Alternative Synthesis and Structures of C-monoacetylenic Phosphaalkenes

Andreas Orthaber,[a][†] Elisabet Öberg,[a][†] Reuben T. Jane,[a] and Sascha Ott*[a]

Keywords: Phosphaalkenes; Sonogashira coupling; Hay coupling; X-ray crystallography

Abstract. An alternative synthesis of C-monoacetylenic phosphaalkenes trans-Mes*P=C(Me)(C=C=CR) (Mes* = 2,4,6-i-Bu3Ph, R = Ph, SiMe3) from C-bromophosphaalkenes cis-Mes*P=C(Me)Br using standard Sonogashira coupling conditions is described. Crystallographic studies confirm cis-trans isomerization of the P=C double bond during Pd-catalyzed cross coupling, leading exclusively to trans-acetylenic phosphaalkenes. Crystallographic studies of all synthesized compounds reveal the extent of π-conjugation over the acetylene and P=C π-systems.

Introduction

Originating from the curiosity of breaking the double bond rule, different synthetic routes have been suggested for the synthesis of low-valent and low-coordinated phosphorus compounds. Furthermore, extensive work has been conducted on synthesis and spectroscopic studies of phosphaalkenes (6,7,3 phosphanes) with pendant π-conjugated systems for potential use in organic electronics, including a range of P=C containing poly- and oligomers. Moreover, the introduction of electro-active centers, such as metalloenes, has been of great interest. The all carbon ene-yne and ene-diyne motifs display interesting opto-electronic and conductive properties that suggest possible applications in single molecule electronics, and the insertion of a heteroatom such as phosphorus offers the possibility of further interesting properties. While the versatility of acetylene bridges in building up large π-conjugated and cross-conjugated molecular structures has been extensively explored in organic chemistry, examples of heavier element analogues thereof are very rare.

Recent work in our laboratory has focused on finding different routes to C-mono- and di-acetylenic phosphaalkenes. Van der Sluis et al. have described coupling reactions of 2-bromo-1-phosphaalkenes, which allow the introduction of various groups bonded directly to phosphaalkenes, including an acetylene moiety. In the present work, we describe an alternative synthesis of 2-acetylenic phosphaalkenes from methyl-substituted 2-bromo-1-phosphaalkenes using standard Sonogashira coupling conditions. This may allow greater functional group tolerance than the original procedure, which employed Grignard reagents. Oxidative acetylene homo-coupling under modified Glaser-type conditions afforded a butadiyne-bridged bis-phosphaethene. All reported phosphaalkenes have been structurally characterized by means of X-ray crystallography.

Results and Discussion

2,2-Dibromophosphaethene (1) was prepared by treatment of Mes*P=Cl with CHBr3 in the presence of LDA, according to published procedures. Substitution of one bromide functionality by a methyl group can be achieved by stirring a solution of 1 with n-BuLi at low temperatures, followed by quenching of the intermediate with MeI (Scheme 1). 2,2-Dihalophosphaethenes bearing the Mes* group are usually selective towards trans functionalization. In order to achieve highest possible selectivity, it is important to perform the lithiation of 2,2-dibromophosphaethene 1 at −130 °C; which yields the cis-phosphaacarbene species exclusively. By doing so, (Z)-2a is obtained as the single isomer in excellent yields without detectable traces of (E)-2a.

Scheme 1. Selective trans metal/halogen exchange of dibromophosphaethene 1. Isomerization of the lithiated intermediate is suppressed at low temperatures. For 2a R1 = CH3, and 2b R1 = C(OH)Ph2; (a) n-BuLi, –130 °C, Trapp mixture, 30 min; (b) MeI (2a) or Ph3C=O (2b), –130 °C, 30 min then to r.t., 2 h. 93 % (2a), 71 % (2b).

