(Z)-1-Methoxy-4-(diphenylphosphino)but-1-ene-3-yne: a versatile synthon for unsymmetrically substituted (diphenylphosphino)diacetylene derivatives

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Abstract

An efficient synthesis of $Ph_2P-C\equiv C-C\equiv C-Li$, **1**, was found, starting from commercially available (Z)-1-methoxybut-1-ene-3-yne and its diphenylphosphino derivative **2**. The lithio compound **1** was condensed with electrophiles to give $Ph_2P-C\equiv C-C\equiv C-\Sigma$ ($\Sigma = SiR_3$, SnR_3, $B(N^iPr)_2$) **3**. Compound **2** was easily transformed into the phosphonium salt **6** and the phosphine oxide **7** using MeI and H_2O_2 respectively. Derivatives **3** ($\Sigma = SiMe_3$, $SnMe_3$) are reactive at phosphorus and at the Σ group; complexation with $W(CO)_5THF$ gave the expected derivatives $W(CO)_5Ph_2P-C\equiv C-C\equiv C-\Sigma$ ($\Sigma = SiMe_3$, $SnMe_3$), **10**, and in the case of $\Sigma = SnMe_3$, coupling reaction between $Ph_2P-C\equiv -C-C\equiv C-SnMe_3$, **3c**, and $(\eta^5-IC_5H_4)Mn(CO)_3$ in the presence of $PdCl_2(CH_3CN)_2$ as a catalyst gave the complex **11**, $Ph_2P-C\equiv C-C\equiv C-(\eta^5-C_5H_4)Mn(CO)_3$.

Keywords: Phosphine; Diyne; Chromium; Tungsten; Lithium; Silyl

1. Introduction

Considerable attention has been devoted to finding organic materials which are efficient and practical for non-linear optical applications (see for instance Ref. [1]). Of interest are materials either for second-order processes, i.e. frequency doubling of laser radiation (typically doubling infrared radiation into the visible) or for third-harmonic generation [1]. In both cases, electron delocalization and π-orbital overlap are desirable for high non-linear optical response. In this context, diacetylenes and the corresponding polydiacetylenes have been shown to be useful candidates (see Ref. [1]; also, $\chi^{(2)}$ see Refs. [2,3] and $\chi^{(3)}$ see Refs. [2,4].)

Over classical substituents attached either to the diacetylene unit or to the polymeric backbone, heteroelement-based or organometallic side groups would allow introduction of either unusual structural constraints or significant electronic changes, and thus modulate the non-linear optical properties in a large range.

Previously, we have synthesized poly[(silylene)di-

acetylenes] and found that these polymers were semiconductors after doping with $FeCl_3$ [5]. The observed values depended on the substituents at silicon; indeed, the following conductivity order was observed: $SiPh_2 > SiMePh > SiMe_2$; electron donor substituents on silicon enhanced the conductivity values compared with a methyl group. Moreover, our experimental data were in favor of a conductivity occurring along the polymer chain rather than from chain to chain [5].

The poly[(silylene)diacetylenes] were also interesting from a thermal point of view. Indeed, polymerization of the diacetylene units occurred easily, at relatively low temperature (from 200 to 315 °C, depending on the substituents at silicon) to give a polymer with ene–yne groups [6]. These thermal properties have been extended to $R_3Si-C\equiv C-C\equiv C-SiR_3$ species, with different R groups, which gave in the same way the polymerization of the diacetylene units [7].

In connection with our on-going studies in the silicon series, we are interested in the usefulness of 1,3-diynes substituted by a wide variety of main group element or organometallic moieties. Accordingly, we report here a new synthesis of the 4-lithio-1-(diphenylphosphino)-butadiyne **1**, starting from (Z)-1-methoxy-4-(diphenyl-

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phosphino)but-1-ene-3-yne **2**, and its coupling reactions with electrophiles to give unsymmetrically disubstituted diacetylenes **3**.

$$Ph_2P-C\equiv C-C\equiv C-\Sigma \quad \mathbf{3}$$

$$\Sigma = R_3Si, R_3Sn, PR_2, P(O)R_2, B(N^iPr_2)_2, \ldots$$

In addition, owing to the presence of the phosphorus atom or to the reactivity of the C–heteroelement bond, **3** can be versatile synthetic intermediates; some relevant data are discussed below.

2. Results and discussion

2.1. Synthesis of $Ph_2P-C\equiv C-C\equiv C-Li$, 1 and $Ph_2P-C\equiv C-C\equiv C-\Sigma$, 3

1-(Diphenylphosphino)butadiyne was first prepared by Cadiot and coworkers, by condensation of chlorodiphenylphosphine with 1-(bromomagnesio)butadiyne at low temperature (Eq. (1)) [8]. This route was used by Bestmann et al. [9] in order to prepare 1-lithio-4-(diphenylphosphino)butadiyne, **1**, via the lithiation of 1-(diphenylphosphino)butadiyne (Eq. (2)).

$$H-C\equiv C-C\equiv C - MgBr + ClPPh_2$$

$$\xrightarrow[-30\,°C]{THF} Ph_2P - C\equiv C - C\equiv C - H \quad (1)$$

$$Ph_2P-C\equiv C-C\equiv C-H + {}^nBuLi$$

$$\xrightarrow[-60\,°C]{THF} Ph_2P-C\equiv C-C\equiv C-Li \quad (2)$$
$$\mathbf{1}$$

Our goal was to develop a more general route to **3** in which both the use of diacetylene itself and of the unstable 1-(diphenylphosphino)diacetylene would be avoided.

