Phosphaorganic Chemistry

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Incorporating Phosphaalkenes into Oligoacetylenes**

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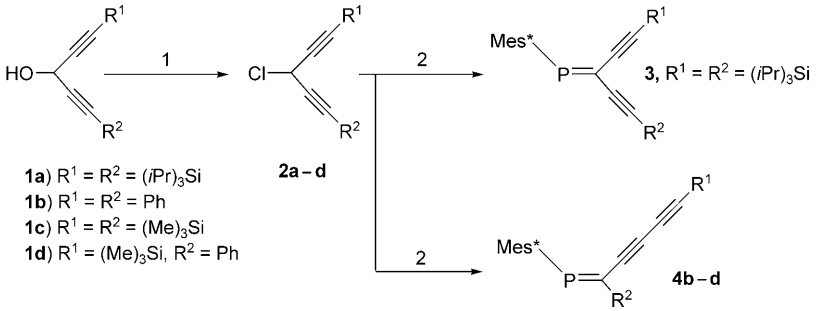
First synthesized and isolated by Becker in 1976, and viewed as something of a curiosity,[1] phosphaalkenes are now well-established entities in organophosphorus chemistry. In many cases, phosphaalkenes display a reactivity that is similar to that of their all-carbon-based counterparts, that is, alkenes.[2,3] Their use as ligands in homogenous catalysis has recently refueled interest in the chemistry of phosphaalkenes,[4,5] a trend that now also reaches into certain areas of material and polymer science.[6] For example, phosphaalkenes have been polymerized in reactions similar to those of ethylenes[7] or incorporated as intact fragments in polyphenylenephosphaalkenes.[8–10] Phosphorus centers that have been implemented into polyaromatic structures in the form of phospholes have been shown to act as n-type dopants that lead to decreased band gaps in π-conjugated assemblies.[11,12] The incorporation of pyridines, thiophenes, and now phospholes is a prominent way to alter the properties of polyaromatic π conjugates. However, conjugated atom chains, that is, oligoacetylene analogues that feature heavier main-group elements, are virtually unknown. We have recently initiated a project with the aim to incorporate phosphorus heteroatoms, in the form of phosphaalkenes (P=C), into fully π-conjugated acetylenic frameworks. In contrast to the classical all-carbon-based designs,[13,14] our approach will enable us to alter the electronic properties of the resulting acetylenic phosphaalkenes (APAs) by coordination of metal fragments to the phosphaalkene ligand. In this first report of a heavy main-group element that is an intrinsic part of an oligoacetylene, we also seek to investigate the effect that the heavy alkene has on the optical and electrochemical properties of the entire π conjugate.

APAs have only emerged very sporadically. A report by Appel et al. describes the synthesis of *P*-acetylenic phosphaalkenes from a *P*-chlorophosphaalkene,[15] whereas the only *C*-acetylenic phosphaalkene was obtained from a *C*-bromophosphaalkene.[16] The non-existence of APAs with more than one acetylene substituent and the lack of more elaborate structures that are based on the APA motif are presumably results of the reluctance of halogenated phosphaalkenes to engage in metal-catalyzed coupling reactions. *C*,*C*-Dibromophosphaalkenes, for example, will isomerize to phosphaalkynes upon exposure to palladium or platinum.[17]

We envisaged that APAs would be accessible through a sequence of three steps from commercially available acetylenes and ethyl formate (Scheme 1). In the preparation of carbinols **1a–d**[18] it is important that the reaction times are kept short and the temperature below room temperature to avoid the previously described base-catalyzed ynol-to-enone rearrangement.[19] Treatment of etheric solutions of the carbinols with thionyl chloride affords the 3-chloropenta-1,4-diynes **2a–d** in acceptable yields.[20] NMR spectroscopic studies of **2a–c** show unambiguously that the compounds are C_2-symmetric and therefore consistent with the assigned structures. Finally, the P=C bond can be established by treating the chlorides with Mes*PCl_2 in the presence of lithium diisopropylamide (LDA).[21] The reaction proceeds presumably through a carbene-type C_5 intermediate which is attainable from 3-chloropenta-1,4-diyne by a base-induced α elimination.[22,23]



Scheme 1. Synthesis of *C*,*C*-diacetylenic phosphaalkene **3** and 1-phosphahex-1-ene-3,5-diyne **4b–d**. 1) $SOCl_2$, Et_2O, 12 h, 20°C. **2a** 82%; **2c** 71%; **2d** 58%. 2) Mes*PCl_2, LDA, THF, 2 h, −100→−20°C. **3** 40%; **4b** 48% over two steps; **4c** 57%; **4d** 52%. Mes* = 2,4,6-(tBu)$_3$C$_6$H$_2$.

