Addition Reactions of Tertiary Silylphosphanes with Acetylenic Ketones and Aldehydes

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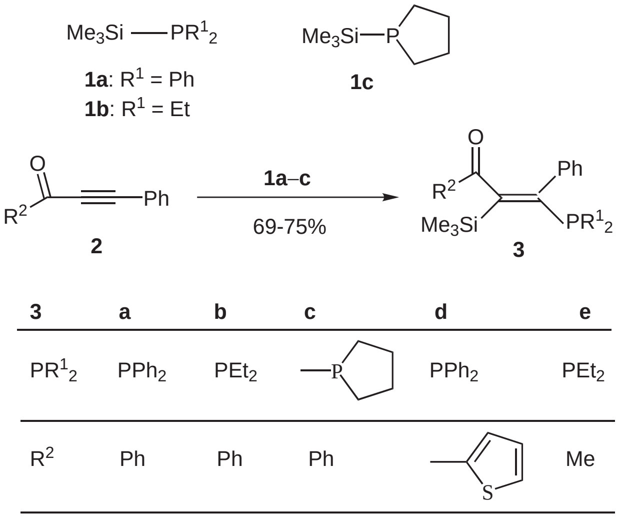
Abstract: (Trimethylsilyl)phosphanes $Me_3Si–PR_2$ (PR_2 = PPh_2, PEt_2, 1-phospholanyl) add smoothly across the C≡C bond of acetylenic ketones RCOC≡CPh to form (*Z*)-3-phosphanyl-2-(trimethylsilyl)prop-2-en-1-ones **3** (3,4-addition). Thermal isomerization of the latter yields the corresponding 3-(trimethylsilyl)oxy-allenylphosphane **6**, formally the product of a 1,4-addition. Mainly 1,2-addition occurs with propiolic aldehydes leading to (1-[(trimethylsilyl)oxy]propargyl)phosphanes **4**. Desilylation reactions of **3b** yield either (3-oxopropyl)phosphanoxide **7** or (3-oxopropenyl)phosphanoxide **8**.

Key words: organophosphorus(III) compounds, organosilicon compounds, nucleophilic addition at alkynones, enones, siloxyallenes

Tertiary silylphosphanes react with α,β-unsaturated olefinic ketones and aldehydes in general by addition across the C=C double bond (3,4-addition).[1] Surprisingly, analogous reactions with acetylenic carbonyl compounds are barely known: Märkl et al. have reported the synthesis of a 4-phosphacyclohexadien-1-one from 1,5-diphenyl-1,4-pentadiyn-3-one and $PhP(SiMe_3)_2$ in the presence of AIBN,[2] and Regitz et al. have described the insertion of acetylenic esters and ketones into the P–Si bond of P-silylated cyclopropenylidenephosphanes[3] and 1,2-dihydro-1,2-phosphasiletes.[4] We report now that more common and readily accessible dialkyl- and diaryl(trimethylsilyl)phosphanes also react smoothly with acetylenic carbonyl compounds and that the formation of 3,4-, 1,2-, and 1,4-addition products is feasible. Reactions of diphenyl(trimethylsilyl)phosphane with terminal and internal alkoxyalkynes have been investigated recently by Russian researchers.[5]

Silylphosphanes **1a**–**c**[6] reacted readily with acetylenic ketones **2a**–**c** in a 3,4-addition mode to furnish 3-phosphanyl-2-(trimethylsilyl)propenones **3a**–**e** in good yield (Scheme 1).[7] Acetonitrile or THF was used as the solvent since related phosphane additions to olefinic substrates were found to be faster in polar solvents.[1] Acetonitrile had the additional advantage that some of the products crystallized directly from the reaction solution.