In order to facilitate the introduction of the acetylenic moieties, we investigated the direct coupling of terminal acetylenes using regular Sonogashira coupling conditions. Phenyl- or tri-methylsilylacetylene undergoes C–C bond formation in the presence of 5 mol-% Pd-catalyst (different types), CuI and base (triethylamine or pyridine) in DMF/THF or NEt3 solutions. In order to assess the E/Z stereochemistry of the product...
we carried out X-ray crystallographic analysis of both products and starting materials. Our investigations clearly show that isomerization of the P=C double bond occurs during the palladium mediated introduction of the acetylene moiety in the case of both phenyl- and trimethylsilylacetylene. This is in line with the findings from van der Sluij et al., who reported similar behavior for the coupling of the related compound cis-Mes*P=C(H)Br (2c), with Grignard reagents, including phenylethynyl magnesium bromide. Moreover, the use of a more efficient catalyst, [PdCl₂(dppf)], which exhibits superior reactivity to [PdCl₂(PPh₃)₂] (complete conversion of 2a within 5 minutes as monitored by TLC), also does not result in retention of the P=C double bond stereochemistry. The proposed mechanism suggests that the coupling proceeds via a cationic palladacycle intermediate (Scheme 2). Hence, introduction of more sterically demanding substituents at R¹ in 2 or the use of other catalysts may lead to a cisoid attack of the acetylene moiety. However, the presence of a more sterically demanding methyl group in 2a in place of the proton in 2c does not result in a retention of the stereochemistry at the P=C double bond. Irrespective of the catalyst ([PdCl₂(dppf)] or [PdCl₂(PPh₃)₂]) or the acetylene (TMS- or phenylacetylene) being used, the coupling leads exclusively to the trans-product. Thus, it is evident that the reactivity of the postulated palladium intermediate is mainly governed by steric effects.

With the aim to increase the steric demand of the substituent and thereby suppress the cis-trans isomerization during the Sonogashira coupling step, we introduced a diphenylhydroxymethane moiety through reaction of 1 with benzophenone to afford 2b (Scheme 1). However, attempts to perform coupling reactions with 2b were unsuccessful, resulting only in partial decomposition of the starting material and no detectable coupling products. It seems that the diphenylhydroxymethyl substituent introduces more steric bulk than the reaction can tolerate, as the bromide may no longer be accessible to the palladium catalyst or the incoming acetylene.

An extended π-conjugated compound was prepared by homocoupling of TMS-acetylenic phosphaalkene 3b. In order to prepare the butadiyne bridged bisphosphaalkene 4, the phosphaalkene 3b is deprotected in situ and the intermediate subsequently subjected to slightly modified Glaser-Eglinton coupling conditions. After chromatographic workup the phosphaalkene dimer 4 is obtained in moderate yields (Scheme 2).

Electronic and steric effects influence the spectroscopic and crystallographic properties of the described phosphaalkenes as compared to those of the structurally well characterized 2,2-dibromophosphaethene. Table 1 shows the 3¹P{¹H} NMR chemical shifts of phosphaethenes 1–4 in CDCl₃. The electronic influence of the substituents on the phosphorus chemical shift is clearly observable: in 1, the two electron-withdrawing bromines connected to the phosphaalkene carbon result in a downfield signal in the 3¹P{¹H} NMR spectrum at δ = 270.5 ppm. In comparison, 2a, which has one bromine and one methyl substituent, has a chemical shift of 242.4 ppm. Diphenylhydroxymethyl substitution in 2b again leads to a downfield shift (276.5 ppm) and the largest 1³JC coupling in this series (71.6 Hz). Increasing the electron delocalization by introducing acetylenic substituents, as in 3a,b, results in even further downfield 3¹P{¹H} NMR shifts to 284.0 ppm and 288.5 ppm, respectively. Dimer 4 exhibits the largest delocalization and a 3¹P{¹H} NMR signal of 302.9 ppm is thus observed.

### Table 1. 3¹P{¹H} and ¹³C NMR chemical shifts and 1³JC of the P=C double bond for phosphaethenes 1–4.

|     | 3¹P{¹H} (ppm) | ³¹JC (Hz) | ¹³C (ppm) |
|-----|---------------|-----------|-----------|
| 1¹⁵ | 270.5         | 57.6      | 139.3     |
| 2a  | 242.4         | 65.0      | 161.2     |
| 2b  | 276.5         | 71.6      | 170.9     |
| 3a  | 284.0         | 33.7      | 160.5     |
| 3b  | 288.5         | 34.6      | 160.8     |
| 4   | 302.9         | 68.8      | 166.0     |

*α) ppm b) Hz.*

The UV/Vis spectrum of TMS-substituted 3b shows a longest wavelength absorption maximum of λ_max = 309 nm in dichloromethane, while the presence of the phenyl group in 3a induces an additional red-shift of 17 nm (for 3a λ_max = 326 nm). Dimer 4 exhibits the lowest energy absorption maximum at λ_max = 359 nm. Compared to our previously reported C,C-diacetylenic phosphaalkenes with both TMS- and phenyl groups, the monoacetylenic phosphaethenes presented here have higher energy absorption maxima.

