Organophosphorus Compounds; 72.[1] The Tri-*tert*-butylcyclopropenyl Group as a Steric Protecting Function for 1-Phosphaallenes

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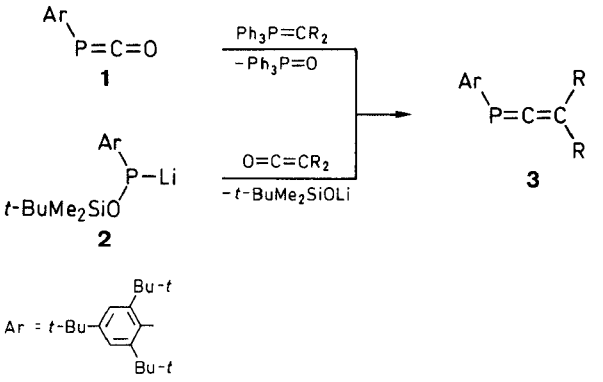
Dedicated to Professor O.J. Scherer on the occasion of his 60th birthday

When the tri-*tert*-butylcyclopropenylphosphane **5** is allowed to react with ketenes **6**, the cyclopropenyl(silyl)vinylphosphanes **7** are obtained. Subsequent acylation proceeds via silyl exchange to furnish the phosphanes **8** while methanolysis gives rise to the secondary phosphanes **9** by way of P/Si bond cleavage. Sodium hydroxide catalyzed elimination of hexamethyldisiloxane from **7** results in the formation of the 1-phosphaallenes **10**. The P/C double bonds of the latter can be saturated by either 1,2-addition (→ **11**, **12**) or by oxidative addition (→ **13**) followed by addition of water (→ **14**). Complexation of **10** with the metal fragments $W(CO)_5$ or $Fe(CO)_4$ moieties yields the novel metal complexes **15** and **16**.

A limited number of 1-phosphaallenes such as **3** have been reported in the literature since the middle of the 1980's.[2] Compounds of this type tend to undergo head-to-tail dimerization of their phosphaalkene bonds to form 2,4-bis(methylene)-1,3-diphosphetanes.[3] The heterocumulenes can, however, be isolated when the P/C double bond is shielded by the presence of a spatially demanding substituent such as the 2,4,6-tri-*tert*-butylphenyl group.



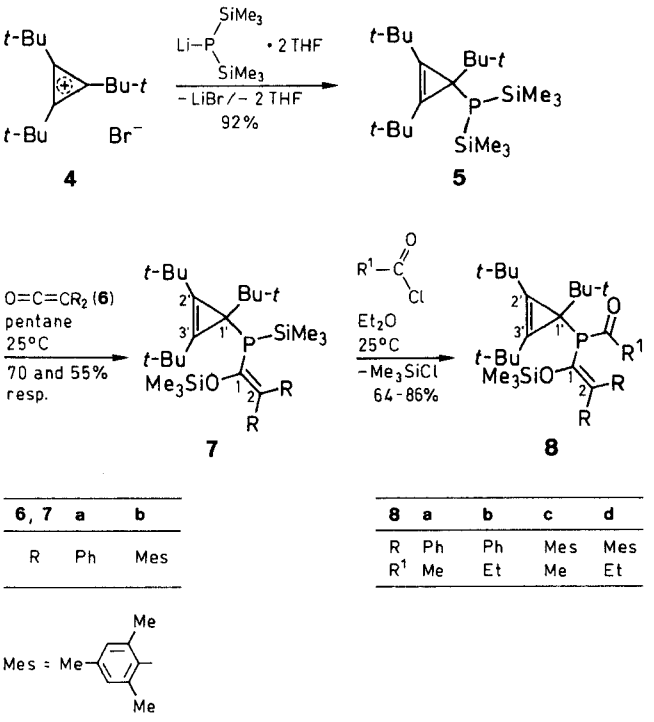
Scheme 1

Well-established synthetic methods are the Wittig reaction of the phosphaketene **1**[4] and the silanolate elimination from suitable precursors which can be obtained from, among others, the phosphides **2** and ketenes.[5] 1-Phosphaallenes of the type **3** have been prepared by these routes. The phosphorus analogue of the well-known, base-catalyzed isomerization of alkynes bearing hydrogen atoms in the 3-position to allenes[6] may also be employed for the preparation of 1-phosphaallenes. Hence, for example, the "phosphapropargyl rearrangement" of (2,4,6-tri-*tert*-butylphenyl)phenylethynylphosphane can be realized with basic aluminum oxide and furnishes the 1-phosphaallene **3** (Ar = 2,4,6-tri-*t*-BuC_6H_2, R = H, R = Ph).[7]

In the present work, we have examined the question of whether a tri-*tert*-butylcyclopropen-1-yl group bonded to phosphorus is able to prevent the P/C double bond of 1-phosphaallenes from undergoing dimerization, as has been previously demonstrated for phosphaalkenes.[8]

Preparation of the Alkenyl(cyclopropenyl)silylphosphanes 7a and b

Starting material for our synthesis of 1-phosphaallenes bearing tri-*tert*-butylcyclopropen-1-yl groups **10** was the cyclopropenylium salt **4**[9] which reacted smoothly with lithiated bis(trimethylsilyl)phosphane[10] to furnish the cyclopropenylbis(trimethylsilyl)phosphane **5**.[8] The decisive step for the further course of the planned reaction is the insertion of diphenyl- or bis(mesityl)ketene **(6a,b)** into the P/Si bond of **5**. This was achieved by reaction of **5** with **6** in pentane at room temperature and furnished **7a** and **b** in good yields. A repetition of the reaction on the still intact P/Si bond of **7**, as has been observed in the case of (2,4,6-tri-*tert*-butylphenyl)bis(trimethylsilyl)phosphane,[3] did not occur. In this context, it should also be mentioned that electron-poor acetylenes also undergo insertion into the P/Si bond of **5**.[11]