Since such a C_5 fragment can react either at the central C^3-position or at the terminal C^1 atom, the products of this reaction have to be analyzed carefully. Common characterization techniques such as ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and mass spectrometry show that acetylenic phosphaalkenes are obtained in all cases. A characteristic chemical shift for the P=C carbon atom at $\delta = 142.6$ ppm can be found in the ^{13}C NMR spectrum of the product arising from **2a**. In contrast, the respective signals of the products arising from **2b–d** are considerably shifted downfield to values beyond $\delta =$ 160 ppm, supporting the notion that the APA portion of these

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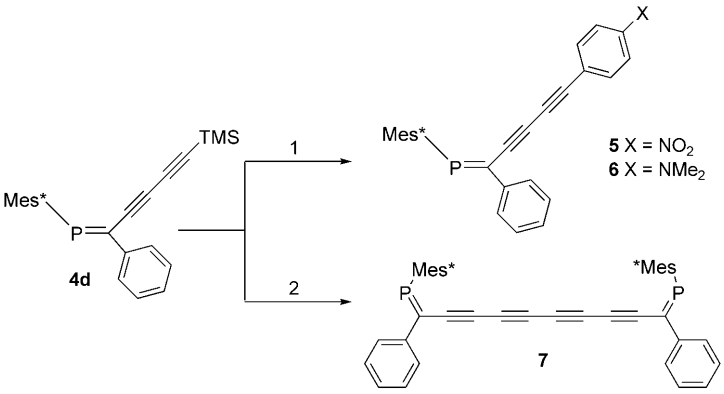
products are regioisomers to **2a**. Confirmation of the product structures was obtained from X-ray crystallography. Analysis of **3** revealed that a *C*,*C*-diacetylenic phosphaalkene had formed, that is, an isomer that stems from the reaction of **2a** at the central position of the C_5 reactant (Figure 1). Since **4b–d** yielded no crystals of sufficient quality, a corresponding $[Co_2(CO)_6]$ complex was prepared. X-ray analysis of $[Co_2(CO)_6(\mathbf{4b})]$ showed that **4b** is a butadiyne-substituted phosphaalkene and thus a regioisomeric analogue of **3** (see the Supporting Information). Remarkably, the reaction is not only regioselective for the C^1-position of the C_5 fragment, but also produces almost exclusively the isomer in which the butadiyne is *trans* to the lone pair of electrons on the phosphorus atom. A similar reactivity leads to **4c** and **4d**, the structures of which were assigned by ^{13}C NMR spectroscopic data and further crystallographic evidence (see below). As the two silyl groups in **2a** and **2c** are electronically very similar, it seems that the selectivity of this reaction is solely determined by the steric bulk of the substituents. Interestingly, Barluenga et al. have recently reported the site-specific olefination of a chromium(0) alkynylcarbene that involves a formal 1,2-migration of a C≡C bond and thus exhibits a regioselectivity that is comparable to that of our system.[24]



Scheme 2. Coupling reactions of **4d**. 1) K_2CO_3, $[Pd(PPh_3)_4]$ or $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, THF, MeOH, 3–4 h, 50 °C. **5** 68%; **6** 59%. 2) K_2CO_3, $Cu(OAc)_2$, MeOH, pyridine, 1 h, 20 °C, 67%. TMS = trimethylsilyl

Having succesfully synthesized **4d**, we explored its suitability as a building block for the construction of more elaborate APAs (Scheme 2). In situ protodesilylation of **4d** with potassium carbonate afforded the terminal acetylene which was found to engage in Sonogashira–Hagihara coupling reactions.

Thus, a solution of compound **4d** in THF/MeOH and Et_3N was treated with 4-iodonitrobenzene and 4-iodo-*N*,*N*-dimethylaniline in the presence of excess potassium carbonate and catalytic amounts of $[PdCl_2(PPh_3)_2]$ and copper iodide in a one-pot reaction to afford compounds **5** and **6** in 68% and 59% yield, respectively. A small amount of an isomeric by-product in which the butadiyne is *cis* to the phosphorus lone pair of electrons was detected after the reaction. This isomerization is presumably aided by temporary coordination of the palladium catalyst to the P=C bond in an η^2 fashion.[17] The electronic effect of the remote substituents in **5** and **6** is communicated to the phosphorous centers as evidenced by a difference of $\Delta\delta = 14$ ppm between their chemical shifts in the respective ^{31}P NMR spectra. It is thus clear that the phosphorus heteroatoms are an intrinsic part of the π-conjugated system.