The identity of enones **3a**–**e** was established by their spectroscopic data (Table). A strong IR absorption at 1629–1687 cm^{-1} indicated the presence of a carbonyl group, and the C=C-C=O unit was recognized by the ^{13}C chemical shifts together with characteristic P,C coupling constants. The ^{29}Si NMR signal of **3b** was observed as a doublet at δ = –8.5 ppm [^3J(Si,P) = 11.4 Hz]. These data exclude the alternative structures of 1,2- and 1,4-addition products featuring Me_3SiO functionalities (vide infra). It is reasonable to assume that the formation of **3** begins with an addition of the nucleophilic phosphorus atom of silylphosphanes **1** at the electron-deficient triple bond of acetylenic ketones **2**. The NMR spectra showed the presence of only one isomer in all cases. The magnitudes of the $^3J(P,C{=}O)$ (19.5–24.2 Hz), $^4J(P,SiC)$ (9.5–10.2 Hz), and $^5J(P,SiCH_3)$ (1.2–1.6 Hz, except for **3d**) coupling constants indicate the same double bond configuration in all cases. However, a definite assignment cannot be made because a rigorous stereochemical proof for related systems[4] is not available and it has been noted that no obvious stereochemical dependence of the ^3J(P,C) coupling constant in vinylphosphanes exists.[8] An X-ray crystal structure analysis of **3b** provided the definite proof of the *Z* configuration (Figure).[9] The ^1H and ^{13}C NMR spectra of **3b** show temperature-dependent signals and coalescence phenomena for the PEt_2 group and the adjacent phenyl ring. This is probably due to steric hindrance between the $SiMe_3$ and the PEt_2 groups which slows down the exchange between the position of the PEt_2 group (see Figure) and a conformation obtained by a 180° rotation around the C(sp^2)–P bond.



Scheme 1 Conditions: CH_3CN or THF, 0→20 °C

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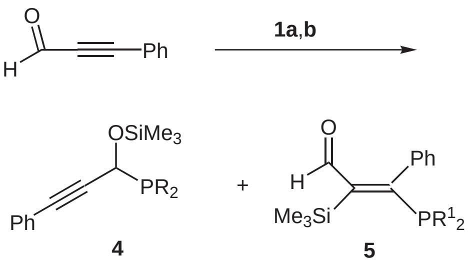
Table Selected IR, $^{13}C\{^1H\}$ NMR, and ^{31}P NMR Data of Compounds **3**, **4**, and **6**

Compound	IR [cm^{-1}] (C=O)	^{13}C NMR (125.77 MHz, $CDCl_3$, TMS), δ [ppm] ($J_{C,P}$ [Hz])				^{31}P NMR, δ [ppm]
		C-1	C-2	C-3	Other Signals	
3a	1663	200.6 (23.9)	151.5 (25.2)	164.8 (52.8)	0.9 (d, $^4J_{C,P}$ = 10.0, $SiMe_3$), 126.0–139.0 (C_{Ph})	2.2
3b[a]	1655	200.5 (20.4)	154.3 (26.7)	164.0 (49.1)	1.8 (d, $^4J_{C,P}$ = 10.1, $SiMe_3$), 10.4 (d, $^2J_{C,P}$ = 16.2, CH_3), 11.1 (d, $^2J_{C,P}$ = 16.0, CH_3), 18.4 (d, $^1J_{C,P}$ = 10.0, PCH_2), 18.5 (d, $^1J_{C,P}$ = 9.4, PCH_2), 125.9–137.2 (C_{Ph})	–17.8
3c	1650	200.8 (19.5)	156.6 (34.0)	159.5 (47.4)	1.4 (d, $^4J_{C,P}$ = 10.0, $SiMe_3$), 25.8 (m, br, PCH_2), 28.2 (s, 2 C, CH_2), 126.0–139.3 (C_{Ph})	–18.2
3d	1629	192.5 (24.2)	152.3 (25.6)	164.1 (55.2)	1.4 (d, $^4J_{C,P}$ = 9.5, $SiMe_3$), 126.1–144.3 (C_{Ph}, C_{Thie})	2.6
3e	1687	208.6 (20.2)	151.1 (26.7)	166.4 (48.0)	1.7 (d, $^4J_{C,P}$ = 10.2, $SiMe_3$), 10.4 (d, $^2J_{C,P}$ = 17.1, CH_3), 18.8 (d, $^1J_{C,P}$ = 11.2, PCH_2), 31.4 (d, $^4J_{C,P}$ = 2.3, CH_3CO), 126.5, 127.6, 127.7, 137.6	–17.2
4a	–	64.4 (–)	88.2, 88.5			4.2
4b	–	61.9 (11.4)	87.2, 87.8			–16.0
6	–	118.3 (23.9)	201.0		0.2 (s, $SiMe_3$), 9.65 (d, $^2J_{C,P}$ = 10.1, CH_3), 9.87 (d, $^2J_{C,P}$ = 16.3, CH_3), 17.4 (d, $^1J_{C,P}$ = 10.1, PCH_2), 17.8 (d, $^1J_{C,P}$ = 13.8, PCH_2), 124.4–137.3	–10.6

[a] The ^{13}C NMR spectrum was recorded at 233 K.