Zweifel and coworkers have previously shown that the treatment of (Z)-1-methoxybut-1-ene-3-yne with one equivalent of ${}^nBuLi$, followed by quenching the reaction mixture with chlorosilanes, afforded the trialkyl-substituted enynes **4** (Eq. (3)) [10,11].

$$\xrightarrow{2\,LDA} R_3Si-C\equiv C-C\equiv C-Li \quad (3)$$
$$\mathbf{5}$$

The deprotonation of **4** with two equivalents of lithiumdiisopropylamide (LDA) produced 1-lithio-4-trialkylsilyl-1,3-butadiyne **5** (Eq. (3)) [10,11].

In a similar way, the lithiation of the commercially available (Z)-1-methoxybut-1-ene-3-yne and its diphenylphosphino derivative **2** provides a convenient

access to 1-lithio-4-diphenylphosphino-1,3-butadiyne **1** (Eq. (4)).

$$\xrightarrow{2\,LDA} Ph_2P-C\equiv C-C\equiv C-Li + MeOLi \quad (4)$$
$$\mathbf{1}$$

Phosphine **2** is stable and was isolated in high yield. The coupling constant $J(HH)$ of 6.5 Hz in the ${}^1H$ NMR spectrum confirmed the (Z) isomer. Phosphine **2** reacted with LDA to give the expected anion **1**, and quenching the reaction mixture with various electrophiles produced the desired diynes **3** (Eq. (5)).

$$Ph_2P-C\equiv C-C\equiv C-Li \xrightarrow{Cl\Sigma} Ph_2P-C\equiv C-C\equiv C-\Sigma \quad (5)$$
$$\mathbf{1} \qquad\qquad\qquad\qquad \mathbf{3}$$

$$\Sigma = B(N^iPr_2)_2, R_3Si, R_3Sn \;(R = Me, Ph)$$

For instance, the reaction of the anion **1** with two equivalents of trimethylchlorosilane (one is trapped by MeOLi, see Eq. (4)) gave **3a** ($\Sigma = Me_3Si$) in 50% yield. Monodesilylation of 1,4-bis(trimethylsilyl)butadiyne using methyllithium [12] followed by the reaction of the formed anion with chlorodiphenylphosphine led also to **3a** ($\Sigma = Me_3Si$) (Eq. (6)).

$$Me_3Si-C\equiv C-C\equiv C-SiMe_3$$

$$\xrightarrow{MeLi-LiBr} Me_3Si-C\equiv C-C\equiv C-Li$$

$$\xrightarrow{Ph_2PCl} Me_3Si-C\equiv C-C\equiv C - PPh_2 \quad (6)$$
$$\mathbf{3a}$$

The lithio derivative **1** reacted with H_2O or MeOH, to give $Ph_2P-C\equiv C-C\equiv C-H$ which was characterized by IR ($\nu(C-H)$ 3303 cm^{-1}) [9] in the crude product, but we were unable to isolate the compound which was too unstable.

We have tried the reaction of **1** with $ClSi(OMe)_3$ and $ClSi(O^iPr)_3$; these functional groups were thought to be good precursors in the synthesis of new organic–inorganic hybrid materials. With $ClSi(O^iPr)_3$, the reaction was not complete; ${}^1H$ NMR of the crude material indicated two isopropyl derivatives, and ${}^{31}P$ NMR a major peak near -29 ppm. However, in both cases, attempts at purification by distillation led to rapid polymerization.

2.2. (Z)-$Ph_2P-C\equiv C-CH=CH(OMe)$, 2 and $Ph_2P-C\equiv C-\Sigma$, 3 as synthetic intermediates

2.2.1. (Z)-$Ph_2P-C\equiv C-CH=CH(OMe)$, 2

Phosphines are known to react with oxidation agents and alkyl halides to give phosphine oxides and phosphonium salts respectively, and indeed, these reactions
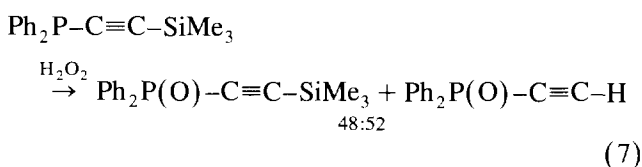
were straightforward with **2**. The expected derivatives, **6** and **7**, were obtained in good yields (Scheme 1).

### 2.2.2. $Ph_2P-C\equiv C-C\equiv C-\Sigma$, 3

Phosphines **3** can react in three different ways: (i) they can act as a phosphine; (ii) give specific reactions of the Σ group; (iii) react with the triple bonds to give, for instance, complexation reactions. We will focus only on the two first points.

2.2.2.1. Acting as a phosphine.
The oxidation reaction to give phosphine oxide was tried with **3a**, $\Sigma = SiMe_3$, and **3b**, $\Sigma = SiPh_3$. In the case of $Ph_2P-C\equiv C-C\equiv-SiPh_3$, **3b**, spectral analyses gave the following information: IR gave $\nu(C\equiv C)$ 2082 (S) and 2204 (S) with $\nu(\equiv C-H)$ 3296 and $\nu(P=O)$ 1191 cm^{-1}. ^{31}P NMR showed two very close peaks at 9.5 and 9.4 ppm, corresponding to phosphine oxides. Finally, a doublet was observed at 2.56 ppm, 1.7 Hz, in the ^1H NMR spectrum. All these data are in agreement with a mixture of $Ph_2P(O)-C\equiv C-C\equiv SiPh_3$ and $Ph_2P(O)-C\equiv C-C\equiv C-H$ (ca. 28%). An analogous result was obtained in the oxidation reaction of $Ph_2P-C\equiv C-C\equiv C-SiMe_3$, **3a**, i.e. formation of a mixture of $Ph_2P(O)-C\equiv C-C\equiv C-SiMe_3$ and $Ph_2P(O)-C\equiv C-C\equiv C-H$ (ca. 43%). Owing to steric hindrance factors, the desilylation reaction is easier with R = Me than with R = Ph.