Scheme 2

The alkenyl(cyclopropenyl)silylphosphanes **7a** and **b** were obtained as crystalline compounds and gave satisfactory elemental analyses. The *O*-silyl groups appeared as singlets at δ = 0.17 and 0.14, respectively, in the ^{1}H NMR spectra while the *P*-silyl groups appeared as doublets at δ = 0.70 and 0.69 with $^3J_{H,P}$ coupling constants of 4.8 and 4.9 Hz, respectively. For both compounds, three magnetically different *tert*-butyl groups were observed which is indicative of hindered

rotation about the bond between the phosphorus atom and the three-membered ring. We did not investigate this phenomenon further as it is not relevant for our synthetic objective. As was expected, the ^{13}C NMR data of the cyclopropenyl units of **7a** and **b** hardly differed from those of **5**.[8] The sp^3-hybridized carbon atoms of the three-membered ring (δ = 45.6 and 46.0, respectively) exhibited typical $^1J_{C,P}$ coupling constants of 30.7 and 32.5 Hz. The ^{13}C NMR spectra also provided evidence that one of the trimethylsilyl groups had migrated: this resonated in both cases as a singlet at δ = 2.9 while the *P*-trimethylsilyl groups each occurred as a doublet at lower field (δ = 3.9 and 4.0, $^2J_{C,P}$ = 15.9 and 15.0 Hz, respectively). The assignment of the olefinic carbon atoms in the three-membered ring was based on a comparison with C2′ and C3′ of **5**.[8] The vinyl carbon atoms C1 and C2 were unambiguously identified by the magnitudes of their couplings with phosphorus. These are for C1 (δ = 153.1 and 152.0) 51.8 and 51.0 Hz, respectively, while those for C2 (δ = 137.3 and 137.0) are, as expected, markedly smaller (38.8 and 40.0 Hz, respectively). In comparison with **5**, the phosphorus resonances of **7a** and **b** have experienced strong shifts to lower field.

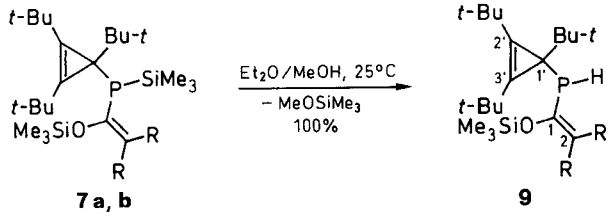
Acylation and Methanolysis of 7a and b

The ready cleavage of the phosphorus/silicon bond and the high bond dissociation energy of the silicon/halogen bond permit the condensation of **7a** and **b** with acyl chlorides[12] and provide additional, chemical indications for the structures of the resultant alkenyl(cyclopropenyl)silylphosphanes.

When acetyl or propionyl chloride was added to a pentane solution of **7a** or **b**, the acyl(alkenyl)cyclopropenylphosphanes **8a–d** were formed with concomitant cleavage of chlorotrimethylsilane.

The deshielding effect of the carbonyl groups on the phosphorus atoms is reflected in the ^{31}P NMR spectra of **8a–d** by large shifts to lower field (**7a,b**: δ = −38.2 and −40.1; **8a–d**: δ = +35.7 to +40.2). The replacement of the trimethylsilyl groups in **7a** and **b** by acyl groups can also be recognized by the disappearance of the $PSiMe_3$ signals in the ^1H NMR spectra of **8a–d**; instead, the CH_2 and/or CH_3 signals of the acyl groups are observed and the proximity of these atoms to phosphorus is documented by $^3J_{H,P}$ couplings of 5.0 to 8.0 Hz. The doublet of the $PSiMe_3$ group is also absent in the ^{13}C NMR spectra of **8a–d** and is replaced by low field signals for the carbonyl carbon atoms (δ = 219.5 to 225.1) with $^1J_{C,P}$ couplings of 39.0–45.0 Hz. The only slightly smaller $^2J_{C,P}$ coupling constants of the carbon atoms attached to the carbonyl group (δ = 34.0 to 40.8, $^2J_{C,P}$ = 35.0–39.0 Hz) are worthy of note. The remaining spectroscopic data require no interpretation and are very similar to those of **7a** and **b**.

The solvolytic elimination of the trimethylsilyl groups bonded to phosphorus in **7a** and **b** further illustrates the ready cleavage of the P/Si bond. Thus **7a** and **b** were converted quantitatively into the secondary phosphanes **9a** and **b** by treatment with an excess of methanol in diethyl ether. The $SiMe_3/H$ exchange is immediately apparent from the NMR spectra: PH signals at δ = 4.50 or 4.48, respectively, with coupling constants of 210 and 219 Hz are observed in the ^1H NMR spectra; the $^1H/^{31}P$ interactions are, of course, also visible in the ^{31}P NMR spectra (see experimental section).

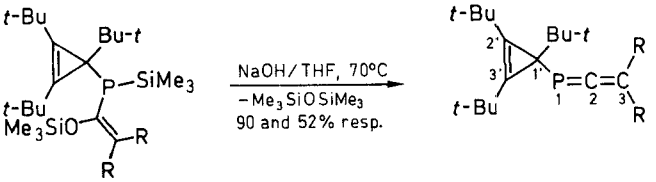


9	a	b
R	Ph	Mes

Scheme 3

The 1-Phosphaallenes 10a and b

The elimination of hexamethyldisiloxane plays a major role in the synthetic chemistry of phosphaalkenes,[13] phosphacumulenes,[2] and phosphaalkynes.[14,15] The reactions are usually catalyzed by sodium hydroxide. In the case of the reactions **7a,b** → **10a,b**, higher temperatures and, above all, the use of tetrahydrofuran as solvent – in addition to the large surface area of the sodium hydroxide catalyst (achieved by melting under high vacuum in a pressure Schlenk tube) – have proved to be advantageous. The 1-phosphaallenes were obtained in the form of yellow, air-stable crystals. The steric shielding by the tri-*tert*-butylcyclopropenyl group efficiently prevents the feasible dimerization and is also responsible for the fact that these heterocumulenes are even stable towards protic nucleophiles such as methanol at room temperature.



