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Gas-Phase Thermolysis of Diallyl(4-Fluorophenyl) and Allyl(*t*-Butylamino)Phenyl Phosphines

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ABSTRACT

Dially(4-fluorophenyl)phosphine and allyl(t-butylamino)phenylphosphine were pyrolyzed in a stirred-flow reactor at 340–420°C/9–19 Torr, using toluene as carrier gas. The primary reaction products were propene, 1-(4-fluorophenyl)-1-phosphabutadiene, and 1-phenyl-2-t-butyliminophosphine. The phosphorus-containing products gave rise to [4 + 2] and [2 + 2] cycloaddition products, respectively. The consumption of these phosphines showed first-order kinetics, with the rate coefficients following the Arrhenius equations: Dially(4-fluorophenyl)phosphine:

$$k(s^{-1}) = 10^{9.00\pm0.32} \exp(-122 \pm 4 \text{ kJ/mol RT})$$

Allyl(t-butylamino)phenylphosphine:

$$k(s^{-1}) = 10^{9.04\pm0.25} \exp(-113 \pm 3 \text{ kJ/mol RT})$$

The results support a six-center cyclic transition-state unimolecular elimination reaction mechanism for both reactants. © *1997 John Wiley & Sons, Inc.*

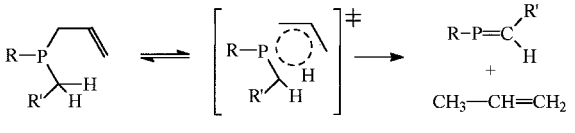
INTRODUCTION

In previous work [1,2], it was shown that thermal decomposition of allyl phosphines, with hydrogen atoms in an α position to the phosphorus atom, would constitute a new route to phosphaalkenes, via a unimolecular retroene-type mechanism, involving a 1,5 hydrogen atom shift in a six-center cyclic transition state (Figure 1).

The reaction is similar to that of homologous oxygen [3–5], sulfur [6,7], and nitrogen systems [8–11], forming propene and the corresponding carbon-heteroatom double-bonded products.

Since this reaction mechanism has possibilities as a new general method to generate reactive dicoordinated phosphorous double-bonded species as intermediates for synthetic phosphorus chemistry [12], it is of interest to investigate the factors bearing on the reactivity and the mechanism of the reaction, in order to generalize this novel access to these reactive species, and also to provide kinetic data in the field of gas-phase phosphorus chemistry, which so far is very scarce [13].

In this work, we report the pyrolyses of diallyl(4-fluorophenyl)phosphine and allyl(*t*-butylamino)-



R= Ph; R'= H, CH=CH$_2$, Ph
R= tBu; R'= CH=CH$_2$

FIGURE 1

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tively), chosen to study, on the one hand, the influence of a substituent on the phenyl ring attached to the phosphorus atom and, on the other hand, the reactivity of the system when the hydrogen atom likely to be transferred is attached to a nitrogen atom, generating an iminophosphine as a product.

RESULTS AND DISCUSSION

Stoichiometry

The gas products formed from AFP over the temperature range 381–420°C consisted of 97 ± 5% propene plus varying amounts of C_2 hydrocarbons and 1,4-hexadiene, the latter being identified by comparison of its gas-liquid chromatography (GLC) retention time with that of an actual sample. In most runs, however, the hexadiene was found only in trace amounts.

The ^{31}P-NMR analysis of the nonvolatile pyrolysis products of AFP showed two AB systems [14] ($\delta_{P1} = -64.8$, $\delta_{P2} = -36.3$, $^1J_{PP} = 251.4$ Hz; and $\delta_{P1} = -23.8$, $\delta_{P2} = 2.7$, $^1J_{PP} = 225.1$ Hz), in a 70:30 ratio, approximately, as main products, and two singlets ($\delta = -35.6$ and $\delta = -35.9$) representing less than 20% of the phosphorated products. Attempts to separate the products were unsuccessful; nevertheless, the AB systems observed by NMR spectroscopy can be attributed to two of the possible isomers of the 1,2-diphospha-3-cyclohexenes **3**, obtained via a [4 + 2] cycloaddition reaction of the phosphabutadiene **2** generated during the pyrolysis (Figure 2), their chemical shifts and coupling constants being analogous to those reported elsewhere for similar compounds [1,2]. The formation of the phosphabutadiene **2** during the pyrolysis is inferred by the presence of **3** in the reaction products mixture.