This multiple reactivity is due to the presence of a $C_{sp}-SiR_3$ (R = Me, Ph) group and to the difference of reactivity between $SiMe_3$ and $SiPh_3$. Indeed, oxidation of the monoacetylenic compound $Ph_2P-C\equiv C-SiR_3$ (R = Me, Ph) with one equivalent of H_2O_2 gave an analogous result: easy oxidation was observed in both cases (R = Ph, 74% yield [13]) and partial $Si-C_{sp}$ bond rupture was observed in the case of R = Me (Eq. (7)).

$$Ph_2P-C\equiv C-SiMe_3$$

$$\xrightarrow{H_2O_2} Ph_2P(O)-C\equiv C-SiMe_3 + Ph_2P(O)-C\equiv C-H$$
$$48{:}52$$

$$\tag{7}$$

H_2O_2 can either react at phosphorus or induce a protodesilylation process. In the latter case, a possible mechanism is activation of the hydrogen peroxide via coordination to the silicon atom, followed by elec-
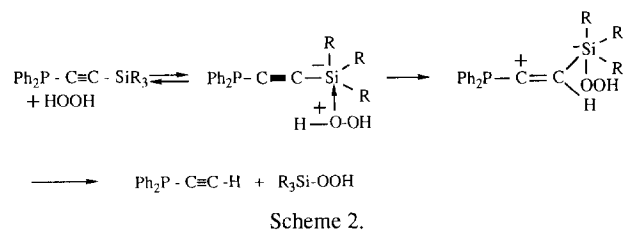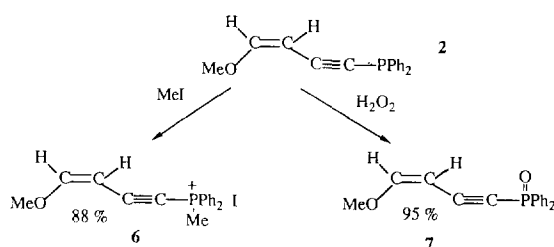
Scheme 2.

trophilic addition to the triple bond, and, finally, elimination of trialkylsilyl peroxide (Scheme 2). The latter is able to oxidize the phosphine into the phosphine oxide, and gave R_3SiOH which was characterized in the reaction mixture in the case of R = Ph (Ph_3SiOH, ^{29}Si NMR, $\delta = -14$ ppm, IR, $\nu(SiOH)$ 3680 cm^{-1}).

The proposed mechanism can be extended to the diacetylene derivatives **3**. It explains both the influence of the steric hindrance of the groups attached to silicon, and the stoichiometry of the reaction, one mole of hydrogen peroxide per mole of compound. To our knowledge, no protodesilylation has been reported previously with H_2O_2 or Me_3SiOOH.
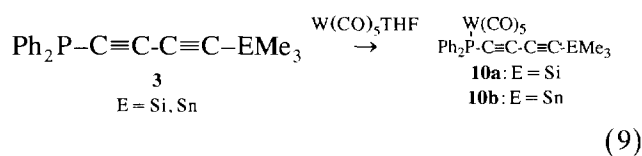
Furthermore, when no silicon group was present, as in the case of the symmetric phosphines $Ph_2P-C\equiv C-PPh_2$ and $Ph_2P-C\equiv C-C\equiv C-PPh_2$, **8**, the oxidation was straightforward and gave the expected phosphine oxides as crystalline compounds in 87% [14] and 40% yields respectively (Eq. (8)).

$$Ph_2P-C\equiv C-C\equiv C-PPh_2 + H_2O_2$$

$$\rightarrow Ph_2\overset{O}{\overset{\|}{P}}-C\equiv C-C\equiv C-\overset{O}{\overset{\|}{P}}Ph_2 \tag{8}$$
$$\mathbf{9}$$
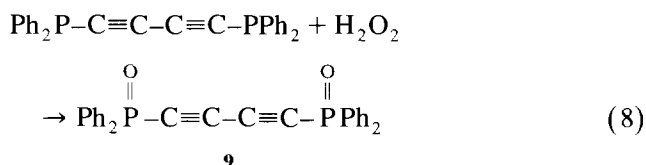
The synthesis of the phosphonium salt $Ph_2P^+(Me)-C\equiv C-C\equiv C-SiMe_3I^-$ was tried with MeI and $Ph_2P-C\equiv C-C\equiv C-SiMe_3$, **3a**; the experimental conditions were those determined in the case of phosphine **2**, but no characterizable compound was obtained from the reaction mixture. This is a quite unexpected result, because of the easy synthesis of $Ph_2P^+(Me)-C\equiv C-PPh_2I^-$ [14].

Phosphines are well-known ligands in coordination chemistry and, in the case of $Ph_2P-C\equiv C-PPh_2$ [15] or $Ph_2P-C\equiv C-C\equiv C-PPh_2$ [16] for instance, several transition metal complexes have been synthesized.

We extended the reaction of $W(CO)_5THF$ to phosphines **3** with $\Sigma = Me_3Si$ and Me_3Sn (Eq. (9)) and obtained the expected complexes in 44%, **10a** (E = Si), and 28%, **10b** (E = Sn), yields.

$$Ph_2P-C\equiv C-C\equiv C-EMe_3 \xrightarrow{\underset{}{W(CO)_5THF}} \underset{W(CO)_5}{Ph_2P-C\equiv C-C\equiv C-EMe_3}$$
$$\mathbf{3} \qquad\qquad\qquad \mathbf{10a}{:}\,E = Si$$
$$E = Si, Sn \qquad\qquad \mathbf{10b}{:}\,E = Sn$$
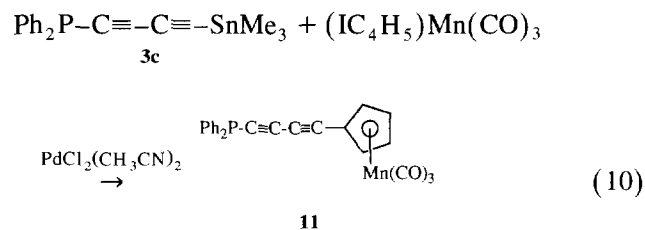
$$\tag{9}$$

Scheme 1.