10	a	b
R	Ph	Mes

Scheme 4

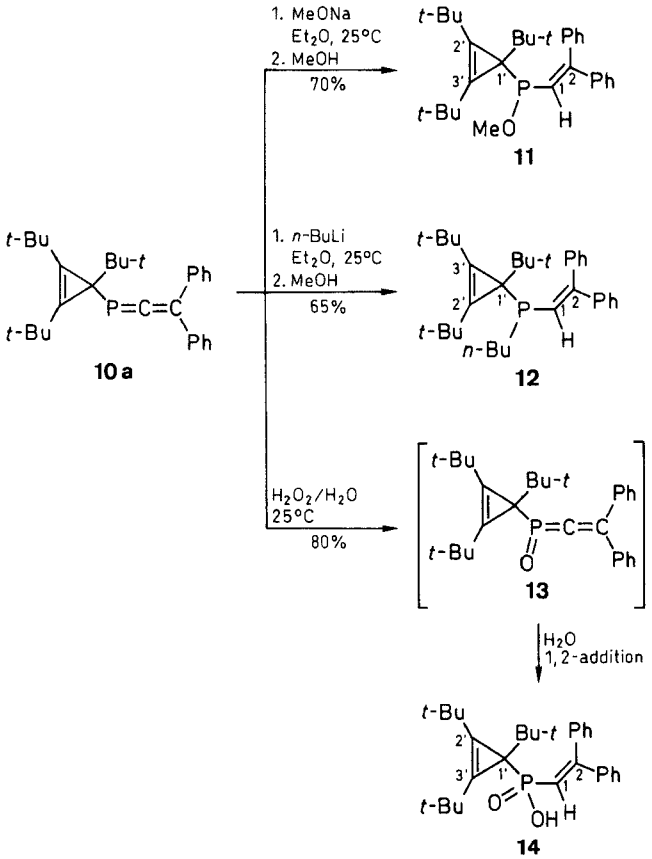
^{31}P NMR spectroscopic monitoring of the elimination reactions reveals their highly selective nature: the conversion from $\lambda^3\sigma^3$- to $\lambda^3\sigma^2$-phosphorus in the reactions **7a,b** → **10a,b** is reflected by the low field shifts of the ^{31}P NMR signals of the two 1-phosphaallenes (δ = 92.7 and 93.2, respectively). The elimination of hexamethyldisiloxane is apparent in the ^1H NMR spectra by the absence of trimethylsilyl signals and the lack of hindrance to rotation of the cyclopropenyl group about the P/C bond which is apparent by the appearance of only two signals in a ratio of 1 : 2 are seen for the *tert*-butyl groups

in **10a** and **b** as compared to the three signals in **7a** and **b**. The ^{13}C NMR resonances of the allene carbon atoms are characteristic for the heterocumulene arrangement of the target molecules: atoms C2 absorb at very low field (δ = 241.0 and 243.2, respectively), which is not unusual for phosphaalkene units, and exhibit $^{1}J_{C,P}$ coupling constants of 24.4 and 28.0 Hz while, on the other hand, atoms C3 give signals in the typical allene region (δ = 134.3 and 127.5, $^{2}J_{C,P}$ = 18.3 and 10.8 Hz, respectively).

The crystal structure analysis[16] performed on **10a** confirms, in principle, the 1-phosphaallene arrangement but the poor quality of the data set and the non-localizable disorder of the *tert*-butyl groups in the molecule (r = 0.14) are not amenable to a discussion of the structure or a deposition of the data.

1,2-Addition and Oxidative Addition to the Phosphaallene 10a

Predictions about the reactivity of the parent compound 1-phosphaallene (**10**; R = H as well as H in place of the cyclopropenyl group) can be deduced from quantum chemical investigations.[17] In addition to the P/C and C/C double bonds, the phosphorus atom itself is also a possible third reactive center and, indeed, reactions have been realized at the first and third locations. The calculations clearly reveal that the phosphaalkene increment is more reactive as compared to the alkene unit. The phosphorus atom possesses a positive partial charge while the α-carbon atom has a negative partial charge.[17]



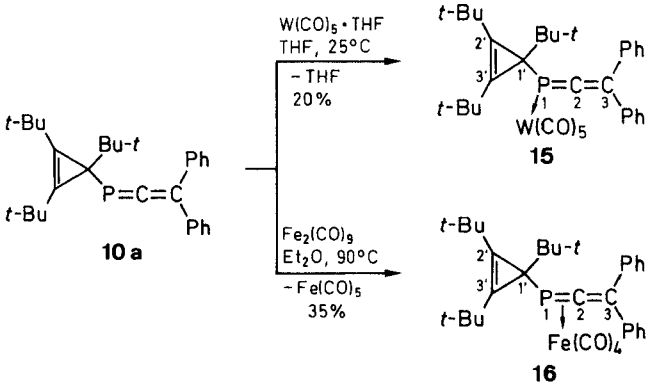
Scheme 5

As mentioned above, methanol does not undergo addition to **10a**; in contrast, the considerably more nucleophilic sodium methoxide does react with the 1-phosphaallene **10a** to furnish, after solvolysis with methanol, the methyl phosphinite **11**. Thus, the orientation of the 1,2-addition is in exact harmony with the predictions. This is also the case in the reaction of **10a** with butyllithium and subsequent methanolysis, the phosphane **12** being the product. Finally, the oxidative addition of "oxygen" via treatment with aqueous hydrogen peroxide and subsequent addition of water produces the phosphinic acid **14** with retention of the original regiochemistry. It may be assumed that, in view of the confirmed resistance of **10a** to solvolysis (see above), oxidative addition of oxygen occurs initially to furnish the highly reactive oxovinylidenephosphorane **13** as the putative intermediate.[18] It is known, at least for methyleneoxophosphoranes [which occur as highly reactive intermediates in Wolff-analogous rearrangements of (α-diazoalkyl)phosphane oxides],[18]that they can add water (as well as other nucleophiles) to yield phosphinic acids and derivatives thereof.[19]

As expected, the transitions from $\lambda^3\sigma^2$-phosphorus in **10a** to $\lambda^3\sigma^3$-phosphorus in **11** (δ = 136.1) and **12** (δ = −30.1) or to $\lambda^5\sigma^4$-phosphorus in **14** (δ = +43.0) are apparent in the ^{31}P NMR spectra. The ^{1}H NMR spectra of **11** and **14** exhibit MeO or HO resonances with coupling to the heteronucleus ($^{3}J_{H,P}$ = 12.0 Hz in the case of **11**). The ultimate proton addition to the sp-hybridized carbon atom of the 1-phosphaallene **10a** is confirmed both by the appearance of doublet signals for the olefinic hydrogen atoms in the ^{1}H NMR spectra and of olefinic carbon signals with $^{1}J_{C,P}$ couplings in the ^{13}C NMR spectra of **11**, **12**, and **14** (see experimental section).

The 1-Phosphaallene Metal Complexes 15 and 16

Previously, both η^2-coordination [$Pt(PR_3)_2$(RP=C=CPh_2)][20] and η^1-ligand bonding [$Ni(CO)_3$(RP=C=CPh)][21] have been realized in transition metal complexes of 1-phosphaallenes. The P=C increment is exclusively involved in both types of coordination. Complexations of $W(CO)_5$ and $Fe(CO)_4$ groups to **10a** gave rise to similar results.



Scheme 6

When the 1-phosphaallene **10a** in tetrahydrofuran was allowed to react with an equimolar amount of

$W(CO)_5 \cdot THF$,[22] the complex **15** was isolated as a yellow-brown resin after column chromatography. The heterocumulene is coordinated through the lone electron pair at phosphorus to the tungsten pentacarbonyl unit in an "end-on" orientation.