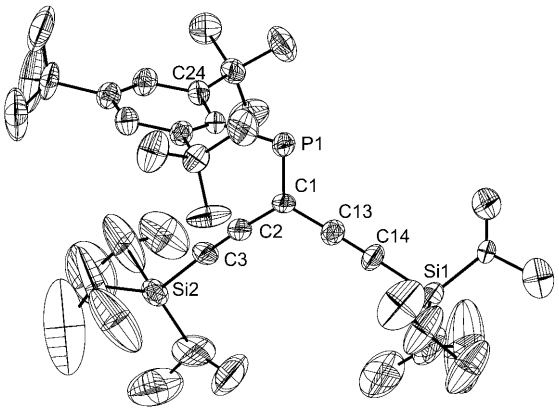


Figure 1. ORTEP view of diacetylenic phosphaalkene **3**. Thermal ellipsoids set at 20% probability level. Hydrogen atoms removed for clarity Selected bond lengths [Å] and angles [°]: P1–C1 1.68, P1–C24 1.85, C1–C2 1.46, C1–C13 1.46, C2–C3 1.20, C13–C14 1.20, P1–C1–C2 127, P1–C1–C13 117, C2–C1–C13 116.

Compound **4d** was also found to undergo homocoupling when exposed to K_2CO_3 under the classical Eglinton conditions. No isomerization of the P=C bond was detected under these conditions and the octatetrayne-linked bis(phosphaalkene) **7** was isolated in 67% yield after chromatographic purification. In the solid state, the octatetrayne in **7** adopts a slightly twisted conformation, with the two phosphorus centers separated by 13.3 Å (Figure 2). Alternating single and triple bonds are evidenced by typical bond lengths of 1.37 and 1.20 Å for the C(sp)–C(sp) and C≡C bonds, respectively.

Figure 3 shows the UV/Vis absorption spectra of compounds **4b** and **5–7**. As expected, **4b** has its longest wavelength absorption maximum at higher energy than the substituted analogues **5–7**. *N*,*N*-Dimethylamino-substitution in **6** leads to a red-shift of the lowest energy absorption band by 65 nm. Octatetrayne **7** absorbs at 485 nm and thus at a wavelength that is even further bathochromically shifted as a result of the large delocalized π system.

The UV/Vis spectra of all the APAs show lowest energy absorption bands that are generally red-shifted compared to all-carbon-based reference compounds. For example, compared to a dodec-1,11-diene-3,5,7,9-tetrayne, which exhibits its longest wavelength absorption maximum at 405 nm,[25] the substitution of the two terminal carbon atoms by phosphorus, as in **7**, leads to a bathochromic shift of the lowest energy absorption maximum of 80 nm, which corresponds to a difference in HOMO–LUMO gap between the two compounds of 0.50 eV. The doping strength of the two phosphaalkenes in **7** is similar to that of two dithiafulvenes that, when implemented at the termini of octatetraynes, result in a shift of the respective absorption maximum to 484 nm.[26] This wavelength is similar to that for the corresponding absorption of compound **7**. In contrast to these studies, however, the doping effect is an intrinsic property of APAs.

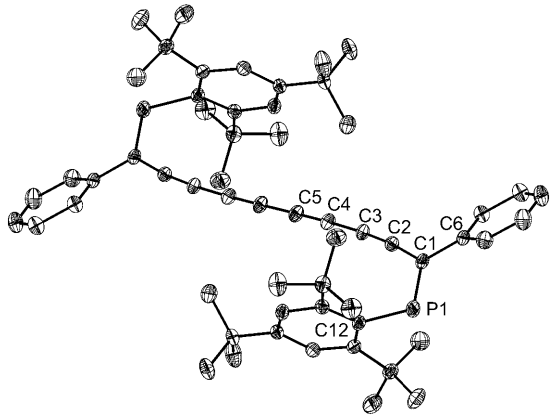


Figure 2. ORTEP view of 1,12-diphosphadodeca-1,11-diene-3,5,7,9-tetrayne **7**. Thermal ellipsoids set at 20% probability level. Hydrogen atoms removed for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.69, P1–C12 1.84, C1–C2 1.42, C1–C6 1.49, C2–C3 1.20, C3–C4 1.37, C4–C5 1.20, P1–C1–C2 121, P1–C1–C6 121, C2–C1–C6 118.