These complexes would be of particular interest to study the influence of an organometallic moieties on the thermal or photochemical polymerization of the diacetylene units.

2.2.2.2. Specific reactions of the Σ group. In the study of specific reactions of the Σ groups, we have focused on the replacement of Me_3Si and Me_3Sn groups.

C_{sp}–Si bonds are easily cleaved with fluoride anion and we tried to extend this reaction to **10a** in order to obtain $W(CO)_5Ph_2P-C\equiv C-C\equiv CH$. The reaction was performed with $^nBu_4NF$ but we were unable to get any identifiable derivative from the reaction mixture.

The coupling reaction between a tin acetylide derivative and an aromatic halide in the presence of a catalytic amount of a Pd(0) or Pd(II) catalyst is well known, and allowed the formation of carbon–carbon bonds. This reaction was extended to the case of aromatic halides substituted by transition metal groups of the type $(IC_5H_4)ML_n$ $(ML_n = Fe(CO)_2Me, Mo(CO)_3Me, W(CO)_3Me, Mn(CO)_3, Re(CO)_3)$ [17–19] and to metal halide as $Cp(CO)_2FeI$ $(Cp = cyclopentadienyl)$; in the latter case a σ metal–acetylide bond was formed [19].

Coupling reactions were tried with **3c**, $Ph_2P-C\equiv C-C\equiv C-SnMe_3$, $PdCl_2(CH_3CN)_2$ as catalyst and $(IC_5H_4)Mo(CO)_3CH_3$ or $(IC_5H_4)Mn(CO)_3$ as halide. In the latter case the reaction gave the expected product **11**, as an oil (Eq. (10)).

$$Ph_2P-C\equiv-C\equiv-SnMe_3 + (IC_4H_5)Mn(CO)_3$$
$$\textbf{3c}$$

$$PdCl_2(CH_3CN)_2 \xrightarrow{\quad} \text{Ph}_2\text{P-C}\equiv\text{C-C}\equiv\text{C}-\overset{}{\underset{Mn(CO)_3}{\bigcirc}}$$

$$\textbf{11}$$

$$(10)$$

With $(IC_5H_4)Mo(CO)_3Me$, the reaction mixture indicated several peaks in the ^{31}P NMR spectrum and we were unable to isolate one of these derivatives.

In the case of the transmetallation reaction between $Ph_2P-C\equiv C-C\equiv C-SnMe_3$, **3c**, and $Cp(CO)_2FeI$, using either $PdCl_2(CH_3CN)_2$ or $Pd(PPh_3)_4$ as catalyst, a mixture of compounds was obtained. Indeed, the ^{31}P NMR spectrum of the crude residue gave nine peaks between +20 and +107 ppm.

These complex reactions may be due to $Ph_2P-C\equiv C-C\equiv C-SnMe_3$ acting as a phosphine towards carbonyl ligands bonded to the metal. This remark may explain the difference observed between $(IC_5H_4)Mn(CO)_3$ and $(IC_5H_4)Mo(CO)_3CH_3$ in the coupling reaction (Eq. (9)); indeed, the replacement of a carbonyl in manganese complexes is known to be difficult (see for instance Ref. [20]), and the reaction of a phosphine with $CpMo(CO)_3Me$ leads to the insertion of a carbonyl group into the Mo–Me bond; indeed, $CpMo(CO)_2(COR)L$ are known to be readily prepared

from $CpMo(CO)_3R$ [21]. Another argument in agreement with the hypothesis of the phosphine acting as ligand was the infrared spectrum; more complex absorption bands in the carbonyl region were observed for the reaction mixture than for the starting organometallic compounds.

In conclusion, we have developed an efficient synthesis of $Ph_2P-C\equiv C-C\equiv C-Li$, **1**, by lithiation of the commercially available (Z)-1-methoxybut-1-ene-3-yne and its diphenylphosphinyl derivative **2**. Further reactions of **1** with electrophiles Σ–Cl afforded a variety of unsymmetrically substituted diacetylenes $Ph_2P-C\equiv C-C\equiv C-\Sigma$ $(\Sigma = SiR_3, SnR_3, B(N^iPr_2)_2)$ **3**. The new compounds have been shown to be versatile synthetic intermediates. At phosphorus, (Z)-$Ph_2P-C\equiv C-CH=CH(OMe)$, **2**, reacted easily with H_2O_2 or MeI to give the expected phosphine oxide, **6**, or phosphonium salt, **7**, respectively. The oxidation of $Ph_2P-C\equiv C-C\equiv C-SiR_3$ **3a,b** and $Ph_2P-C\equiv C-SiMe_3$ were less straightforward and gave a mixture of $Ph_2P(O)-C\equiv C-C\equiv C-SiR_3$ and $Ph_2P(O)-C\equiv C-C\equiv C-H$, or $Ph_2P(O)-C\equiv C-SiMe_3$ and $Ph_2P(O)-C\equiv C-H$. The derivatives $Ph_2P-C\equiv C-C\equiv C-EMe_3$ $(E = Si, Sn)$ gave the tungsten complexes, **10**, $W(CO)_5Ph_2P-C\equiv C-C\equiv C-EMe_3$ $(E = Si, Sn)$. The reactivity at the Σ groups was exemplified with the coupling between $Ph_2P-C\equiv C-C\equiv C-SnMe_3$, **3c**, and $(IC_5H_4)Mn(CO)_3$ using $PdCl_2(CH_3CN)_2$ as catalyst which led to **11**, $(Ph_2P-C\equiv C-C\equiv C-(C_5H_4)Mn(CO)_3$ through carbon–carbon bond formation.