When silylphosphanes **1a**,**b** were combined with phenylpropargyl aldehyde, the nucleophilic 1,2-addition at the aldehyde function dominated by far over the 3,4-addition, and propargylphosphanes **4**, accompanied by traces of acrylic aldehyde derivatives **5**, were obtained[10] (Scheme 2).

The direct 1,4-addition of silylphosphanes **1** at the conjugated system of alkynones **2**, leading to 1-phosphanyl-3-siloxyallenes, was not observed in any of the reactions described above. However, when enone **3b** was heated in toluene at 150 °C in toluene in a closed thick-walled Schlenk tube, thermal rearrangement into allene **6** took place through a 1,3(C→O) $SiMe_3$ shift (Scheme 3). The isomerization was almost complete after 40 h; at this stage, the ^{31}P NMR spectrum showed the signals of **6** and **3b** in a ratio of 99.4:0.6, accompanied by ca 2% of a signal at δ = 47.7 ppm ($POEt_2$).[11] The formation of **6** is in accord with the NMR data (Table) which show the disappearance of the olefinic carbon signals of the enone while the singlet signal of the central allenic carbon (δ = 201.0 ppm) replaces the doublet signal of the carbonyl carbon of **3b** (δ = 200.5 ppm). Also indicative of the formation of the trimethylsilyloxy function is the small high-field shift of the ^1H and ^{13}C signals of the $SiMe_3$ group both of which no longer show a long-range coupling with the P nucleus.



Scheme 2 Conditions: CH_3CN or THF, 0→20 °C

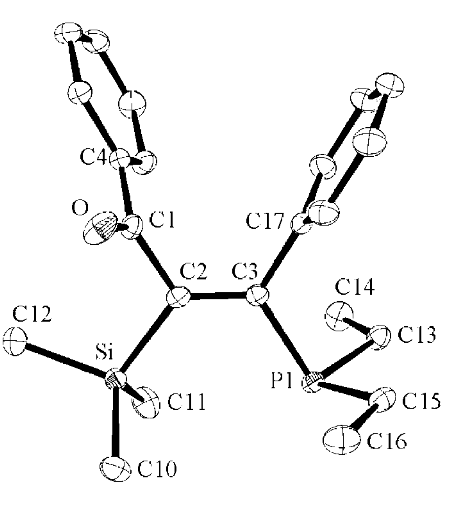
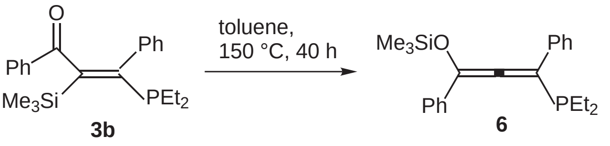
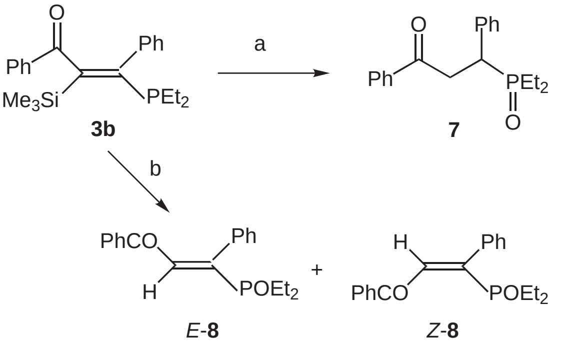


Figure Molecular structure of **3b** in the solid state (ORTEP plot); the ellipsoids of thermal vibration represent a 50% probability



Scheme 3

Due to the presence of different functional groups, compounds **3** should be amenable to various further transformations. In an effort to remove the $SiMe_3$ group, we found that treatment of **3b** with acids gave the (3-oxopropyl)phosphanoxide **7**[12] formally resulting from desilylation and addition of water (Scheme 4). This trans-formation represents a novel method to prepare compounds of type **7**.[13] Protodesilylation with conservation of the olefinic bond was achieved when **3b** was kept in wet acetone; not unexpectedly, concomitant oxidation of the phosphanyl function also took place. The resulting (3-oxopropenyl)phosphanoxide **8** was obtained as a *E*,*Z* mixture which could be separated by column chromato-graphy.[14] The stereochemical assignment can be based reliably on $^3J_{P,H}$ and $^3J_{P,C}$ coupling constants (*trans* > *cis*).[8]



Scheme 4 a) CF_3COOH, $CHCl_3$, 24 h, 59% yield; b) wet acetone, r.t., 3–5 days, yield: 38% *E*-**8**, 21% *Z*-**8** (ca. 10% of residual **3b**).