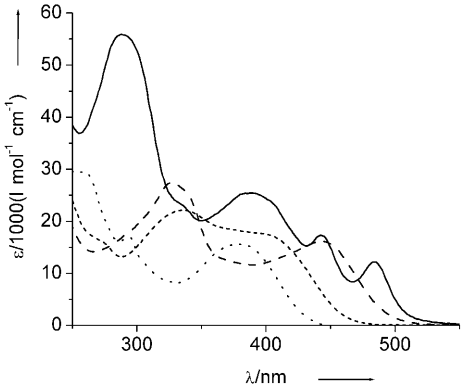


Figure 3. UV/Vis spectra of solutions of compounds **4b** (••••), **5** (----), **6** (– – –), and **7** (——) in CH_2Cl_2 at 25 °C.

Further information about how phosphorus influences the electronic properties of the APAs was sought using voltammetric measurements (Table 1). As anticipated, electron-rich **6** features the most negative reduction potential of the series at −2.04 V. In contrast, the first reversible reduction of electron-deficient **5** occurs at −1.40 V. This reduction is assigned to a localized electron uptake of the nitrophenyl substituent.[27] The second reversible reduction of **5**, however, can safely be assigned to the conjugated backbone of the molecule. In spite of the charge of the radical anion, this second process occurs at a potential that is 140 mV more positive than the first reductive process of phenyl-substituted **4b**. A further anodic shift of the potential required for the reduction of the π-conjugated framework occurs in octatetrayne **7**, which is reduced at −1.62 V. The subsequent electron uptake at −1.96 V is assigned to a second reduction of the strongly coupled, dimeric APA portion of **7**. The reduction potential is thus a sensitive measure of the electronic content of the entire π conjugate, including the substituents at the butadiyne. In contrast, the irreversible oxidations of **4b** and **5**–**7** are largely invariant to the substitution pattern. The cyclic voltammogram of the anilino-substituted compound **6** features a preceding oxidation at 0.47 V that can be assigned to the redox-independent anilino group.[26]

Table 1: Electrochemical data for solutions of **4b**, **5**–**7**.[a]

Compound	Reduction $E^{1/2}$ [V]		Oxidation $E_{p,a}$ [V]	
	$C_6H_4NO_2$	P=C–C_4	$C_6H_4NMe_2$	P=C–C_4
4b		−1.98		1.05
5	−1.40	−1.84		1.08
6		−2.04	0.47[b]	1.07
7		−1.62, −1.96		1.06

[a] 1 mM solutions in CH_2Cl_2 (0.1 M NBu_4PF_6), $\nu = 100\ mV s^{-1}$. All potentials are given versus ferrocene/ferrocenium. [b] The irreversible oxidation becomes reversible at scan rates higher than $1\ V s^{-1}$.

The common potential found for the oxidations of **4b** and **5**–**7** points towards a localization of this process on the phosphorus heteroatom. In agreement with the electronic absorption spectra, the electrochemical data show that octatetrayne **7** is the APA with the smallest HOMO–LUMO gap of the series and comparable to the bis(dithiafulvene)-substituted octatetrayne reference.[26]

In summary, we have introduced the first heavy alkene into an oligoacetylene framework and have thus established an access to a new class of π-conjugated molecules. The synthesis was aided by the ambivalent reactivity of a carbene-type C_5 intermediate that leads to *C*,*C*-diacetylenic, as well as to butadiyne-substituted phosphaalkenes. Compounds of the latter type have been shown to engage in various coupling reactions and are thus appealing building blocks for the construction of larger assemblies based on the APA motif. As evident from the electrochemical data, the HOMO of the APAs is mainly localized on the phosphorus center, while the LUMO has significant π* character. In comparison with all-carbon-based reference compounds, it was established that the phosphorus centers act as n-dopants to the conjugated acetylene scaffold and lead to decreased HOMO–LUMO gaps in the APAs. Future work will include an in-depth investigation of the reactivity of the C_5 carbene, the construction of cyclic assemblies based on the APA building blocks, and the synthesis of other members of the APA family, that is, *P*,*C*-diacetylenic and peracetylenic phosphaalkenes.