The thermal study, i.e. polymerization and mineralization processes, of the new diacetylene compounds is under investigation.

3. Experimental

3.1. General

All reactions were carried out under argon using a vacuum line and Schlenk tubes. Solvents were dried and distilled before use. Tetrahydrofuran (THF) was distilled over sodium benzophenone.

The chlorosilanes used were purchased from Janssen, Aldrich or Lancaster and distilled over magnesium before use. Triphenyl- and trimethyl-tin chloride were purchased from Aldrich, methyllithium-lithium bromide solution in diethyl ether from Aldrich, butyllithium in hexane and LDA in THF–heptane from Janssen. Diphenylchlorophosphine, tungsten hexacarbonyl, palladium dichloride and tetrakis(triphenylphosphine)palladium were purchased from Aldrich. Cyclopentadienyldicarbonylironiodide was purchased from Alfa Products. (Z)-1-Methoxybut-1-ene-3-yne from Aldrich was purified according to the literature (see Refs.

[10,22]). The following derivatives were prepared according to published methods: Li–C≡C–C≡C–Li [5], $Ph_2P–C≡C–SiMe_3$ [13], $ClB(N^iPr_2)_2$ [24], $PdCl_2(CH_3CN)_2$ [25], $W(CO)_5THF$ [26], $(\eta^5\text{-}IC_5H_4)Mn(CO)_3$ [17], $(\eta^5\text{-}IC_5H_4)Mo(CO)_3CH_3$ [17].

Photochemical reactions were performed with a 450 W medium-pressure Hanovia mercury lamp. ^1H NMR spectra were obtained on a Brucker AW-80 or AC-250 instrument and ^{13}C, ^{31}P, ^{119}Sn, ^{29}Si and ^{11}B NMR spectra on a Brucker AC-200 or AC-250 spectrometer; the chemical shifts δ are relative to tetramethylsilane (TMS) (^1H, ^{13}C, ^{29}Si), H_3PO_4 (^{31}P), tetramethylstannane (^{119}Sn) and BF_3–Et_2O (^{11}B). IR spectra were recorded on a Perkin–Elmer 1600 FT spectrometer at 4 cm^{-1} resolution. The mass spectra were recorded on a Jeol JMS-DX300 instrument using electron impact.

3.2. Synthesis

3.2.1. (Z)-MeOCH=CHC≡C–PPh_2 2

A solution of ^nBuLi (17.7 ml, 44.2 mmol) was added dropwise to a solution of (Z)-MeOCH=CHC≡CH in THF (100 ml) cooled to −50°C and the mixture was stirred for 1/2 h. After cooling to −78°C, neat ClPPh$_2$ (48.6 mmol) was added dropwise and the mixture was allowed to reach 0°C and was kept at that temperature for 4 h. The mixture was hydrolyzed using a saturated solution of NH$_4$Cl, extracted with THF and dried over magnesium sulfate. The volatiles were removed under vacuum and the remaining viscous oil was distilled using a small column to give the title compound **2** in 74% yield. B.p.$_{0.01}$: 175°C. IR (CCl$_4$, cm^{-1}): ν(C≡C) 2148 (s); ν(C=C) 1632 (vs); 3057, 2935, 2856, 1480, 1435. ^1H NMR (CDCl$_3$, δ, ppm): 3.84 (s, 3H, CH_3O), 4.76 (dd, 1H, J_{HH} = 6.5 Hz, $^4J_{HP}$ = 2.2 Hz, =CH–C≡), 6.37 (d, 1H, J_{HH} = 6.4 Hz, MeOCH=), 7.30–7.74 (m, 10H, Ph). ^{13}C NMR: the compound was analyzed using the decoupled, coupled and polarization transfer techniques: (CDCl$_3$, δ, ppm): 60.83 (dq, $^1J_{CH}$ = 145 Hz, $^3J_{CH}$ = 6 Hz, CH$_3$O), 85.29 (ddd, $^1J_{CH}$ = 169 Hz, $^2J_{CH}$ = 11.9 Hz, $^3J_{CP}$ = 1.4 Hz, =CH–C≡), 88.62 (dd, $^1J_{CP}$ = 3.3 Hz, $^3J_{CH}$ = 4.7 Hz, ≡C–P), 103.63 (dd, $^2J_{CP}$ = 5.5 Hz, $^2J_{CH}$ = 11.3 Hz, C≡C–P), 128.82 (d, $^3J_{CP}$ = 7.5 Hz, $C^{3,5}$), 129.14 (d, $^4J_{CP}$ = 0.3 Hz, C^4), 132.72 (d, $^2J_{CP}$ = 20.9 Hz, $C^{2,6}$), 137.13 (d, $^1J_{CP}$ = 7.2 Hz, C^{ipso}), 158.59 (dm, $^1J_{CH}$ = 180 Hz, MeOCH=). ^{31}P NMR (CDCl$_3$, δ, ppm): −29.64. Anal. Found: C, 76.79; H, 5.68; O, 6.62; P, 11.37. C$_{17}$H$_{15}$OP. Calc.: C, 76.68; H, 5.68; O, 6.60; P, 11.63%.