The nature of the products showing signals at $\delta = -35.5$ and $\delta = -35.9$ in the ^{31}P-NMR spectrum remains, until now, unclear. Since the mass spectrum of the mixture shows only peaks that can be attributed to a dimer of the phosphabutadiene, we think that they may be due to two of the possible isomers of the phosphetanes **4** arising from a [2 + 2] cycloaddition reaction of the phosphabutadiene (Figure 3).

The high synthetic potential of dicoordinated phosphorus compounds, obtained in this way, prompted us to try to generate iminophosphines by thermal elimination of propene from allylaminophosphines. The pyrolysis of BAP **5** (Figure 4) was carried out at temperatures between 343°C and 386°C. The gas products mixture was composed of 94 ± 5% of propene, about 5% of isobutene plus traces of C_2 hydrocarbons. The analysis of the reaction mixture by ^{31}P-NMR spectroscopy at ambient temperature showed a signal at $\delta = 153$ as a major product and somewhat less than 10% of two other compounds giving minor signals at $\delta = 232$ and $\delta = 109$. No important changes were observed when the ^{31}P-NMR analysis was made at −70°C. The propene comes from the expected reaction (Figure 4), and the small amount of isobutene may be formed via a four-center elimination reaction (Figure 5), as it is known for *t*-butylamines [15].

The signal at $\delta = 153$ was assigned to the 1,3-di-*t*-butyl-2,4-diphenyldiazadiphosphetidine **8** arising from a [2 + 2] cycloaddition reaction of the iminophosphine **6** (Figure 6). This assignment was based on the ^{13}C-NMR analysis that showed triplet signals for the *t*-butyl carbons [16]. The mass spectrum of the nonvolatile products fraction showed peaks corresponding to the fragmentation of the dimer [16]. No peaks that could be attributed to other oligomers (trimers, tetramers, etc.) were observed in the mass spectrum.