Experimental Section

Compounds **3** and **4b**–**d** were synthesized from **2a**–**d** in a procedure similar to that described for the synthesis of Mes*P=CBr_2.[21]

3: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.8$–0.9 (m, 21H; *i*Pr), 1.12 (s, 21H; *i*Pr), 1.31 (s, 9H; *t*Bu), 1.51 (s, 18H; *t*Bu), 7.43 ppm (s, 2H; CH–Mes*); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 11.4$, 11.6, 18.7, 18.9, 31.5, 33.3 (d, ^4J(P,C) = 6.5 Hz), 35.2, 38.3, 97.7 (d, J(P,C) = 15.4 Hz), 103.2 (d, J(P,C) = 11.9 Hz), 105.8 (d, J(P,C) = 19.6 Hz), 107.8 (d, J(P,C) = 25.8 Hz), 122.5, 135.1 (d, ^1J(P,C) = 57.3 Hz), 142.6 (d, ^1J(P,C) = 33.8 Hz), 150.4, 153.7 ppm; ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta =$ 331.0 ppm; EI MS (70 eV): *m*/*z* (%): 650.43 (100) [M^+]. Elemental analysis (%) calcd for ($C_{41}H_{71}PSi_2$): 75.63, 10.99; found: C 75.89, H 11.13.

4d: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.19$ (s, 9H; TMS), 1.45 (s, 9H; *t*Bu), 1.56 (s, 18H, *t*Bu), 7.36–7.4 (m, 3H; Ph), 7.56 (s, 2H, CH–Mes*), 7.85–7.89 ppm (m, 2H, Ph); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta =$ −0.2, 31.6, 33.3 (d, ^4J(P,C) = 6.5 Hz), 35.2, 38.2, 75.7 (d, J(P,C) = 21.1 Hz), 88.4 (d, J(P,C) = 8.5 Hz), 91.1 (d, J(P,C) = 10.4 Hz), 96.9 (d, J(P,C) = 3.5 Hz), 122.6, 125.5 (d, ^3J(P,C) = 20.4 Hz), 128.7 (d, J(P,C) = 1.5 Hz), 128.9 (d, J(P,C) = 5.8 Hz), 135.3 (d, ^1J(P,C) = 52.7 Hz), 139.9 (d, J(P,C) = 21.1 Hz), 150.9, 154.1, 162.2 ppm (d,

^1J(P,C) = 43.4 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 313.6 ppm; EI MS (70 eV): *m*/*z* (%): 486.54 (38) [M^+], 472 (15) [$M-CH_3$]$^+$, 430 (93) [MH−*t*Bu]$^+$, 276 (100) [Mes*P]$^+$. Elemental analysis (%) calcd for 5 ($C_{32}H_{43}PSi$)·CH_3OH: 78.42, 8.95; found: C 78.45, H 8.80.

5: [$Pd(PPh_3)_2Cl_2$] (6.5 mg, 9.25 μmol, 3 mol%), CuI (3.5 mg, 18.5 μmol, 6 mol%), and aqueous K_2CO_3 (1M, 3 mL) were added to a degassed solution of 4-iodonitrobenzene (0.077 g, 0.31 mmol) and **4d** (0.15 g, 0.31 mmol) in THF (30 mL), MeOH (10 mL), and triethylamine (10 mL). The reaction was monitored by thin-layer chromatography (TLC; 5% EtOAc in pentane) and quenched after 3 h by the addition of brine (40 mL). The reaction mixture was extracted with EtOAc (3 × 30 mL), the combined organic phases dried over Na_2SO_4, filtered, and concentrated in vacuo. The product was purified by column chromatography (silica, 5% EtOAc in pentane) and recrystallized from CH_2Cl_2 and MeOH. Yellow solid, yield 68%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.36 (s, 9H; *t*Bu), 1.53 (s, 18H; *t*Bu), 7.36–7.40 (m, 3H; Ph), 7.5 (d, ^3J(H,H) = 8.9 Hz, 2H; *p*-NO_2Ph), 7.52 (s, 2H; CH−Mes*), 7.81–7.86 (m, 2H; Ph), 8.17 ppm (d, ^3J(H,H) = 8.9 Hz, 2H; *p*-NO_2Ph); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 31.5, 33.3 (d, ^4J(P,C) = 6.5 Hz), 35.2, 38.2, 79.7 (d, J(P,C) = 8.5 Hz), 83.6 (d, J(P,C) = 20.8 Hz), 85.5 (d, J(P,C) = 4.6 Hz), 89.4 (d, J(P,C) = 10.0 Hz), 122.6, 123.8, 125.5 (d, ^3J(P,C) = 19.6 Hz), 128.9 (d, J(P,C) = 1.5 Hz), 129.1 (d, J(P,C) = 5.8 Hz), 129.4 (d, J(P,C) = 1.9 Hz), 132.8 (d, ^7J(P,C) = 1.5 Hz), 135.1 (d, ^1J(P,C) = 52.7 Hz), 139.6 (d, J(P,C) = 20.8 Hz), 147.3, 151.0, 154.2, 161.4 ppm (d, ^1J(P,C) = 44.6 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 318.7 ppm; EI MS (70 eV): *m*/*z* (%): 535 (10) [M^+], 479 (28) [MH−*t*Bu]$^+$, 277 (100) [Mes*PH]$^+$. Elemental analysis (%) calcd for $C_{35}H_{38}NO_2P$: 78.48, 7.15, 2.61; found: C 78.41, H 7.16, N 2.60.