Note: ^1H NMR indicated pure (Z)-isomer. Superheating during distillation can lead to partial isomerization. ^1H NMR of the (E)-isomer determined in a mixture of (Z):(E), 80:20 (CDCl$_3$, δ, ppm): 3.55 (s, 3H, CH_3O), 5.06 (dd, 1H, J_{HH} = 12.8 Hz, $^4J_{HP}$ = 2.5 Hz, =CH–C≡), 7.00 (d, 1H, J_{HH} = 12.8 Hz, MeOCH=), 7.30–7.74 (m, 10H, Ph).

3.2.2. Ph_2P–C≡C–C≡CLi 1

A solution of LDA (19 mmol) was added dropwise to a cooled solution (−50°C) of 2.52 g (9.48 mmol) (Z)-MeOCH=CHC≡C–PPh$_2$, **2**, dissolved in 40 ml of THF; the mixture was stirred at that temperature for 2 h and allowed to reach room temperature. During the reaction the solution turned deep red. ^{31}P NMR of the solution (THF–C$_6$D$_6$, δ, ppm): −29.9.

3.2.3. Ph_2P–C≡C–C≡C–SiMe_3 3a

3.2.3.1. Method A. A solution of LDA (19 mmol) was added dropwise to a cooled solution (−50°C) of 2.52 g (9.48 mmol) (Z)-MeOCH=CHC≡C–PPh$_2$, **2**, dissolved in 40 ml of THF; the mixture was stirred at that temperature for 2 h and allowed to reach room temperature. During the reaction the solution turned deep red. The solution was cooled to −50°C and 2.4 ml of Me$_3$SiCl (19 mmol) in 20 ml of THF were added dropwise and the mixture was allowed to reach room temperature. After hydrolysis using a saturated solution of NH$_4$Cl and extraction with pentane, the solution was dried over magnesium sulfate. The volatiles were removed under vacuum to leave a violet residue. IR (CHCl$_3$, cm^{-1}): ν(C≡C) 2071(s); 3058, 1587, 1251. ^1H NMR (CDCl$_3$, δ, ppm): 0.27 (s, 9H, CH$_3$), 7.34–7.66 (m, 10H, Ph). ^{31}P NMR (CDCl$_3$, δ, ppm): −29.87.

3.2.3.2. Method B. A solution of MeLi–LiBr (1.6 M) (9.8 ml, 15.7 mmol) was added to 3.02 g (15.57 mmol) of Me$_3$Si–C≡C–C≡C–SiMe$_3$ dissolved in 40 ml diethyl ether and the mixture was stirred overnight. The green solution was added to a solution of Ph$_2$PCl (3 ml, 16.35 mmol) in 20 ml of Et$_2$O at −20°C. The mixture turned yellow and a precipitate appeared; after stirring overnight, the solvent was removed under vacuum and the residue treated with hexane; filtration followed by evaporation of the volatiles led to a yellow residue. Traces of Me$_3$Si–C≡C–C≡C–SiMe$_3$ were removed by sublimation (40–50°C, 5 × 10^{-2} mm Hg) and the product **3a** was crystallized from MeOH. 58% yield. M.p. 57–57.5°C. IR (CHCl$_3$, cm^{-1}): ν(C≡C) 2070 (s); 3059, 2963, 1586, 1430, 1253. ^1H NMR (CDCl$_3$, δ, ppm): 0.14 (s, 9H, Me), 7.26–7.53 (m, 10H, Ph). ^{13}C NMR (CDCl$_3$, δ, ppm): −0.4 (s, CH_3, Si satellites: $^2J_{HSi}$ = 56.7 Hz), 76.29 (d, $^1J_{CP}$ = 14.3 Hz, P–C≡), 88.25 (d, $^3J_{CP}$ = 2 Hz, Si–C≡C), 92.12 (d, $^2J_{CP}$ = 5 Hz, P–C≡C–), 96.95 (Si–C≡), 129.18 (d, $^3J_{CP}$ = 7.8 Hz, $C^{3,5}$), 129.80 (s, C^4), 133.22 (d, $^2J_{CP}$ = 21.2 Hz, $C^{2,6}$), 137.17 (d, $^4J_{CP}$ = 5.8 Hz, C^{ipso}). ^{31}P NMR (CDCl$_3$, δ, ppm): −29.81. ^{29}Si NMR (CHCl$_3$, δ, ppm): −15.68. Mass spectrum (EI; m/e, (relative intensity)): 306 (M$^+$; 30), 291 (M$^+$–CH$_3$; 8), 276 (M$^+$–2CH$_3$; 3), 261 (M$^+$–3CH$_3$; 3), 233 (M$^+$–SiMe$_3$; 11) 73 (SiMe$_3$, 100). Anal. Found: C, 74.19; H, 6.22. C$_{19}$H$_{19}$PSi. Calc.: C, 74.48; H, 6.25%.