Even though the metal complex **15** could not be obtained completely free of tungsten hexacarbonyl [the starting material for the generation of $W(CO)_5 \cdot THF$], the spectroscopic data do permit an unambiguous structure elucidation. They are very similar to those of the uncomplexed 1-phosphaallene **10a** and this is compatible with an "end-on" but not a "side-on" coordination (see also complex **16**). Thus, both the phosphorus (**10a**: $\delta = 92.7$; **15**: $\delta = 81.7$) and the carbon C2 (**10a**: $\delta = 241.0$; **15**: $\delta = 226.3$) atoms experience only relatively minor diamagnetic shifts. The $^1J_{P,W}$ coupling constant of 111 Hz is also in favor of the above-described coordination of the metal fragment.

Interestingly, the coordination of the $Fe(CO)_4$ fragment to the 1-phosphaallene **10a** does not occur in the same way as described above for the $W(CO)_5$ ligand. When **10a** was allowed to react with diiron nonacarbonyl, the analytically characterized metal complex **16** was obtained after column chromatographic work-up. The following spectroscopic observations are in favor of the η^2-coordination of the metal to the P/C double bond. The ^{31}P NMR signal of the phosphorus nucleus in **16** is dramatically shifted to higher field (by ca. 197 ppm) relative to that of **10a** (see experimental section); this reflects the "side-on" coordination.[20] Also, the relatively high field position of the ^{13}C NMR signal of the phosphaalkene carbon atom ($\delta = 156.8$, $^1J_{C,P} = 26.5$ Hz) is only compatible with the structural type **16**.

Melting points were determined with a Mettler FP 61 apparatus (heating rate: 2°C/min). Microanalyses were performed with a Perkin-Elmer 397 apparatus. Compounds **7a,b, 8a–d, 9a,b, 10a,b, 11, 12, 14** and **16** gave C, H ± 0.3% except **8b**, H–0.33 and **16**, C–0.32%. ^1H NMR spectra were recorded on Varian EM 360, Varian EM 390, and Bruker WP 200 spectrometers with tetramethylsilane as internal standard, ^{13}C NMR spectra were measured on Bruker WP 200 and Bruker AM 400 spectrometers with tetramethylsilane as internal standard, and ^{31}P NMR spectra using Bruker WP 200 and Bruker AM 400 spectrometers with 85% orthophosphoric acid as external standard. All reactions were carried out under argon (Schlenk tube technique); prior to use, the reaction vessels were evacuated, baked out, and purged with argon. The solvents used were anhydrous and were distilled and stored under argon prior to use.

Alkenyl(cyclopropenyl)silylphosphanes 7a and b; General Procedure:

The phosphane **5**[8] (580 mg, 1.5 mmol) was dissolved in pentane (20 mL) in a pressure Schlenk tube, the ketene **6a**[23] or **6b**[24] (1.5 mmol) was added, and the mixture stirred for 12 h at r.t. After evaporation of the mixture at 30°C/10^{-3} mbar, the residue was recrystallized from pentane at −78°C.

(2,2-Diphenyl-1-trimethylsiloxyvinyl)(1,2,3-tri-tert-butylcyclopropenyl)trimethylsilylphosphane (**7a**):

Yield: 610 mg (70%); colorless crystals; mp 54°C.

IR (KBr): ν = 2950, 2900, 2860, 1655, 1450, 1335, 1250, 1020, 850 cm^{-1}.

^1H NMR (C_6D_6): δ = 0.14 [s, 9H, $OSi(CH_3)_3$], 0.70 [d, $^3J_{H,P}$ = 4.8 Hz, 9H, $PSi(CH_3)_3$], 1.25, 1.36, 1.52 [each s, each 9H, $C(CH_3)_3$], 7.1–7.3 and 7.4–7.5 (m, 10 H_{arom}).

^{13}C NMR (C_6D_6): δ = 2.9 [s, $OSi(CH_3)_3$], 3.9 [d, $^2J_{C,P}$ = 15.9 Hz, $PSi(CH_3)_3$], 30.9, 31.7, 31.9 [each s, $C(CH_3)_3$], 31.8 [s, $C(CH_3)_3$], 38.6 [d, $^2J_{C,P}$ = 13.0 Hz, $C(CH_3)_3$], 45.6 (d, $^1J_{C,P}$ = 30.7 Hz, C1'), 126.0–132.2 (C_{arom}), 130.6 (d, $^2J_{C,P}$ = 14.1 Hz, C2'/C3'), 137.3 (d, $^2J_{C,P}$ = 38.8 Hz, C2), 143.2 (d, $^3J_{C,P}$ = 9.6 Hz, $C1_{arom}$), 144.5 (d, $^3J_{C,P}$ = 10.0 Hz, $C1_{arom}$), 153.1 (d, $^1J_{C,P}$ = 51.8 Hz, C1).

^{31}P NMR (C_6D_6): δ = −38.2.

(2,2-Dimesityl-1-trimethylsiloxyvinyl)(1,2,3-tri-tert-butylcyclopropenyl)trimethylsilylphosphane (**7b**):

Yield: 540 mg (55%); colorless crystals; mp 67°C.

IR (KBr): ν = 2950, 2900, 2865, 1660, 1440, 1330, 1010 cm^{-1}.

^1H NMR (C_6D_6): δ = 0.14 [s, 9H, $OSi(CH_3)_3$], 0.69 [d, $^3J_{H,P}$ = 4.9 Hz, 9H, $PSi(CH_3)_3$], 1.25, 1.37, 1.52 [each s, each 9H, $C(CH_3)_3$], 2.14, 2.16 (each s, each 3H, *p*-CH_3), 2.67, 2.69 (each s, each 6H, *o*-CH_3), 6.88, 6.90 (each s, each 2H, *m*-H_{arom}).

^{13}C NMR (C_6D_6): δ = 2.9 [s, $OSi(CH_3)_3$], 4.0 [d, $^2J_{C,P}$ = 15.0 Hz, $PSi(CH_3)_3$], 21.0, 22.0 (each, s, *p*-CH_3), 25.0, 25.1 (each s, *o*-CH_3), 30.8, 31.7 [each s, $C(CH_3)_3$], 31.8 [s, $C(CH_3)_3$], 38.5 [d, $^2J_{C,P}$ = 12.0 Hz, $C(CH_3)_3$], 46.0 (d, $^1H_{C,P}$ = 32.5 Hz, C1'), 125.0–132.0 (C_{arom}), 130.5 (d, $^2J_{C,P}$ = 13.0 Hz, C2'/C3'), 130.0–135.0 (C_{arom}), 137.0 (d, $^2J_{C,P}$ = 40.0 Hz, C2), 142.0 (d, $^3J_{C,P}$ = 10.0 Hz, $C1_{arom}$), 144.0 (d, $^3J_{C,P}$ = 9.0 Hz, $C1_{arom}$), 152.0 (d, $^1J_{C,P}$ = 51.0 Hz, C1).