In conclusion, we have shown that tertiary trimethylsilylphosphanes add smoothly in a *syn* fashion to the triple bond of acetylenic ketones, and we have furnished an unequivocal proof for the *Z* configuration of the products **3**. In contrast, the reaction of $Me_3Si–PPh_2$ with internal alkoxyalkynes requires much more forcing conditions and was reported to give anti-addition products.[5] The presence of several different functional groups in compounds **3**, which are α,β-unsaturated phosphanes, silanes, and carbonyl compounds simultaneously, provides opportunities for various synthetic transformations. First examples are given here by their thermal isomerization leading to siloxyallenes **6** and desilylation reactions leading to phosphanoxides **7** or **8**.

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(7) (*Z*)-3-(Diphenylphosphanyl)-1,3-diphenyl-2-(trimethylsilyl)prop-2-en-1-one(**3a**); general procedure: A solution of 1,3-diphenylprop-2-yn-1-one (**2a**, 3.1 g, 15.0 mmol) in THF (100 mL) was cooled at 0 °C and diphenyl(trimethylsilyl)phosphane (**1a**, 3.87 g, 15.0 mmol) was added. The reaction mixture was kept with stirring at 0 °C for 2 h, then at 20 °C for 12 h. The solvent was evaporated at 15 mbar and the solid residue was recrystallized from CH_3CN to furnish **3a** as colorless crystals (5.22 g, 75%), mp 127–128 °C. IR (KBr): 1663 s, 1243 s, 1233 s, 858 s, 842 s cm^{-1}. ^1H NMR ($CDCl_3$, 500.14 MHz): $\delta = 0.51$ (d, $^5J_{H,P} = 1.2$ Hz, 9 H, $SiMe_3$), 6.3–7.8 (20 H_{Ph}). MS (EI, 70 eV): *m/z* (%) = 466 (9), 465 (33), 464 (100) [all M^+].
3b: From **1b** and **2a**; large pale-yellow crystals, 69% yield, mp 100 °C. IR (KBr): 1655 s, 1237 s, 844 s, 703 m cm^{-1}. ^1H NMR ($CDCl_3$, 500.14 MHz, 233 K): $\delta = 0.35$ (d, $^5J_{H,P} = 1.6$ Hz, 9 H, $SiMe_3$), 1.0–1.4 (m, 10 H_{ethyl}), 6.6–7.6 (10 H_{Ph}). ^{29}Si NMR ($CDCl_3$, 99.37 MHz): $\delta = –8.5$ (d, $^3J_{Si,P} = 11.4$ Hz). MS (EI, 70 eV): *m/z* (%) = 370 (5), 369 (10), 368 (39) [all M^+], 279 (100). $C_{22}H_{29}OSiP$ (368.53): calcd C 71.70, H 7.93; found C 71.38, H 8.12.
3c: From **1c** and **2a**; pale-yellow crystals, 69% yield, mp 99 °C. IR (KBr): 1667/1650 vs, 1230 vs, 1174 vs, 702 vs cm^{-1}. ^1H NMR ($CDCl_3$, 500.14 MHz): $\delta = 0.35$ (d, $^5J_{H,P} = 1.5$ Hz, 9 H, $SiMe_3$), 1.08–1.25 (m, coalescing, 2 H), 1.35–1.45 (m, 2 H), 1.65–1.90 (m, 4 H), 6.7–7.7 (10 H_{Ph}). MS (EI, 70 eV): *m/z* (%) = 368 (2), 367 (7), 366 (25) [all M^+], 279 (100). $C_{22}H_{27}OPSi$ (366.51): calcd C 72.10, H 7.42; found C 71.80, H 7.55.
3d: From **1a** and **2b**; 70% yield, amorphous solid, mp 149 °C. IR (KBr): 1629 vs, 1413 s, 1261 s, 1246 s, 846 vs, 743 vs, 725 s, 702 vs cm^{-1}. ^1H NMR ($CDCl_3$, 500.14 MHz): $\delta = 0.44$ (s, 9 H, $SiMe_3$), 6.4–7.5 (18 H_{arom}). MS (EI, 70 eV): *m/z* (%) = 472 (13), 471 (36), 470 (100) [all M+], 469 (39). $C_{28}H_{27}OPSSi$ (470.64): calcd C 71.46, H 5.78; found C 71.52, H 5.62.
3e: From **1b** and **2c**, malodorous colorless oil, isolated by bulb-to-bulb distillation at 80–100 °C/0.0001 mbar; 76% yield. IR (KBr): 1687 s, 1245 s, 1187 s, 841 s cm^{-1}. ^1H NMR ($CDCl_3$, 500.14 MHz): $\delta = 0.49$ (d, $^5J_{H,P} = 1.5$ Hz, 9 H, $SiMe_3$), 1.19 (dt, 6 H, CH_2CH_3), 1.35 (m, 4 H, PCH_2), 1.86 (d, $^5J_{H,P} = 1.4$ Hz, $COCH_3$), 6.90–7.00 (m, 2 H_{Ph}), 7.32–7.43 (m, 3 H_{Ph}). MS (EI, 70 eV): *m/z* (%) = 308 (2), 307 (9), 306 (43) [all M^+], 217 (100). $C_{17}H_{27}OPSi$ (306.46): calcd C 66.63, H 8.88; found C 67.31, H 8.25.