3.2.4. $Ph_2P-C\equiv C-C\equiv C-SiPh_3$ 3b

$Ph_2P-C\equiv C-C\equiv CLi$, 1, (vide supra) was prepared from 2.72 g (10.22 mmol) of (Z)-MeOCH=CHC≡C–PPh$_2$, 2, and the solution was cooled to −50 °C. A solution of 6.03 g (20.5 mmol) of Ph$_3$SiCl in THF (20 ml) was added and the mixture was stirred overnight at room temperature. The mixture was hydrolyzed with a saturated solution of NH$_4$Cl, extracted from Et$_2$O, dried over MgSO$_4$ and the volatiles were removed under vacuum. The violet oil obtained precipitated from pentane. The title compound 3b was obtained as a violet-red powder in 53% yield. M.p. 121–122 °C. IR (CHCl$_3$, cm^{-1}): ν(C≡C) 2071; 3072, 3020, 1586, 1430, 1114. ^{1}H NMR (CDCl$_3$, δ, ppm): 7.30–7.80 (m, Ph). ^{13}C NMR (CDCl$_3$, δ, ppm): 78.30 (d, $^1J_{CP}$ = 16.3 Hz, P–C≡), 85.72 (d, $^3J_{CP}$ = 1.5 Hz, Si–C≡C), 92.0 (d, $^2J_{CP}$ = 3.1 Hz, P–C≡C–), 92.13 (d, $^4J_{CP}$ = 0.7 Hz, Si–C≡), 128.55 (SiPh, $C^{2,6}$), 129.24 (d, $^3J_{CP}$ = 7.9 Hz, PPh, $C^{3,5}$), 129.89 (PPh, C^4), 130.70 (SiPh, C^4), 133.31 (d, $^2J_{CP}$ = 21.1 Hz, PPh, $C^{2,6}$), 134.82 (d, $^1J_{CP}$ = 6.3 Hz, PPh. C^{ipso}), 135.81 (s, SiPh, C^4), 136.04 (s, SiPh, $C^{3,5}$). ^{31}P NMR (CDCl$_3$, δ, ppm): −29.83. ^{29}Si NMR(CHCl$_3$, δ, ppm): −28.35. Mass spectrum (EI; m/e (relative intensity)): 492 (M$^+$; 67), 415 (M$^+$− Ph, 11), 307 (M$^+$− PPh$_2$, 100), 259 (Ph$_3$Si, 89), 233 (M$^+$− SiPPh$_3$, 8). Anal. Found: C, 81.63; H, 5.28; P, 5.25; Si, 5.70. C$_{34}$H$_{25}$PSi. Calc.: C, 82.90; H, 5.11; P, 6.28; Si, 5.70%.

3.2.5. $Ph_2P-C\equiv C-C\equiv C-SnPh_3$ 3c

$Ph_2P-C\equiv C-C\equiv CLi$, 1, (vide supra) was prepared from 2.7 g (10.14 mmol) of (Z)-MeOCH=CHC≡C–PPh$_2$, 2, and the solution was cooled to −50 °C. A solution of Me$_3$SnCl (20.3 ml, 20.28 mmol) in THF was added dropwise and the mixture was allowed to reach room temperature and stirred overnight. THF was removed under vacuum and the residue was washed with hexane to remove LiCl. Recrystallization from pentane gave pale brown crystals of the title compound 3c in 62% yield. M.p. 65 °C. IR (CHCl$_3$, cm^{-1}): ν(C≡C) 2054; 3078, 3058, 2974, 2923, 1586, 1436. ^{1}H NMR (CDCl$_3$, δ, ppm): 7.23–7.55 (m, 10H, Ph), 0.27 (s, 9H, Me, tin satellites: $^2J_{H^{119}Sn}$ = 60.0 Hz; $^2J_{H^{117}Sn}$ = 58.3 Hz). ^{13}C NMR (CDCl$_3$, δ, ppm): −7.23 (CH$_3$, tin satellites: $^1J_{C^{119}Sn}$ = 405.3 Hz, $^1J_{C^{117}Sn}$ = 387.2 Hz), 73.56 (d, $^1J_{CP}$ = 12.4 Hz, P–C≡), 91.64 (d, $^3J_{CP}$ = 1.9 Hz, P–C≡C–C≡), 92.35 (d, $^2J_{CP}$ = 5.4 Hz, P–C≡C–), 92.99 (C≡C–Sn), 129.1 (d, $^3J_{CP}$ = 7.8 Hz, $C^{3,5}$), 129.66 (C^4), 133.15 (d, $^2J_{CP}$ = 21.1 Hz, $C^{2,6}$), 135.53 (d, $^1J_{CP}$ = 6.0 Hz, C^{ipso}). ^{31}P NMR (CDCl$_3$, δ, ppm): −29.33. ^{119}Sn NMR (CDCl$_3$, δ, ppm): −56.87 (d, $^5J_{SnP}$ = 5.3 Hz). Mass spectrum (EI; m/e (relative intensity)): 398 (M$^+$; 19), 383 (M$^+$− CH$_3$; 29), 368 (M$^+$− 2CH$_3$; 4) 353 (M$^+$− 3CH$_3$; 42) 233 (M$^+$− SnCH$_3$; 100). Anal. Found: C, 57.91; H, 5.0; P, 8.08; Sn, 28.73. C$_{19}$H$_{19}$PSn. Calc.: C, 57.48; H, 4.82; P, 7.80; Sn, 29.9%.

3.2.6. $Ph_2P-C\equiv C-C\equiv C-SnPh_3$ 3d

$Ph_2P-C\equiv C-C\equiv CLi$, 1, (vide supra) was prepared from 1.48 g (5.56 mmol) of (Z)-MeOCH=CHC≡C–PPh$_2$, 2, and the solution was cooled to −50 °C. A solution of Ph$_3$SnCl (2.14 g, 5.56 mmol) in THF (20 ml) was added dropwise and the mixture was allowed to reach room temperature and stirred overnight. THF was removed under vacuum and the residue was washed with hexane to remove LiCl. Concentration of the solution gave the title compound 3d as a pale pink solid in 50% yield. M.p. 111–112 °C. IR (CHCl$_3$, cm^{-1}): ν(C≡C) 2058; 3069, 3057, 1482, 1432, 1076. ^{1}H NMR (CDCl$_3$, δ, ppm): 7.31 (m, 15H, Ph), 7.53 (m, 10H, Ph). ^{13}C NMR (CDCl$_3$, δ, ppm): 74.8 (d, $^1J_{CP}$ = 14 Hz, P–C≡), 89.48 (Sn–C≡), 92.4 (d, $^2J_{CP}$ = 5.1 Hz, P–C≡C), 94.08 (C≡C–Sn), 129.16 (d, $^3J_{CP}$ = 7.8 Hz, $C^{3,5}$), 129.34 (tin satellites: $^1J_{CSn}$ = 60 Hz, $C^{2,6}$), 129.76 (C^4, PPh), 130.23 (C^4, SnPh), 133.24 (d, $^2J_{CP}$ = 21.1 Hz, $C^{2,6}$), 135.25 (d, $^1J_{CP}$ = 5.9 Hz, C^{ipso}), 136.26 (C^{ipso}, SnPh) 137.13 (tin satellites: $^2J_{CSn}$ = 43.8 Hz, $C^{3,5}$). ^{31}P NMR (CDCl$_3$, δ, ppm): −29.66. ^{119}Sn NMR (CDCl$_3$, δ, ppm): −170.22. Mass spectrum (EI; m/e (relative intensity)): 584 (M$^+$; 27), 507 (M$^+$− Ph; 24), 351 (SnPh$_3$; 75), 233 (M$^+$− SnPh$_3$; 100). Anal. Found: C, 69.63; H, 4.20; P, 5.10. C$_{34}$H$_{25}$PSn. Calc.: C, 70.0; H, 4.3; P, 5.3%.