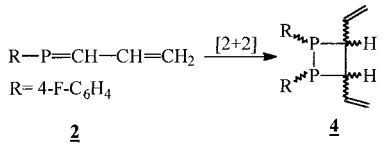

FIGURE 3

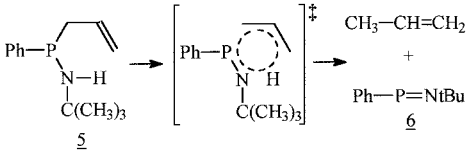

FIGURE 4

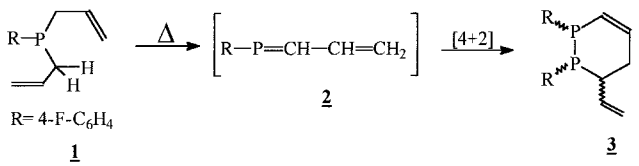

FIGURE 2

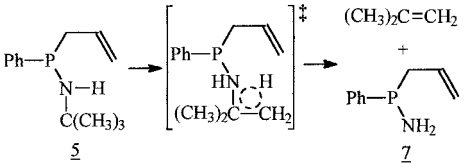

FIGURE 5

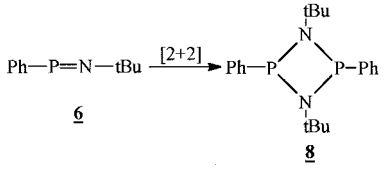

FIGURE 6

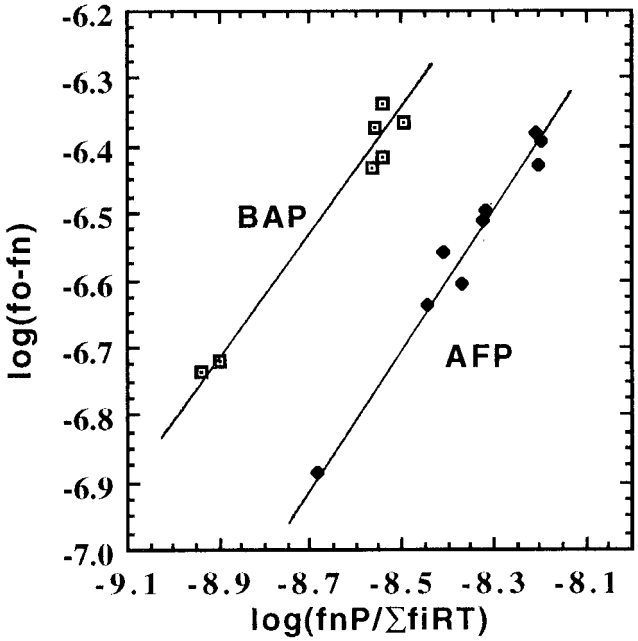

FIGURE 7 Phosphines order plots. *fo*: reactant inflow; *fn*: reactant outflow; Σ*fi*: total outflow; *P*: total pressure; *T*: absolute temperature; *R*: gas constant.

Concerning the ^{31}P-NMR analysis, it is well known that *cis* and *trans* diazadiphosphetidines show very different chemical shifts. Typical ranges for the signals [17] are 80–120 for one of the isomers, often the *cis,* and 180–240 for the other, often the *trans* isomer. The value $\delta = 153$ lies between these two ranges; however, some examples are known where the chemical shift for a diazadiphosphetidine falls in this range [17]. For example, 1,3-di-t-butyl-2,4-dibutylamino-1,3,2,4-diazadiphosphetidine has $\delta = 165$ [18], and several other N-aryl–substituted diazadiphosphetidines have resonance signals around 160 [19]. Due to the small quantities present, it was not possible to isolate the products giving signals at 232 and 109, but it may be assumed that the compound with $\delta = 232$ corresponds to the other isomer of **8**, since formation of small amounts of this compound is observed during the distillation of the starting material **5**. The other signal at $\delta = 109$ may be due to a mixed diazadiphosphetidine arising from a [2 + 2] cycloaddition reaction between **6** and the iminophosphine product of the pyrolysis of the allyl aminophosphine **7**, generated during the reaction (Figure 5).

The information provided by the above analysis suggests the formation of the transient iminophosphine by propene elimination.

Kinetics

The initial order for the consumption of AFP, measured at 392°C for conversions up to 29% and a 3.7-fold increase of reactant inflow, was 0.99 ± 0.06. For BAP, at 365°C, for conversions of up to 34% and a 2.8-fold increase of reactant inflow, the measured order was 0.91 ± 0.04. An order one was then assumed for the reactions of both phosphines. The order plots are shown in Figure 7. Tables 1 and 2 show the temperature variation of the rate coefficients, as well as the experimental conditions, for a representative number of runs made with AFP and BAP, respectively. For the calculation of the rate coefficients, it was assumed that the phosphaalkene and the iminophosphine leave the reactor as monomers in the same concentration as the propene; hence, the total reaction product outflow was assumed to be twice that of propene. Least-squares linear fits of the respective rate coefficients produced the Arrhenius parameters given in Table 3. The error limits correspond to the standard error.