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(9) Crystal data for **3b**: Triclinic, space group $P\bar{1}$, a = 9.432 (3), b = 9.611 (2), c = 12.548 (3) Å, α = 98.82 (3), β = 102.21 (3), γ = 101.69 (3); Z = 2, D_{calc} = 1.149 g·cm^{-3}. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-187712. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336033).

(10) Yield of crude **4a**,**b**: ~90%; since both compounds are extremely malodorous oils, we refrained from further purification. Data for **4a**: ^{1}H NMR (CDCl$_3$, 500.14 MHz): δ = 0.17 (s, SiMe$_3$), 5.33 (d, $^2J_{H,P}$ = 1.2 Hz, HCC≡C), 7.23–7.70 (m, 5 H$_{Ph}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 50.32 MHz): δ = 0.2 (s, SiMe$_3$), 64.4 (s, H*C*C≡C), 88.21 (d, $J_{C,P}$ = 10.6 Hz) and 88.63 (d, $J_{C,P}$ = 5.0 Hz) (*C*≡*C*). This product was isolated as a 6.2:1 mixture (^{31}P NMR) with **5a** [δ(^{1}H) = 0.43 (d, $^5J_{H,P}$ = 1.5, SiMe$_3$); δ(^{13}C) = 1.8 (d, $^4J_{C,P}$ = 9.1, SiMe$_3$), 198.0 ($^3J_{C,P}$ = 17.4, CHO); δ(^{31}P) = 3.4].

Data for **4b**: IR (film): 1679 m, 1599 m, 1251 vs, 1065 vs, 868 vs, 844 vs, 754 m cm^{-1}. ^{1}H NMR (CDCl$_3$, 200.13 MHz): δ = 0.16 (s, 9 H, SiMe$_3$), 0.90–1.15 (dt, 6 H, CH$_2$C*H*$_3$), 1.30–1.70 (m, 4 H, PCH$_2$), 4.78 (d, $J_{H,P}$ = 5.0 Hz, HCC≡C), 7.15–7.40 (m, 5 H$_{Ph}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 50.32 MHz): δ = 0.09 (s, SiMe$_3$), 9.85 and 9.95 (each d, $J_{C,P}$ = 15.1 Hz, CH$_2$CH$_3$), 16.4 (d, $J_{C,P}$ = 15.1 Hz, PCH$_2$), 16.7 (d, $J_{C,P}$ = 14.1 Hz, PCH$_2$), 61.9 (d, $J_{C,P}$ = 11.6 Hz, H*C*C≡C), 87.2 (s) and 87.9 (d, $J_{C,P}$ = 4.0 Hz) (*C*≡*C*). This product was isolated as a 94:6 mixture (^{31}P NMR) with **5b** [δ(^{1}H) = 0.32 (d, $^5J_{H,P}$ = 1.6 Hz, SiMe$_3$); δ(^{13}C) = 2.3 (d, $^4J_{C,P}$ = 10.7 Hz, SiMe$_3$)].

(11) Allene **6** was obtained as an oil (~97% purity by ^{31}P NMR) which could not be purified further by chromatography or vacuum distillation without decomposition. ^{1}H NMR (CDCl$_3$, 500.14 MHz): δ = 0.21 (s, 9 H, SiMe$_3$), 1.04 and 1.42 (each dt, 3 H, PCH$_2$CH$_3$), 1.58–1.74 (m, 4 H, PCH$_2$), 7.24–7.38 (m, 6 H$_{Ph}$), 7.61 (dd, 2 H$_{Ph}$), 7.64 (dd, 2H$_{Ph}$).