We were able to grow single crystals of compounds 2–4 that were suitable for X-ray diffraction by slow diffusion or slow evaporation of suitable solvent mixtures. The solid state structures confirm that the isomerization of the P=C double bond occurs during the coupling step in all cases (Figure 1, Figure 2).
Alternative Synthesis and Structures of C-monoacetylenic Phosphaalkenes

Figure 1. ORTEP plot of phosphaalkenes 2a (left) and 2b (right) (ellipsoids are drawn at a probability level of 50%). Hydrogen atoms and a disordered tert-butyl group with occupancy of less than 0.5 in 2a are omitted for clarity. For 2b only one of the two independent molecules is displayed.

Figure 2. ORTEP plot of phosphaalkenes 3a (top left), 3b (top right) and 4 (bottom) (ellipsoids are drawn at a probability level of 50%). Hydrogen atoms and a disordered tert-butyl group (3b) with occupancy of less than 0.5 are omitted for clarity. For 3a and 4 only one of the two independent molecules is displayed.

Selected structural parameters of phosphaalkenes 1–4 are shown in Table 2. Replacement of the first bromine atom by an electron donating methyl group leads to a significant elongation of the P=C double bond. Introducing the bulkier diphenylhydroxymethyl moiety barely affects the P=C bond length, but increases the bond angle to approximately 124°. Interestingly, there is only a slight elongation upon coupling with trimethylsilyl- or phenylacetylene. Concomitant with acetylene coupling and consequent isomerization is a shortening of the C1(methyl)–C2 bond length. Inversion of the relative geometry of the P=C bond also leads to a widening of the P=C2–C1 bond angle from 121.6(5)° to approximately 128°. Interestingly, the Cipso-P=C angle is also influenced by the different substituents, either for steric or electronic reasons. In the case of phosphaalkene 3a, the solid state structure clearly shows the extended conjugation of the π-system over the P=C double bond and the phenyl unit, which are almost coplanar (the acute angle between the least squares (l.s.) planes is 9.2(2)°). In the phosphaalkene dimer 4, we observe an s-trans arrangement of the P=C units.

Conclusions

In summary, we have demonstrated that isomerization to the thermodynamically favored trans-Mes*P=C(Me)(C≡CR)3a,b occurs during the Pd-catalyzed cross coupling of cis-Mes*P=C(Me)Br 2a, and cannot be suppressed by the use of more efficient catalysts. Further increase of the steric bulk at the phosphaalkene as in 2b completely inhibits coupling. Crystallographic investigations reveal an almost planar arrangement over the whole acetylenic phosphaethene portion of the molecule, giving rise to extended conjugation pathways and bathochromically shifted lowest energy absorption maxima.

Experimental Section

General: Syntheses were carried out under a dry nitrogen atmosphere using modified Schlenk techniques. NMR spectra were recorded in CDCl3 using a JEOL Eclipse+ 400 MHz or a Varian Mercury+ spectrometer operating at a proton frequency of 399.8 MHz and 300.02 MHz, respectively. 1H- and 13C NMR spectra were internally referenced to solvent residual peaks (7.16 ppm and 77.1 ppm, respectively); 31P{1H} NMR spectra were externally referenced to 85% aqueous H3PO4. Solvents and starting materials were purchased from Sigma Aldrich, ABCR, or VWR and used as received, except for THF, which was dried with sodium and benzophenone, and freshly distilled prior to use. Column chromatography was performed on Merck silica gel SI-60 Å (35–70). High-resolution mass spectral analyses (HRMS) were performed on a high-resolution and FTMS+pNSI mass spectrometer (orbitrapXL) or on a MicroTOF spectrometer with ESI core. Compound 1 was prepared according to a previously described procedure.[15]