6: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.44 (s, 9H; *t*Bu), 1.57 (s, 18H; *t*Bu), 3.01 (s, 6H; CH_3), 6.6 (d, ^3J(H,H) = 8.8 Hz, 2H; *p*-$N(Me)_2$−Ph), 7.29 (d, ^3J(H,H) = 8.8 Hz, 2H; *p*-$N(Me)_2$−Ph), 7.35–7.41 (m, 3H; Ph), 7.56 (s, 2H; CH−Mes*), 7.88–7.93 ppm (m, 2H; Ph); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 31.6, 33.3 (d, ^4J(P,C) = 6.5 Hz), 35.2, 38.2, 40.2, 73.2 (d, J(P,C) = 8.5 Hz), 80.6 (d, J(P,C) = 21.9 Hz), 90.5 (d, J(P,C) = 4.2 Hz), 92.4 (d, J(P,C) = 10.0 Hz), 108.7 (d, J(P,C) = 1.9 Hz), 111.7, 122.5, 125.6 (d, ^3J(P,C) = 20.4 Hz), 128.7, 128.7, 133.6 (d, J(P,C) = 1.2 Hz), 135.8 (d, ^1J(P,C) = 52.3 Hz), 140.3 (d, J(P,C) = 21.14 Hz), 150.5, 150.7, 154.1, 163.2 ppm (d, ^1J(P,C) = 42.7 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 304.3 ppm. Elemental analysis (%) calcd for $C_{37}H_{44}NP$: C 83.26, H 8.31, N 2.62; found: C 83.14, H 8.36, N 2.60.

7: $Cu(OAc)_2$ (1.5 g, 8.23 mmol) and K_2CO_3 (0.85 g, 6.17 mmol) were suspended in argon-degassed, distilled pyridine (17 mL) and MeOH (17 mL). **4d** (0.1 g, 0.2 mmol) was added in one portion under a stream of argon. After stirring the reaction mixture at room temperature for 1 h, it was quenched by the addition of water (120 mL). The aqueous layer was extracted with *n*-pentane (3 × 50 mL) and Et_2O (2 × 50 mL), the combined organic phases dried over Na_2SO_4 and concentrated in vacuo (40 °C). The product was purified by column chromatography (silica, eluent *n*-pentane). Orange solid, yield: 57 mg, 67%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.38 (s, 18H; *t*Bu), 1.51 (s, 36H; *t*Bu), 7.36–7.40 (m, 6H; Ph), 7.51 (s, 4H; CH−Mes*), 7.78–7.82 ppm (d, $^3J_{H,H}$ = 5.9 Hz, 4H, Ph); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 31.5, 33.3 (d, ^4J(P,C) = 5.7 Hz), 35.3, 38.2, 67.3 (d, J(P,C) = 5.3 Hz), 75.1, 78.4 (d, J(P,C) = 20.7 Hz), 91.7 (d, J(P,C) = 7.3 Hz), 122.9, 125.5 (d, J(P,C) = 19.9 Hz), 128.9, 129.1 (d, ^5J(P,C) = 4.6 Hz), 134.7 (d, ^1J(P,C) = 53.4 Hz), 139.2 (d, J(P,C) = 21.1 Hz), 151.3, 154.2, 160.8 ppm (d, ^1J(P,C) = 45.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 330.5 ppm; EI MS (70 eV): *m*/*z* (%): 770 (16) [$M-t$Bu]$^+$, 714 (57) [MH−2*t*Bu]$^+$, 658 (40) [$M-3t$Bu+2H]$^+$, 602 (32) [$M-4t$Bu+3H]$^+$. Elemental analysis (%) calcd for $C_{58}H_{68}P_2 \cdot {}^1/_2\,CH_3OH$: C 83.34, H 8.37; found: C 83.31, H 8.58.

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