(12) **7**: colorless crystals, mp 89 °C. IR (KBr): 1688 (s, C=O), 1266 m, 1158 (s, P=O) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400.13 MHz): δ = 1.01 (dt, $^3J_{P,H}$ = 17.0 Hz, $^3J_{H,H}$ = 7.7 Hz, 3 H, CH$_2$C*H*$_3$), 1.23 (dt, $^3J_{P,H}$ = 17.2 Hz, $^3J_{H,H}$ = 7.7 Hz, 3 H, CH$_2$C*H*$_3$), 1.49–1.74 (m, 2 H, PCH$_2$), 1.84–2.05 (m, 2 H, PCH$_2$), 3.80 (m$_c$, 2 H, COCH$_2$), 3.95 (m$_c$, 1 H, PCH), 7.26–7.55 (m, 8 H$_{arom}$), 7.96 (dd, 2 H$_{arom}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 100.61 MHz): δ = 5.88/5.92 (2 d, $J_{P,C}$ = 44.3/44.3 Hz, PCH$_2$*C*H$_3$), 18.51/19.25 (2 overlapping d, PCH$_2$), 38.6 (s, COCH$_2$), 39.1 (d, $J_{P,C}$ = 61.4 Hz, *C*HPOEt$_2$), 127.2–137.5 (C$_{Ph}$), 196.9 (d, $J_{P,C}$ = 10.2 Hz, CO). ^{31}P (CDCl$_3$): δ = 54.8. $C_{19}H_{23}O_2P$ (314.36): calcd C 72.59, H 7.37; found C 72.82, H 7.51.

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(14) (*Z*)-**8**: Colorless oil. IR(film): 1669 (s, C=O), 1225 (s), 1174 (s, P=O) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400.13 MHz): δ = 1.14 (dt, $^3J_{P,H}$ = 17.4 Hz, $^3J_{H,H}$ = 7.7 Hz, 6 H, PCH$_2$C*H*$_3$), 1.80–1.97 (m, 4 H, POCH$_2$), 7.24 (d, $^3J_{P,H}$ = 30.5 Hz, 1 H, COCH=), 7.35–7.60 (3 m, 8 H$_{arom}$), 7.97–8.00 (dd, 2 H$_{arom}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 100.61 MHz): δ = 5.67 (d, $J_{P,C}$ = 5.3 Hz, PCH$_2$*C*H$_3$), 21.9 (d, $J_{P,C}$ = 69.1 Hz, PCH$_2$), 128.1–128.8 (several C), 133.8 (CH), 137.0, 138.8 (d, $J_{P,C}$ = 9.1 Hz), 142.3 ($J_{P,C}$ = 5.4 Hz, CO*C*H=), 145.8, 146.5, 192.9 (d, $J_{P,C}$ = 4.9 Hz, C=O). ^{31}P: δ = 46.4. $C_{19}H_{21}O_2P$ (312.35): calcd C 73.06, H 6.78; found C 72.68, H 6.94. (*E*)-**8**: Colorless crystals, mp 80 °C. IR (solid, ATR): 1659 (s, C=O), 1254 (s), 1188 (s, P=O) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400.13 MHz): δ = 1.25 (dt, $^3J_{P,H}$ = 16.9 Hz, $^3J_{H,H}$ = 7.6 Hz, 6 H, PCH$_2$C*H*$_3$), 1.67–1.86 (m, 4 H, POCH$_2$), 7.09–7.52 (4 m, 8 H$_{arom}$), 7.82 (d, $^3J_{P,H}$ = 17.8 Hz, 1 H, COCH=), 7.87 (dd, 2 H$_{arom}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 100.61 MHz): δ = 5.42 (d, $J_{P,C}$ = 5.7 Hz, PCH$_2$*C*H$_3$), 19.6 (d, $J_{P,C}$ = 69.8 Hz, PCH$_2$), 127.6–128.9 (several C), 133.5 (CH), 134.9 (d, $J_{P,C}$ = 9.1 Hz), 136.6, 140.3 ($J_{P,C}$ = 5.7 Hz, CO*C*H=), 145.8, 146.5, 191.9 (d, $J_{P,C}$ = 14.8 Hz, C=O). ^{31}P: δ = 44.2. $C_{19}H_{21}O_2P$ (312.35): calcd C 73.06, H 6.78; found C 73.11, H 6.83.