^{31}P NMR (C_6D_6): δ = −40.1.

Acyl(alkenyl)cyclopropenylphosphanes 8a–d; General Procedure:

To a solution of **7a** or **7b** (1 mmol) in pentane (5 mL) was added the acyl chloride (1 mmol). The mixture was stirred at room temperature and then concentrated at 30°C/10^{-3} mbar. The residue was allowed to stand at −78°C whereupon the analytically pure product separated out.

Acetyl(2,2-diphenyl-1-trimethylsiloxyvinyl)(1,2,3-tri-tert-butylcyclopropenyl)phosphane (**8a**):

Reaction time: 30 min; yield: 430 mg (86%); colorless crystals; mp 70°C.

IR (KBr): ν = 2950, 2890, 1655, 1435, 1250, 1195, 1120, 850, 700 cm^{-1}.

^1H NMR (C_6D_6): δ = 0.17 [s, 9H, $OSi(CH_3)_3$], 1.41 [s, 9H, $C(CH_3)_3$], 1.43 [s, 18H, $C(CH_3)_3$], 2.60 (d, $^3J_{H,P}$ = 8.0 Hz, 3H, $COCH_3$), 7.13–7.63 (m, 10 H_{arom}).

^{13}C NMR (C_6D_6): δ = 1.8 [s, $OSi(CH_3)_3$], 30.6, 30.8 [each s, $C(CH_3)_3$], 31.7 [s, $C(CH_3)_3$], 34.0 (d, $^1J_{C,P}$ = 39.0 Hz, $COCH_3$), 39.1 [d, $^2J_{C,P}$ = 20.2 Hz, $C(CH_3)_3$], 45.2 (d, $^1J_{C,P}$ = 35.5 Hz, C1'), 127.1–132.5 (C_{arom}, C2'/C3'), 141.2 (d, $^2J_{C,P}$ = 37.0 Hz, C2), 142.3 (d, $^3J_{C,P}$ = 9.2 Hz, $C1_{arom}$), 143.0 (d, $^3J_{C,P}$ = 8.3 Hz, $C1_{arom}$), 151.5 (d, $^1J_{C,P}$ = 39.3 Hz, C1), 220.6 (d, $^1J_{C,P}$ = 41.0 Hz, CO).

^{31}P NMR (C_6D_6): δ = 39.3.

(2,2-Diphenyl-1-trimethylsiloxyvinyl)propionyl(1,2,3-tri-tert-butylcyclopropenyl)phosphane (**8b**):

Reaction time: 6 h; yield: 450 mg (80%); colorless crystals; mp 74°C.

IR (KBr): ν = 2940, 2880, 2850, 1640, 1430, 1350, 1240, 1190, 1110, 835, 755 cm^{-1}.

^1H NMR (C_6D_6): δ = 0.22 [s, 9H, $OSi(CH_3)_3$], 1.40 [s, 9H, $C(CH_3)_3$], 1.40 (t, $^3J_{H,H}$ = 4.8 Hz, 3H, CH_2CH_3), 1.43][s, 18H, $C(CH_3)_3$], 3.12 (dq, $^3J_{H,H}$ = 4.8 Hz, $^3J_{H,P}$ = 5.7 Hz, 3H, CH_2CH_3), 7.16–7.67 (m, 10 H_{arom}).

^{13}C NMR (C_6D_6): δ = 1.8 [s, $OSi(CH_3)_3$], 9.0 (d, $^3J_{C,P}$ = 4.7 Hz, CH_2CH_3), 30.7, 30.9 [each s, $C(CH_3)_3$], 31.8 [s, $C(CH_3)_3$], 39.1 [d, $^2J_{C,P}$ = 19.6 Hz, $C(CH_3)_3$], 39.3 (d, $^2J_{C,P}$ = 38.6 Hz, CH_2CH_3), 45.1 (d, $^1J_{C,P}$ = 36.4 Hz, C1'), 127.1–132.5 (C_{arom}, C2'/C3'), 141.0 (d, $^2J_{C,P}$ = 37.4 Hz, C2), 141.7 (d, $^3J_{C,P}$ = 9.1 Hz, $C1_{arom}$), 142.6 (d, $^3J_{C,P}$ = 9.1 Hz, $C1_{arom}$), 151.0 (d, $^1J_{C,P}$ = 40.8 Hz, C1), 223.0 (d, $^1J_{C,P}$ = 44.0 Hz, CO).

^{31}P NMR (C_6D_6): δ = 35.7.

Acetyl(2,2-dimesityl-1-trimethylsiloxyvinyl)(1,2,3-tri-tert-butylcyclopropenyl)phosphane (**8c**):

Reaction conditions: 24 h/50°C; yield: 400 mg (64%); colorless crystals; mp 78°C.

IR (KBr): ν = 2960, 2900, 2890, 1450, 1440, 1195, 1130, 900, 850 cm^{-1}.

^1H NMR (C_6D_6): δ = 0.19 [s, 9H, $OSi(CH_3)_3$], 1.42 [s, 9H, $C(CH_3)_3$], 1.44 [s, 18H, $C(CH_3)_3$], 2.20, 2.23 (each s, each 3H, *p*-CH_3), 2.60, 2.65 (each s, each 6H, *o*-CH_3), 2.66 (d, $^3J_{H,P}$ = 8.0 Hz, 3H, $COCH_3$), 6.95 (m, 4 H_{arom}).

^{13}C NMR (C_6D_6): δ = 1.8 [s, $OSi(CH_3)_3$], 21.5, 21.9 (each s, *p*-CH_3), 25.5, 25.9 (each s, *o*-CH_3), 30.8, 30.9 [each s, $C(\underline{C}H_3)_3$], 31.5 [s, $\underline{C}(CH_3)_3$], 34.9 (d, $^2J_{C,P}$ = 35.0 Hz, $CO\underline{C}H_3$), 41.2 [d, $^2J_{C,P}$ = 23.0 Hz, $\underline{C}(CH_3)_3$], 45.1 (d, $^1J_{C,P}$ = 24.0 Hz, C1'), 128.1–134.3 (C_{arom}, C2'/C3'), 140.8 (d, $^2J_{C,P}$ = 35.0 Hz, C2), 143.2 (d, $^3J_{C,P}$ = 9.5 Hz, $C1_{arom}$), 144.1 (d, $^3J_{C,P}$ = 8.5 Hz, $C1_{arom}$), 152.1 (d, $^1J_{C,P}$ = 35.0 Hz, C1), 219.5 (d, $^1J_{C,P}$ = 39.0 Hz, CO).