According to the kinetic data shown in Table 3, substitution of a fluorine atom for hydrogen in position **4** of the benzene ring of diallylphenylphosphine produces a decrease of about 20 kJ mol^{-1} in *Ea* and a decrease of about 30 units in the entropy of activation. These variations cause only a slight reactivity increase, as indicated by the rate coefficients calculated at 375°C and 400°C, by using the respective Arrhenius equations. A slight increase in electron density at the P–C bond about to be broken, due to the +M effect of the *p*-fluorine atom, would assist this process in the transition state. The high polarizability of the phosphorus atom, however, would make this effect less marked than expected. The greatly enhanced reactivity of BAP in relation to all the other phosphines, sulfides, amines, and ethers shown in Table 3 seems to agree with Dewar's suggestion [20] whereby the 1–5 shift of a hydrogen atom from a heteroatom to a carbon atom should be more facile than from one carbon atom to another. In such a mechanism, the bond-making and bond-breaking steps would tend to be concerted and synchronous. As mentioned above, the formation of about 5% of isobutene in the pyrolysis of BAP probably takes place by a unimolecular, four-center cyclic transition-state mechanism, similar to that proposed

TABLE 1 Stirred Flow Pyrolysis of Diallyl-4-fluorophenylphosphine

T(°C)	$k \times 10^4$ s^{-1a}	Θ s^b	%r (C_3H_6)^c	P torr	$fr^\circ \times 10^{8d}$	$f_c/fr^{\circ e}$
381.0	1770	1.77	23.80	9.96	48.58	65
382.0	1836	1.19	18.00	19.3	133.9	68
391.4	2738	1.53	29.52	13.9	78.0	65
391.9	2692	1.53	29.16	14.3	44.7	117
392.7	2778	1.28	26.28	16.8	117.2	62
392.8	2677	1.19	24.20	16.8	167.2	47
411.3	4610	0.689	24.10	15.1	268.7	44
410.9	4432	0.728	24.40	12.0	131.7	68
420.8	6612	0.772	33.80	14.0	133.4	73
421.2	6569	0.778	33.83	13.0	123.4	72

[a]Rate coefficient.
[b]Residence time.
[c]Percent reaction based on propene measurement.
[d]Reactant inflow, mol s^{-1}.
[e]Toluene to reactant flow ratio.

TABLE 2 Stirred Flow Pyrolysis of Allyl(t-butylamino)phenylphosphine

T(°C)	$k \times 10^4$ s^{-1a}	Θ s^b	%r (C_3H_6)^c	P torr	$fr^\circ \times 10^{8d}$	$f_c/fr^{\circ e}$
343.0	3067	0.885	21.35	9.71	107.2	61
343.5	3056	0.804	19.74	11.3	129.0	65
355.1	4532	0.794	26.47	11.8	128.6	68
355.8	4458	0.773	25.63	9.48	100.1	72
365.3	6883	0.776	34.83	11.8	131.9	66
365.4	6418	0.803	34.07	9.97	56.0	129
365.3	6564	0.785	34.00	9.46	124.3	56
366.0	5844	0.647	27.45	11.5	134.8	76
377.1	9792	0.750	42.33	11.8	116.6	76
376.6	9700	0.845	45.04	8.65	71.0	82
380.2	10062	0.872	46.75	11.2	107.1	67
386.3	12774	0.799	50.13	11.2	101.2	77
386.5	13076	0.831	52.08	12.3	111.6	74

[a]Rate coefficient.
[b]Residence time.
[c]Percent reaction based on propene measurement.
[d]Reactant inflow, mol s^{-1}.
[e]Toluene to reactant flow ratio.

for aryl *t*-butyl amines [15]. This reaction, however, can be expected to have an activation energy of about 230 $kJ \cdot mol^{-1}$; hence, its occurrence at the present temperature range is not significant. The corresponding phosphorus-containing product of the latter reaction, the allylaminophenylphosphine, can be expected to decompose twice as fast as the BAP by the six-center transition-state mechanism, forming propene and iminophenylphosphine.

