34.41 (d. <sup>3</sup>*J*<sub>CP</sub>= 8.0 Hz, CH<sub>2</sub>), 69.86 (d. <sup>1</sup>*J*<sub>CP</sub>=101.2 Hz, C1), 113.90 (d. <sup>1</sup>*J*<sub>CP</sub>=90.0 Hz, arom.), 117.70 (d. <sup>3</sup>*J*<sub>CP</sub>=9.7 Hz, C=<u>C</u>), 123.79 (d. <sup>2</sup>*J*<sub>CP</sub>=12.1 Hz, arom), 124.14 (d. <sup>3</sup>*J*<sub>CP</sub>= 8.9 Hz, arom.), 127.95 (s, arom.), 128.58 (d. <sup>3</sup>*J*<sub>CP</sub>= 8.1 Hz, arom.), 132.97 (d. <sup>2</sup>*J*<sub>CP</sub>=10.4 Hz, arom.), 140.24 (d. <sup>3</sup>*J*<sub>CP</sub>= 4.9 Hz, arom.), 131.58 (s, arom.), 132.88 (d, <sup>3</sup>*J*<sub>CP</sub>= 4.9 Hz, arom.), 187.46 (d. <sup>2</sup>*J*<sub>CP</sub>= 5.6 Hz, CO). <sup>31</sup>P NMR (CDCl<sub>3</sub>), δ: 2.77 s. Anal. Calcd for C<sub>34</sub>H<sub>31</sub>OP: C, 83.95; H, 6.38. Found: C, 84.01; H, 6.22. MS, *m/z*: 486 [M]<sup>+</sup>.

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**Supporting Information Available:** <sup>1</sup>H, <sup>31</sup>P, <sup>13</sup>C NMR spectra of the new compounds furan **5** and phosphinolines **6–19**, X-ray analysis of the molecular structures of **8** and **19** and a table of the most relevant distances as well as CIF files of compounds **8** and **19**, and detailled experimental procedures for the preparation of **6**, **7**, **9**, **10–16**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.