^{31}P NMR (C_6D_6): δ = 40.2.

(2,2-Dimesityl-1-trimethylsiloxyvinyl)propionyl(1,2,3-tri-tert-butylcyclopropenyl)phosphane **(8d)**:

Reaction conditions: 48 h/50 °C; yield: 440 mg (69 %); colorless crystals; mp 81 °C.

IR (KBr): ν = 2940, 2870, 1650, 1540, 1420, 1360, 1250, 1195, 1120, 840, 760 cm^{-1}.

^1H NMR (C_6D_6): δ = 0.18 [s,9H, $OSi(CH_3)_3$], 1.39 [s, 9H, $C(CH_3)_3$], 1.40 (t, $^3J_{H,H}$ = 5.0 Hz, 3H, $CH_2\underline{C}H_3$), 1.42 [s, 18H, $C(CH_3)_3$], 2.25, 2.28 (each s, each 3H, *p*-CH_3), 2.65, 2.69 (each s, each 6H, *o*-CH_3), 3.20 (dq, $^3J_{H,H}$ = 5.0 Hz, $^3J_{H,P}$ = 7.0 Hz, 2H, $C\underline{H}_2CH_3$), 7.10 (br s, 4 H_{arom}).

^{13}C NMR (C_6D_6): δ = 1.6 [s, $OSi(CH_3)_3$], 8.6 (d, $^3J_{C,P}$ = 4.0 Hz, $CH_2\underline{C}H_3$), 21.1, 21.4 (each s, *p*-CH_3), 25.3, 25.6 (each s, *o*-CH_3), 30.5, 32.0 [each s, $C(\underline{C}H_3)_3$], 32.2 [s, $\underline{C}(CH_3)_3$], 38.9 [d, $^2J_{C,P}$ = 22.0 Hz, $\underline{C}(CH_3)_3$], 40.8 (d, $^2J_{C,P}$ = 37.5 Hz, $\underline{C}H_2CH_3$), 46.0 (d, $^1J_{C,P}$ = 36.5 Hz, C1'), 126.5–133.0 (C_{arom}, C2'/C3'), 139.5 (d, $^2J_{C,P}$ = 35.0 Hz, C2), 139.8 (d, $^3J_{C,P}$ = 9.0 Hz, $C1_{arom}$), 140.9 (d, $^3J_{C,P}$ = 9.0 Hz, $C1_{arom}$), 152.3 (d, $^1J_{C,P}$ = 42.0 Hz, C1), 225.1 (d, $^1J_{C,P}$ = 45.0 Hz, CO).

^{31}P NMR (C_6D_6): δ = 38.5.

Alkenyl(cyclopropenyl)phosphanes 9a and b; General Procedure:

To a solution of **7a** or **7b** (1 mmol) in Et_2O (20 mL) was added MeOH (0.4 mL, 10 mmol) and, after 2 h, the mixture was evaporated at 25 °C/12 mbar. The products were obtained in quantitative yields and were recrystallized from pentane at −78 °C.

(2,2-Diphenyl-1-trimethylsiloxyvinyl)(1,2,3-tri-tert-butylcyclopropenyl)phosphane **(9a)**:

Colorless crystals; mp 67 °C.

IR (KBr): ν = 2970, 2900, 2860, 2300, 1630, 1450, 1330, 1020, 820 cm^{-1}.

^1H NMR (C_6D_6): δ = 0.12 [s, 9H, $OSi(CH_3)_3$], 1.18, 1.25, 1.37 [each s, each 9H, $C(CH_3)_3$], 4.50 (d, $^1J_{H,P}$ = 216 Hz, 1H, PH), 7.25 (br s, 10 H_{arom}).

^{13}C NMR (C_6D_6): δ = 1.0 [s, $OSi(CH_3)_3$], 30.7, 30.8, 31.2 [each s, $C(\underline{C}H_3)_3$], 31.7, 31.8 [each s, $\underline{C}(CH_3)_3$], 38.3 [d, $^2J_{C,P}$ = 24.1 Hz, $\underline{C}(CH_3)_3$], 42.8 (d, $^1J_{C,P}$ = 31.0 Hz, C1'), 126.0–132.4 (C_{arom}), 129.2 (d, $^2J_{C,P}$ = 4.7 Hz, C2'/C3'), 135.2 (d, $^2J_{C,P}$ = 11.8 Hz, C2), 142.0, 143.1 (each s, $C1_{arom}$), 153.6 (d, $^1J_{C,P}$ = 27.6 Hz, C1).

^{31}P NMR (C_6D_6): δ = 32.0 (d, $^1J_{P,H}$ = 210 Hz).

(2,2-Dimesityl-1-trimethylsiloxyvinyl)(1,2,3-tri-tert-butylcyclopropenyl)phosphane **(9b)**:

Colorless crystals; mp 75 °C.

IR (KBr): ν = 2960, 2900, 2850, 2300, 1640, 1320, 1000, 810 cm^{-1}.

^1H NMR (C_6D_6): δ = 0.13 [s, 9H, $OSi(CH_3)_3$], 1.20, 1.26, 1.37 [each s, each 9H, $C(CH_3)_3$], 2.15, 2.17 (each s, each 3H, *p*-CH_3), 2.73, 2.76 (each s, each 6H, *o*-CH_3), 4.48 (d, $^1J_{H,P}$ = 219 Hz, 1H, PH), 6.90, 6.95 (each s, each 2 H_{arom}).

^{13}C NMR (C_6D_6): δ = 1.2 [s, $OSi(CH_3)_3$], 21.3, 22.0 (each s, *p*-CH_3), 25.5, 25.8 (each s, *o*-CH_3), 30.3, 30.6, 31.9 [each s, $C(\underline{C}H_3)_3$], 32.5, 377 [each s, $\underline{C}(CH_3)_3$], 39.4 [d, $^2J_{C,P}$ = 23.0 Hz, $\underline{C}(CH_3)_3$], 43.5 (d, $^1J_{C,P}$ = 28.0 Hz, C1'), 126.0–134.1 (C_{arom}, C2'/C3'), 136.5 (d, $^2J_{C,P}$ = 13.0 Hz, C2), 143.0, 143.5 (each s, $C1_{arom}$), 155.2 (d, $^1J_{C,P}$ = 28.1 Hz, C1).