That the frequency factors for the phosphines studied so far (Table 3) have an average value of $10^{9.6 \pm 0.6}$ s^{-1}, just at the lower limit of the range expected for six-center transition-state reactions [21,22] ($10^{10.5 \pm 1.5}$), would indicate either very rigid transition-state structures for these reactions or to be the result of radical-induced chain decomposition of the phosphines. The presence of small amounts of 1,4-butadiene as product from the pyrolyses of AFP and allylmethylphenylphosphine [1] suggests that at least a small degree of P–C bond cleavage, originating allyl- and phosphorus-centered free radicals, is taking place. The allyl radicals, being resonance stabilized, are not likely to promote chain reactions, and less so in the presence of high concentrations of toluene acting as diluent gas and free radical inhibitor; thus, these radicals dimerize to form the observed 1,4-butadiene. A way [21] of assessing the Arrhenius parameters for AFP and BAP reactions is by using the experimental values of the rate coefficients at the middle of the temperature range (400°C for AFP and 365°C for BAP), as being less subject to experimental errors, and a frequency factor of 10^{10} s^{-1}. One calculates values of activation energies of 135 and 124.5 $kJ \cdot mol^{-1}$, for the AFP and BAP reactions, respectively. If one assumes a frequency factor of 10^{11} s^{-1}, the calculated activation energies would be 148 and 137 $kJ \cdot mol^{-1}$, respectively. In the present experimental system, a maximum error of about ± 12 $kJ \cdot mol^{-1}$ may be expected in the activation energy, due to the scatter in rate coefficient measurements above and below the middle of the temperature range considered. The above considerations would suggest an upper limit of about 10^{10} s^{-1} for the frequency factors of the AFP and BAP reactions.

EXPERIMENTAL

The pyrolyses were made in a stirred-flow reactor [23] of 234 mL capacity, fitted with a 315-BHS-1000 pressure transducer from MKS instruments, by injecting 10 mL of 0.1–0.2 M solutions in toluene over periods of 15–30 minutes by means of a peristaltic pump. The experimental technique, reaction-order measurement, rate coefficient calculation, and analytical methods have been described previously [10–23]; ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AM-300 instrument. Mass spectra were obtained on a Kratos GLC-MS RFA25 instrument. Dichloro(4-F-phenyl)phosphine was prepared by a published method [24]; PCl_3, $AlCl_3$, $PhPCl_2$, and *t*-$BuNH_2$ were purchased from Aldrich.

Dially(*4-fluorophenyl*)*phosphine* **1**

A solution of 0.242 mol of allylmagnesium bromide (obtained from 0.242 mol of allyl bromide and 0.484

TABLE 3 Kinetics Parameters for Pyrolysis of Heteroatom Allyl Compounds

Reactant	*log A*	*Ea kJ mol⁻¹*	*− Δ S‡[a]*	k_{375}[b]	k_{400}[b]	*Ref.*
CH_3–S–C–C = C	11.23 ± 0.25	160 ± 3	41	0.75	2.2	[6]
S(C–C = C)$_2$	11.01 ± 0.06	138.2 ± 0.7	49	19.0	48.0	[6]
$PhCH_2$–S–C–C = C	10.93 ± 0.18	141 ± 2	50	19.0	49.0	[6]
$PhP(CH_3)$(C–C = C)	9.61 ± 0.61	144 ± 9	76	0.34	0.91	[1]
Ph–P(C–C = C)$_2$	10.57 ± 0.31	143 ± 4	57	2.8	7.5	[1]
Ph–P(CH_2Ph)(C–C = C)	9.71 ± 0.47	135 ± 6	74	3.4	8.6	[1]
p-FPh–P(C–C = C)$_2$	9.00 ± 0.32	122 ± 4	87	3.7	8.6	[c]
t-C_4H_9NH–P(C–C = C)	9.04 ± 0.25	113 ± 3	87	86.1	187.5	[c]
CH_3NH(C–C = C)	11.4	182	41	0.02	0.06	[8]
H–N(C–C = C)$_2$	11.04 ± 0.13	155 ± 1	48	0.96	2.8	[8]
N(C–C = C)$_3$	11.74 ± 0.07	160.1 ± 0.8	35	0.38	1.2	[9]
c-C_6H_9–NH(C–C = C)	11.44 ± 0.21	176 ± 2	41	0.10	0.61	[26]
CH_3–O–C–C = C	11.09 ± 0.02	174 ± 3	47	0.04	0.13	[3]
O(C–C = C)$_2$	11.91 ± 0.10	171.1 ± 0.1	37	0.33	1.1	[3]
$PhCH_2$–O–C–C = C	11.53 ± 0.03	172.4 ± 0.4	33	0.22	0.71	[3]