Crystallographic Studies: All measurements were performed using graphite-monochromatized Mo-Kα radiation at 100(1) K with a Bruker

| Table 2. Selected structural parameters of phosphaalkenes 1–4. |
|------------------|------------------|------------------|------------------|------------------|
| R1 | R2 | P=Ca | C1-Meb | P=C-Meb |
| Br | Br | 1.65(2) | - | - |
| Me | C(OH)PH2 | 1.680(8) | 1.548(11) | 121.6(5) |
| Br | Br | 1.675(9) | 1.537(12) | 123.5(6) |
| Me | Ph | 1.676(9) | 1.542(12) | 124.5(6) |
| Br | Br | 1.693(2) | 1.504(3) | 128.3(2) |
| Me | Ph | 1.691(1) | 1.510(2) | 128.5(1) |
| Me | TMS | 1.681(7) | 1.498(15) | 127.8(7) |
| Me | n.a. | 1.720(8) | 1.612(19) | 131.5(10) |

a) distances in Å b) angles in degrees; c) substituent cis to Mes*.
The organic phase was dried with MgSO₄ and filtered. The solvent para-C, para-cooling bath containing 4:1:1 THF:Et₂O:pentane or a bath containing pentane was put at the external bisector of the C–C–C angle at a C–H distance of 0.95 Å. The hydrogen atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with tetrahedral angles, enabling rotation around the X–C bond, and C–H distances of 0.98 Å.

Synthesis of Phosphaalkene (2a): Phosphaalkene 2a was prepared using modifications to the procedures reported by Appel et al.[11] and van der Sluis et al.[10] MesP=CBr₂ (2.6 g, 5.8 mmol) was dissolved in THF (100 mL), Et₂O (25 mL), and pentane (25 mL). The mixture was cooled to –120 °C with dry ice and liquid nitrogen in a cooling bath containing 4:1:1 THF:Et₂O:pentane or a bath containing only pentane. n-BuLi (2.5 M, 2.3 mL, 5.80 mmol) was added dropwise and the yellow to orange reaction mixture was kept at –120 °C for 30 min. MeI (0.72 ml, 11.6 mmol) was added dropwise, during which the color of the reaction mixture became slightly paler. The reaction was stirred for 30 min. The mixture was then heated at reflux for 20 min. After cooling to room temperature, the solution was filtered through a plug of silica (pentane) to yield a white solid (2.07 g, 5.40 mmol). Yield: 93%. Recrystallization from dichloromethane/acetonitrile yielded white crystals.

1H NMR (399.8 MHz, CDCl₃): δ = 1.36 (s, 9H, para-tert-butyl), 1.50 (s, 18H, ortho-tert-butyl), 2.68 (d, J₉H = 24.4 Hz, 3H, CH₃) 7.43 (s, 2H, Ar). 31P[1H] NMR (161.8 MHz, CDCl₃): δ = 242.4. 13C NMR (100.5 MHz, CDCl₃): δ = 31.3 (d, J₁C=35.2 Hz, CH₃), 31.4 (s, para-C(CH₃)₃), 32.6 (s, ortho-C(CH₃)₃), 32.7 (s, ortho-C(CH₃)₃), 35.0 (s, para-C(CH₃)₃), 37.8 (s, ortho-C(CH₃)₃), 122.0 (s, meta-C), 138.7 (d, P-C, J₉PC =52.2 Hz), 150.7 (s, para-C), 152.9 (s, ortho-C), 161.2 (d, P=C, J₉PC = 57.0 Hz). ESI MS: m/z [2M+Ag⁺] + 872.95 (100), [M+Ag⁺] + 490.96 (50).