^{31}P NMR (C_6D_6): δ = −35.2 (s, $^1J_{P,H}$ = 219 Hz).

1-Phosphaallenes 10a and b; General Procedure:

Two NaOH pellets were melted under high vacuum in a pressure Schlenk tube. A solution of **7a** or **b** (0.5 mmol) in THF (5 mL) was then added and the mixture stirred for 24 or 62 h at 70 °C. Evaporation at 40 °C/10^{-3} mbar gave the crude products.

3,3-Diphenyl-1-(1,2,3-tri-tert-buylcyclopropenyl)-1-phosphaallene **(10a)**:

Recrystallization from pentane at −78 °C gave yellow, cubic crystals; yield: 190 mg (90 %), mp 96 °C.

IR (KBr): ν = 2965, 2890, 2860, 1670, 1600, 1490, 1475, 1460, 1445, 1390, 1360, 1070, 1030, 770, 750, 700 cm^{-1}.

^1H NMR (C_6D_6): δ = 1.30 [s, 9H, $C(CH_3)_3$], 1.32 [s, 18H, $C(CH_3)_3$], 7.07–7.37 and 7.62–7.78 (m, 10 H_{arom}).

^{13}C NMR (C_6D_6): δ = 30.1 [d, $^3J_{C,P}$ = 3.5 Hz, $C(\underline{C}H_3)_3$], 30.6 [s, $C(\underline{C}H_3)_3$], 31.7 [s, $\underline{C}(CH_3)_3$], 37.6 [d, $^2J_{C,P}$ = 18.1 Hz, $\underline{C}(CH_3)_3$], 48.2 (d, $^1J_{C,P}$ = 61.3 Hz, C1'), 127.5 (d, $^2J_{C,P}$ = 10.8 Hz, C3), 127.3–128.6 (C_{arom}, C2'/C3'), 136.5 (d, $^3J_{C,P}$ = 8.9 Hz, $C1_{arom}$), 241.0 (d, $^1J_{C,P}$ = 24.4 Hz, C2).

^{31}P NMR (C_6D_6): δ = 92.7.

3,3-Dimesityl-1-(1,2,3-tri-tert-butylcyclopropenyl)-1-phosphaallene **(10b)**:

Column chromatography on silica gel with pentane (and, if necessary recrystallization from the same solvent) gave yellow crystals; yield: 140 mg (52 %), mp 99 °C.

IR (KBr): ν = 2980, 2880, 2870, 1650, 1600, 1480, 1475, 1460, 1390, 1350, 1070, 780, 760, 700 cm^{-1}.

^1H NMR (C_6D_6): δ = 1.32 [s, 9H, $C(CH_3)_3$], 1.35 [s, 18H, $C(CH_3)_3$], 2.15 (s, 6H, *p*-CH_3), 2.60 (s, 12H, *o*-CH_3), 6.80 (br s, 4 H_{arom}).

^{13}C NMR (C_6D_6): δ = 20.5 (s, *p*-CH_3), 24.9 (s, *o*-CH_3), 30.2 [d, $^3J_{C,P}$ = 3.0 Hz, $C(\underline{C}H_3)_3$], 30.5 [s, $C(\underline{C}H_3)_3$], 31.2 [s, $\underline{C}(CH_3)_3$], 35.9 [d, $^2J_{C,P}$ = 19.5 Hz, $\underline{C}(CH_3)_3$], 46.5 (d, $^1J_{C,P}$ = 64.0 Hz, C1'), 126.2–130.8 (C_{arom}, C3, C2'/C3'), 135.4 (d, $^3J_{C,P}$ = 10.0 Hz, $C1_{arom}$), 243.4 (d, $^1J_{C,P}$ = 28.0 Hz, C2).

^{31}P NMR (C_6D_6): δ = 93.2.

Methyl (2,2-Diphenylvinyl)(1,2,3-tri-*tert*-butylcyclopropenyl)phosphinite (11):

To a solution of **10a** (300 mg, 0.7 mmol) in Et_2O (10 mL) was added with stirring sodium methoxide (475 mg, 7.0 mmol). After 1 h, MeOH (3 mL) was added and the mixture evaporated at 25 °C/12 mbar. Column chromatography of the residue on silica gel with pentane gave the product as a colorless oil; yield: 220 mg (70 %).

^1H NMR (C_6D_6): δ = 1.00 [s, 18H, $C(CH_3)_3$], 1.20 [s, 9H, $C(CH_3)_3$], 3.00 (d, $^3J_{H,P}$ = 12.0 Hz, OCH_3), 6.51 (d, $^2J_{H,P}$ = 20.2 Hz, 1 H_{olefin}), 6.80–7.60 (m, 10 H_{arom}).

^{13}C NMR (C_6D_6): δ = 29.7, 30.1, 30.2 [each s, $C(\underline{C}H_3)_3$], 30.4, 30.6 [each s, $\underline{C}(CH_3)_3$], 37.1 [d, $^2J_{C,P}$ = 25.3 Hz, $\underline{C}(CH_3)_3$], 49.0 (d, $^2J_{C,P}$ = 21.2 Hz, C1'), 54.2 (d, $^2J_{C,P}$ = 10.6 Hz, OCH_3), 127.3–129.1 (C_{arom}, C2'/C3'), 134.3 (d, $^2J_{C,P}$ = 18.3 Hz, C2), 137.9, 139.8 (each s, $C1_{arom}$), 153.2 (d, $^1J_{C,P}$ = 15.4 Hz, C1).

^{31}P NMR (C_6D_6): δ = 136.1.

Butyl (2,2-Diphenylvinyl)(1,2,3-tri-*tert*-butylcyclopropenyl)phosphane (12):

To a solution of **10a** (350 mg, 0.8 mmol) in Et_2O (10 mL) was added a 1.6 N solution of butyllithium in hexane (0.75 mL, 1.2 mmol).[23] After 30 min, MeOH (3 mL) was added and the mixture evaporated at 25 °C/10^{-3} mbar. Column chromatography of the residue on silica gel eluting with pentane gave the product as a colorless oil; yield: 240 mg (65 %).

^1H NMR (C_6D_6): δ = 0.50–1.30 [m, 9H, $(CH_2)_3CH_3$], 0.80 [s, 9H, $C(CH_3)_3$], 0.95 [s, 18H, $C(CH_3)_3$], 6.30 (d, $^2J_{H,P}$ = 6.0 Hz, 1 H_{olefin}), 6.75–7.40 (m, 10 H_{arom}).