[a]Entropy of activation, J °K^{-1} mol^{-1} at 375°C.
[b]Rate coefficient calculated at 375 and 400°C, s^{-1}, statistically correctd × 10^2.
[c]This work.

mol of magnesium turnings in 150 mL of freshly distilled ether [25]) was added dropwise to a stirred solution of 0.11 mol of dichloro(4-F-phenyl)phosphine in 150 mL of freshly distilled ether cooled at −10°C. When the addition was finished, the reaction mixture was stirred at room temperature for 2 hours, filtered, the solvent evaporated, and the product distilled under reduced pressure through a 15 cm vigreux column (77% yield). Bp: 83°C/0.05 torr. ^{31}P NMR {^{1}H} (121.496 MHz, $CDCl_3$, H_3PO_4 ext) δ = −29.2. ^{1}H NMR (300.133 MHz, $CDCl_3$, TMS ext) δ = 2.5 (m, CH_2P, 4H) δ = 4.9 (m, CH_2 = CH, 4H) δ = 5.6 (m, CH_2 = CH, 2H) δ = 7.0–7.5 (m, arom, 4H). ^{13}C NMR {^{1}H} (75.469 MHz, $CDCl_3$, TMS ext) δ = 32.2 (d, $^1J_{PC}$ = 15, CH_2) δ = 115.2 (d, $^2J_{PC}$ = 7.2) δ = 115.5 (d, $^3J_{PC}$ = 7.4) δ = 117 (d, $^3J_{PC}$ = 8.9, CH_2 = CH) δ 132.7 (d, $^2J_{PC}$ = 6.9, CH = CH_2) δ = 134.1 (d, $^1J_{PC}$ = 7.8) δ = 134.4 (d, $^2J_{PC}$ = 7.9) δ = 163.4 (d, $^1J_{CF}$ = 248). Mass *m/e* (%). 209 (18.8 M^+), 167 (21.5, M–C_3H_6), 114 (10.3 M–C_6H_4F); 190 (4.9, M–F).

(*t-Butylamino*)*phenylchlorophosphine*

A solution of 0.31 mol of *t*-butylamine in 200 mL of freshly distilled ether was added dropwise to a solution of 0.14 mol of dichlorophenylphosphine in 200 mL of freshly distilled ether at −78°C. After the addition had been completed, the mixture was stirred for 30 minutes at ambient temperature, filtered through celite, the solvent evaporated, and the product distilled under reduced pressure through a 15 cm vigreux column (83% yield). Bp: 93–97°C/0.02 torr; ^{31}P RMN {^{1}H} (121.496 MHz, $CDCl_3$, H_3PO_4 ext) δ = 116. ^{1}H NMR (300.133 MHz, $CDCl_3$ TMS ext) δ = 1.4 (5.1, CH_3 9H) δ = 3.3 (bs, N–H, 1H) δ = 7.4–7.8 (m, arom, 5H). ^{13}C NMR {^{1}H} (75.469 MHz, $CDCl_3$, TMS ext) δ = 31.5 (d, $^3J_{PC}$ = 10.6 (H_3C)$_3$C) δ = 52.4 (d, $^2J_{PC}$ = 10.5, (H_3C)$_3$*C*) δ = 128.4 (d, $^3J_{PC}$ = 5.4) δ = 129.8 (d, $^2J_{PC}$ = 7.6) δ = 130.1 (s) δ = 141.9 (d, $^1J_{PC}$ = 25.3).