Crystal Structure Analysis of (2a): Single crystals of 2a suitable for X-ray diffraction were obtained by slow evaporation of a saturated dichloromethane/acetonitrile solution. Compound 2a crystallized in the monoclinic space group P2₁/n (No. 14), C₂H₅BrP: M = 383.33, crystal dimensions = 0.15 × 0.30 × 0.30 mm, a = 6.1700(5) Å, b = 25.056(2) Å, c = 13.0356(10) Å, β = 90.041(1)°, V = 2015.3(3) Å³, Z = 4, 2θmax = 52.74°, ρ = 1.263 g/cm³, μ(Mo-Kα) = 2.116 mm⁻¹, F(000) = 808. 29543 reflections measured, 4123 unique (Rint = 0.0453), R1 = 0.0892(I>2σ(I)), Rw = 0.2333, Goof = 1.406, 210 parameters, 0 restraints.

Synthesis of Phosphaalkene (2b): To a cold (−100 °C) solution of I (155 mg, 0.35 mmol) in THF (15 mL) was added one equivalent of n-BuLi (14 mL, 2.5 M) and the solution stirred for approximately 30 min. After addition of benzophenone (75 mg, 0.41 mmol) the temperature was maintained for another 30 min and then gradually allowed to reach rt. The slurry was quenched with aqueous NaHCO₃ solution and extracted with ethyl acetate. After drying (MgSO₄) and removal of the solvent, the crude product was purified on a silica gel column (ethyl acetate/dichloromethane 3:1) Recrystallization from methanol/ethyl acetate gave phosphaalkene 2b as a white solid (137 mg, 0.25 mmol). Yield: 71%.

1H NMR (300.0 MHz, CDCl₃, 25 °C): δ = 1.32 (s, 9H, para-tert-butyl), 1.48 (s, 18H, meta-tert-butyl), 3.33 (br. s, 1H, OH), 7.33 (m, 6 H, Ph), 7.40 (d, J₁PC = 1.6 Hz, 2H, Me⁺⁺), 7.53 (dd, 1.9 Hz, 8.0 Hz, Ph). 13C NMR (75.5 MHz, CDCl₃, 25 °C): δ = 31.40 (s, para-C(CH₃)₃), 33.13 (d, J₁EC = 7.3 Hz, meta-C(CH₃)₃), 35.05 (s, para-C(CH₃)₃), 37.98 (br. s, meta-C(CH₃)₃), 85.61 (d, J₁EC = 22.9 Hz, COH), 122.48 (s, Mes⁺), 127.81 (s, Ph), 128.26 (d, 2.6 Hz, Mes⁺), 130.12 (s, Ph), 132.47 (s, Ph), 137.67 (s, Ph), 144.17 (d, 7.9 Hz, Mes⁺⁺), 150.90 (s, Mes⁺) 153.23 (d, 3.0 Hz, Mes⁺⁺), 170.87 (d, J₁PC = 71.6 Hz, Ph-C). 31P[1H] NMR (125.5 MHz, CDCl₃, 25 °C): δ = 276.5 (s).
14.1 Hz, P=Cs-C3H3), 31.3 (s, para-C(CH3)3), 32.6 (d, JPC = 6.2 Hz, meta-C(CH3)3), 35.0 (s, para-C(CH3)3), 38.0 (s, meta-C(CH3)3), 94.7 (d, JPC = 28.2 Hz, acetylenic-C), 96.9 (d, JPC = 18.9 Hz, acetylenic-C), 121.7 (s, arom-meta-C, Mes*), 123.8 (d, JPC = 6.9 Hz, arom-ipso-C, Ph), 128.0 (s, para-C, Ph), 128.2 (s, meta-C, Ph), 131.5 (d, JPC = 5.3 Hz, arom-ortho-C, Ph), 135.90 (d, JPC = 60.4 Hz, arom-ipso-C), 150.5 (s, arom para-C, Mes*), 153.8 (s, arom ortho-C, Mes*), 160.5 (d, JPC = 33.7 Hz, P=Cs). 31P{1H} NMR (161.8 MHz, CDCl3, 23 °C): δ = 284.0 (s).

Crystal Structure Analysis of (3a): Single crystals of 3a suitable for X-ray diffraction were obtained by slow evaporation of a saturated dichloromethane/acetone/tetrahydrofuran solution. Compound 3a crystallized in the monoclinic space group C2/c (No. 15), C2H2P·P, M = 404.55, crystal dimensions 0.18 mm, the reaction mixture was filtered through a plug of silica (pentane/ethyl acetate 95:5), yielding pure bisphosphaalkene 4 as a slightly yellow solid in moderate yields (29 mg, 0.044 mmol). Yield: 52 %.