^{13}C NMR (C_6D_6): δ = 27.5–31.0 [m, $(CH_2)_3CH_3$], 30.9, 31.0, 31.4 [each s, $C(\underline{C}H_3)_3$], 31.6, 32.2 [each s, $\underline{C}(CH_3)_3$], 38.7 [d, $^2J_{C,P}$ = 33.1 Hz, $\underline{C}(CH_3)_3$], 42.1 (d, $^1J_{C,P}$ = 30.0 Hz, C1'), 127.6–128.8 (C_{arom}), 131.3 (d, $^2J_{C,P}$ = 4.0 Hz, C2'/C3'), 134.7 (d, $^2J_{C,P}$ = 22.0 Hz, C2), 142.2, 144.9 (each s, $C1_{arom}$), 153.7 (d, $^1J_{C,P}$ = 20.2 Hz, C1).

^{31}P NMR (C_6D_6): δ = −30.1.

(2,2-Diphenylvinyl)(1,2,3-tri-*tert*-butylcyclopropenyl)phosphinic Acid (14):

To a solution of **10a** (200 mg, 0.5 mmol) in Et_2O (5 mL) was added 30% aqueous hydrogen peroxide (0.2 mL, 1.8 mmol) and the mixture was stirred at r.t. for 3 h. After evaporation at 30 °C/12 mbar a yellow solid residue was obtained, yield: 180 mg (80%), mp 150 °C.

IR (KBr): ν = 3080, 3020, 2900, 2850, 2210, 1660, 1560, 1460, 1440, 1370, 1350, 1200, 900, 800, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.95 [s, 9 H, $C(CH_3)_3$], 1.15 [s, 18 H, $C(CH_3)_3$], 5.90 (br, 1 H, OH), 6.35 (d, $^2J_{H,P}$ = 40.0 Hz, 1 H_{olefin}), 7.10–7.90 (m, 10 H_{arom}).

^{13}C NMR (C_6D_6): δ = 31.1, 31.2 [each s, $C(\underline{C}H_3)_3$], 31.6 [s, $\underline{C}(CH_3)_3$], 35.4 [d, $^2J_{C,P}$ = 29.0 Hz, $\underline{C}(CH_3)_3$], 43.6 (d, $^1J_{C,P}$ = 30.0 Hz, C1'), 120.1–135.3 (C_{arom}, C2'/C3'), 143.8 (d, $^1J_{C,P}$ = 41.0 Hz, C1), 154.8 (s, C2).

^{31}P NMR (C_6D_6): δ = 43.0.

[3,3-Diphenylvinyl-(1,2,3-tri-*tert*-butylcyclopropenyl)-1-phosphaallene]pentacarbonyltungsten (15):

A solution of tungsten hexacarbonyl[23] (300 mg, 0.85 mmol) in THF (50 mL) was irradiated (Philips HPK 125 W mercury high-pressure lamp) until the ratio of $W(CO)_5 \cdot THF$ to $W(CO)_6$ and $W(CO)_4 \cdot (THF)_2$ was optimal (IR monitoring[22]). The phosphaallene **10a** (350 mg, 0.8 mmol) in THF (10 mL) was added and, after 2 h, the mixture evaporated at 35 °C/12 mbar. Column chromatography of the residue on silica gel eluting with petroleum ether (35–70 °C)/Et_2O (1:1) gave a yellow-brown resin which still contained some tungsten hexacarbonyl; yield: 120 mg (20%).

IR (film): ν = 3050, 2900, 2300, 2080, 1900, 1450, 1400, 1340, 1260, 1000, 810, 700, 640 cm^{-1}.

^{1}H NMR (C_6D_6): δ = 1.0 [s, 18 H, $C(CH_3)_3$], 1.1 [s, 9 H, $C(CH_3)_3$], 7.0–7.5 (m, 10 H_{arom}).

^{13}C NMR (C_6D_6): δ = 30.7, 31.2 [each s, $C(\underline{C}H_3)_3$], 31.8, 34.9 [each s, $\underline{C}(CH_3)_3$], 38.2 (d, $^1J_{C,P}$ = 30.0 Hz, C1'), 127.5–129.2 (C_{arom}, C3, C2'/C3'), 135.1 (d, $^3J_{C,P}$ = 18.0 Hz, $C1_{arom}$), 191.1 (s, *cis*-CO), 197.0 ($^2J_{C,P}$ = 7.1 Hz, *trans*-CO), 226.3 (d, $^1J_{C,P}$ = 18.0 Hz, C2).

^{31}P NMR (C_6D_6): δ = 81.7 (d, $^1J_{P,W}$ = 110.8 Hz).

[3,3-Diphenylvinyl-(1,2,3-tri-*tert*-butylcyclopropenyl)-1-phosphaallene]tetracarbonyliron (16):

To a suspension of diiron nonacarbonyl[23] (260 mg, 0.7 mmol) in pentane (5 mL) in a pressure Schlenk tube was added with stirring at r.t. a solution of the phosphaallene **10a** (300 mg, 0.7 mmol) in Et_2O (5 mL). The mixture was heated briefly on an oil bath at 90 °C until a clear solution had formed. The solution was allowed to cool to r.t., filtered, and the filtrate evaporated at 40 °C/12 mbar. The residue was purified by suspension in a small amount of pentane to furnish a red-brown solid; yield: 130 mg (35%).

^{1}H NMR (C_6D_6): δ = 1.15 [s, 9 H, $C(CH_3)_3$], 1.35 [s, 18 H, $C(CH_3)_3$], 6.80–7.50 (m, 10 H_{arom}).

^{13}C NMR ($CDCl_3$): δ = 35.4, 42.5 [each s, $C(\underline{C}H_3)_3$], 43.6 [d, $^2J_{C,P}$ = 16.0 Hz, $\underline{C}(CH_3)_3$], 44.2 [s, $\underline{C}(CH_3)_3$], 44.5 (d, $^1J_{C,P}$ = 53.5 Hz, C1'), 127.1–131.4 (C_{arom}, C2'/C3'), 140.1 (d, $^2J_{C,P}$ = 20.1 Hz, C3), 144.0 (d, $^3J_{C,P}$ = 33.0 Hz, $C1_{arom}$), 156.8 (d, $^1J_{C,P}$ = 26.5 Hz, C2), 212.0 (s, CO).

^{31}P NMR (C_6D_6): δ = −103.9.

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