Allyl(*t-butylamino*)*phenylphosphine* **5**

A filtered solution of 0.13 mol of allylmagnesium bromide [25] in 100 mL of freshly distilled ether was added dropwise to a stirred solution of 0.12 mol of *t*-butylaminophenylchlorophosphine in 400 mL of freshly distilled ether at 0°C. After the addition had been completed, the mixture was stirred at room temperature for 1 hour, filtered, the solvent evaporated, and the product distilled under reduced pressure through a 15 cm vigreux column (57% yield). Bp 86–88°C/0.025 torr. ^{31}P NMR {^{1}H} (121.496 MHz, $CDCl_3$, H_3PO_4 ext) δ = 7.5. ^{1}H NMR (300.133 MHz, $CDCl_3$, TMS ext) δ = 1.2 (s, CH_3, 9H) δ = 1.8 (bs, N–H, 1H) δ = 2.4 (m., CH_2, 2H) δ = 4.9 (m, C$\underline{H}_2$ = CH, 2H) δ = 5.3 (m, C$\underline{H}$ = CH_2, 1H) δ = 7.2–7.5 (m, arom, 5H). ^{13}C NMR {^{1}H} (75.469 MHz $CDCl_3$, TMS ext) δ = 31.7 (d, $^1J_{PC}$ = 15.3, CH2 δ = 32.2 [d, $^3J_{PC}$ = 8.1, $\underline{C}H_3$, δ = 50.5 (d, $^2J_{PC}$ = 18.8, (CH_3)$_3\underline{C}$)] δ 116.3 (d, $^3J_{PC}$ = 5.5, CH = CH_2) δ = 127.3 (s, CH_2 = CH) δ = 127.8 (d, $^3J_{PC}$ = 13.2) δ = 128.9 (d, $^2J_{PC}$ = 18.4) δ = 131.4 (s) δ = 143.6 (d, $^1J_{PC}$ = 16.5). Mass *m/e* (%):

222 (14.7, M^+), 180 (77.5, M–C_3H_6), 166 (11.3, M–*t*Bu), 124 (76.1, M–*t*Bu–C_3H_6).

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[14] Selected data for **3**: ^{31}P NMR {^{1}H} (121.496 MHz, $CDCl_3$, H_3PO_4 ext), $\delta_{P1} = -64.8$ and $\delta_{P2} = -36.3$ ($^1J_{PP}$ = 251.4 Hz), $\delta_{P1} = -23.8$ and $\delta_{P2} = -2.7$ ($^1J_{PP}$ = 225.1 Hz). Mass *m/e* (%) 332 (62.5, M^+), 205 (100), 253 (3.2), 237 (2.5), 313 (34.8), 304 (21.7), 292 (10.8), 166 (5.5).
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[16] Selected data for **8**: ^{31}P NMR {^{1}H} (121.496 MHz, $CDCl_3$, H_3PO_4 ext.): $\delta = 153$. ^{1}H NMR (300.133 MHz, $CDCl_3$, TMS ext) $\delta = 1.35$ (s, CH_3, 9H) $\delta = 7.4$–7.8 (m, arom, 5H). ^{13}C NMR {^{1}H} (75.469 MHz, $CDCl_3$, TMS ext): $\delta = 28.8$ (t, $^3J_{PC} = 7.2$, $(\underline{C}H_3)_3$), $\delta = 52.1$ (t, $^2J_{PC} = 15.4$, $\underline{C}(CH_3)_3$), $\delta = 127.2$ ($\overline{t}$, $^3J_{PC} = 3$), $\delta = 129.4$ (s), $\delta = \overline{130}.5$ (m), $\delta = 146.7$ (dd, $^1J_{PC} = 50.1$, $^3J_{PC} = 3.7$). Mass *m/e* (%): 358 (40.3, M^+), 302 (13.4), 281 (90), 253 (19.3), 180 (38.3).
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