Synthesis of Phosphaalkene Dimer (4): Phosphine 3a (40 mg, 0.10 mmol) was dissolved in deaerated THF:DMF (5:5 mL). After addition of the catalyst, either [PdCl2(PPh3)] (3.5 mg, 0.005 mmol) or [PdCl2(dpdp)]·CH2Cl2 (4 mg, 0.005 mmol) and CuI (2 mg, 0.01 mmol), NEt3/pyridine (1 mL of a 3:1 mixture) and ethynyltrimethylsilane were added (35 mg 0.36 mmol). The reaction was monitored by TLC and was complete after 12 h. The reaction mixture was filtered through a plug of silica (pentane/ethyl acetate 95:5) and purified on a short silica column (pentane/ethyl acetate 95:5), yielding pure bisphosphaalkene 4 as a slightly yellow solid in moderate yields (29 mg, 0.044 mmol). Yield: 52 %.

Acknowledgment

The work was supported by COST initiative PhoSciNet (CM0802), Uppsala University U3MEC Molecular Electronics Priority Initiative, Swedish Research Council, the Göran Gustafsson Foundation. A.O. would like to thank the Austrian Science Fund (FWF) for financial support through an Erwin-Schrödinger Fellowship (J 3193). We thank H. Luftmann for HR-MS.

References

[1] a) V. A. Wright, B. O. Patrick, C. Schneider, D. P. Gates, J. Am. Chem. Soc. 2006, 128, 8836–8844; b) V. A. Wright, D. P. Gates, Angew. Chem. Int. Ed. 2002, 41, 2389–2392; c) D. P. Gates, in
New Aspects in Phosphorus Chemistry V, Vol. 250 (Ed.: J.-P. Majoral), Springer, 2005, p. 107; d) R. C. Smith, J. D. Protasiewicz, J. Am. Chem. Soc. 2004, 126, 2268–2269; e) R. C. Smith, X. Chen, J. D. Protasiewicz, Inorg. Chem. 2003, 42, 5468–5470; f) T. Baumgartner, R. Reau, Chem. Rev. 2006, 106, 4681–4727.

[2] a) R. Pietschnig, E. Niecke, M. Nieger, K. Airola, J. Organomet. Chem. 1997, 529, 127–133; b) C. Moser, A. Ortheber, M. Nieger, F. Belaj, R. Pietschnig, Dalton Trans. 2006, 3879–3885; c) S. Shah, T. Concolino, A. L. Rheingold, J. D. Protasiewicz, Inorg. Chem. 2000, 39, 3860–3867; d) S. Shah, J. D. Protasiewicz, Chem. Commun. 1998, 1585–1586; e) A. Ortheber, R. Herber, R. Pietschnig, J. Organomet. Chem. 2012, 719, 36–40.

[3] M. B. Nielsen, F. Diederich, Chem. Rev. 2005, 105, 1837–1868.

[4] G. C. Solomon, D. Q. Andrews, R. H. Goldsmith, T. Hansen, M. R. Wasielewski, R. P. Van Duyne, M. A. Ratner, J. Am. Chem. Soc. 2005, 127, p. 107; d) R. C. Smith, J. D. Protasiewicz, Inorg. Chem. 1999, 38, 1350–1377; b) A. M. Boldi, J. Anthony, V. Gramlich, C. B. Knobler, C. Boudon, J.-P. Gisselbrecht, M. Gross, F. Diederich, Helv. Chim. Acta 1995, 78, 779–796; c) J. Anthony, A. M. Boldi, C. Boudon, J.-P. Gisselbrecht, M. Gross, F. Seiler, C. B. Knobler, F. Diederich, Helv. Chim. Acta 1995, 78, 797–817.

[5] a) M. M. Haley, R. R. Tykwiniski, Carbon-Rich Compounds: from Molecules to Materials, Wiley-VCH Verlag, Weinheim, 2006; b) F. Diederich, P. J. Stang, R. R. Tykwiniski, Acetylene Chemistry: Chemistry, Biology, and Material Science, Wiley-VCH Verlag, Weinheim, 2005.

[6] K. B. Dillon, F. Matthey, J. F. Nixon, Phosphorus: The Carbon Copy: From Organophosphorus to Phospha-organic Chemistry, John Wiley & Sons, New York, 1998.

[7] a) R. E. Martin, F. Diederich, Angew. Chem. Int. Ed. 1999, 38, 1350–1377; b) A. M. Boldi, J. Anthony, V. Gramlich, C. B. Knobler, C. Boudon, J.-P. Gisselbrecht, M. Gross, F. Diederich, Helv. Chim. Acta 1995, 78, 779–796; c) J. Anthony, A. M. Boldi, C. Boudon, J.-P. Gisselbrecht, M. Gross, F. Seiler, C. B. Knobler, F. Diederich, Helv. Chim. Acta 1995, 78, 797–817.

[8] T. Sato, Y. Mizuhata, N. Tokihiro, Chem. Commun. 2010, 46, 4402–4404.

[9] a) E. Öberg, X.-L. Geng, M.-P. Santoni, S. Ott, Org. Biomol. Chem. 2011, 9, 6246–6255; b) X.-L. Geng, S. Ott, Chem. Eur. J. 2011, 17, 12153–12162; c) X.-L. Geng, Q. Hu, B. Schäfer, S. Ott, Org. Lett. 2010, 12, 692–695; d) E. Öberg, B. Schäfer, X.-L. Geng, J. Pettersson, Q. Hu, M. Kritikos, T. Rasmussen, S. Ott, J. Org. Chem. 2009, 74, 9265–9273; e) X.-L. Geng, S. Ott, Chem. Commun. 2009, 7206–7208; f) B. Schäfer, E. Öberg, M. Kritikos, S. Ott, Angew. Chem. Int. Ed. 2008, 47, 8228–8231.

[10] M. van der Sluis, A. Klootwijk, J. B. M. Wit, F. Bickelhaupt, N. Veldman, A. L. Spek, P. W. Jolly, J. Organomet. Chem. 1997, 529, 107–119.

[11] R. Appel, C. Casser, M. Immenkeppel, Tetrahedron Lett. 1985, 26, 3551–3554.

[12] a) M. Yoshifjii, H. Kawanami, Y. Kawai, K. Toyota, M. Yasunami, T. Nitsu, N. Inamoto, Chem. Lett. 1992, 21, 1053–1056; b) M. Yoshifjii, S. Ito, K. Toyota, M. Yasunami, Bull. Chem. Soc. Jpn. 1995, 68, 1206–1212.

[13] a) M. van der Sluis, J. B. M. Wit, F. Bickelhaupt, Organometallics 1996, 15, 174–180; b) E. Niecke, M. Nieger, O. Schmidt, D. Gu- dat, W. W. Schoeller, J. Am. Chem. Soc. 1999, 121, 519–522; c) M. Yoshifjii, S. Ito, in New Aspects in Phosphorus Chemistry II, Vol. 223 (Ed.: J.-P. Majoral), Springer Berlin Heidelberg, 2003, pp. 67–89.

[14] a) I. A. Litvinov, I. E. Boldeskul, G. N. Koidan, A. P. Marchenko, A. M. Pinchuk, J. Struct. Chem. 1992, 33, 314–317; b) M. Nieger, E. Niecke, B. Schmidt, Private Communication to CCDC ed., 1990.

[15] K. Toyota, S. Kawasakii, M. Yoshifjii, J. Org. Chem. 2004, 69, 5065–5070.

[16] a) Bruker AXS Inc., Madison, Wisconsin, USA, 2007; b) Bruker AXS Inc., Madison, Wisconsin, USA, 2001.

[17] a) G. M. Sheldrick, University of Göttingen, Germany, 2008; b) G. Sheldrick, Acta Crystallogr., Sect. A 2008, 64, 112–122.

[18] L. J. Farrugia, J. Appl. Crystallogr. 1999, 32, 837–838.

[19] L. J. Farrugia, J. Appl. Crystallogr. 1997, 30, 565.

Received: July 11, 2012
Published Online: October 9, 2012