3.2.7. $Ph_2P-C\equiv C-C\equiv C-B(N^iPr_2)_2$ 3e

$Ph_2P-C\equiv C-C\equiv CLi$, 1, (vide supra) was prepared starting from 1.02 g (3.82 mmol) of (Z)-MeOCH=CHC≡C–PPh$_2$, 2, and the solution was cooled to −50 °C. A solution of ClB(N^{i}Pr$_2$)$_2$ (0.94 g, 3.82 mmol) in 20 ml of THF was added dropwise and the mixture was allowed to reach room temperature, stirred for 36 h and refluxed for an additional hour. The solvent was removed under vacuum and the residue was washed with hexane to remove LiCl. Evaporation of the solvent under vacuum gave the title compound 3e as a viscous violet oil in 68% yield. IR (CHCl$_3$, cm^{-1}): ν(C≡C) 2081; 3077, 3059, 2965, 2930, 2870, 1586. ^{1}H NMR (CDCl$_3$, δ, ppm): 7.51–7.27 (m, 10H, Ph), 3.33 (sept., 4H, $^3J_{HH}$ = 6.8 Hz, CH), 1.15 (d, 24H, $^3J_{HH}$ = 6.8 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$, δ, ppm): 24.57 (CH$_3$), 47.18 (CH), 77.76 (d, $^1J_{CP}$ = 9.9 Hz, P–C≡), 89.63 (broad, B–C≡C and B–C≡C), 93.44 (d, $^2J_{CP}$ = 6.2 Hz, P–C≡C), 129.06 (d, $^3J_{CP}$ = 7.7 Hz, $C^{3,5}$), 129.55 (C^4), 133.13 (d, $^2J_{CP}$ = 21.13 Hz, $C^{2,6}$), 135.86 (d, $^1J_{CP}$ = 6.2 Hz, C^{ipso}). ^{31}P NMR (CDCl$_3$, δ, ppm): −29.42. ^{11}B NMR (CDCl$_3$, δ, ppm): 25.53. Mass spectrum (EI; m/e (relative intensity)): 444 (M$^+$; 27), 429 (M$^+$− CH$_3$; 100), 401 (M$^+$− ^{i}Pr; 100), 358 (M$^+$− 2^{i}Pr; 24), 344 (M$^+$− N^{i}Pr$_2$; 100), 244 (M$^+$− 2N^{i}Pr$_2$; 9), 233 (M$^+$− B(N^{i}Pr$_2$)$_2$; 35), 185 (PPh$_2^+$; 49).

3.2.8. (Z)-MeOCH = CHC≡C–P(Me)Ph$_2^+$I$^-$ 6

The phosphonium salt was prepared according to the procedure of Charrier et al. [8]. MeI was added drop-

wise to a solution of 1.27 g (4.77 mmol) (Z)-MeOCH=CHC≡C–PPh$_2$, **2**, dissolved in 20 ml of diethyl ether. A precipitate appeared during stirring (20 h). After filtration, the solid was washed with diethyl ether and gave a fine, off-white powder of **6**. 1.71 g, 88% yield. M.p.: 126.5–128 °C. IR (CDCl$_3$, cm^{-1}): ν(C≡C) 2149 (s); ν(C=C) 1615(s). ^{1}H NMR (CDCl$_3$, δ, ppm): 2.9 (d, 3 H, $^2J_{HP}$ = 14 Hz, CH_3), 3.95 (s, 3H, CH_3O), 4.94 (dd, J_{HH} = 6.4 Hz, $^4J_{HP}$ = 3.8 Hz, =CH–C≡), 7.06 (dd, 1H, J_{HH} = 6.4 Hz, $^5J_{HP}$ = 1.1 Hz, MeOCH=), 7.60–8.10 (2m, 10H, Ph). ^{13}C NMR (CDCl$_3$, δ, ppm): 14.73 (d, $^1J_{CP}$ = 63.5 Hz, CH_3), 63.13 (s, CH_3O), 81.22 (d, $^3J_{CP}$ = 5.3 Hz, =CH–C≡), 72.02 (d, $^1J_{CP}$ = 188 Hz, ≡C–P), 116.09 (d, $^2J_{CP}$ = 33.8 Hz, C≡C–P), 132.65 (d, $^2J_{CP}$ = 12.8 Hz, $C^{2,6}$), 130.73 (d, $^3J_{CP}$ = 14.1 Hz, $C^{3,5}$), 135.46 d, $^4J_{CP}$ = 3.1 Hz, C^4), 120.5 (d, $^1J_{CP}$ = 99.1 Hz, C^{ipso}), 168.13 (d, $^4J_{CP}$ = 3 Hz, OCH). ^{31}P NMR (CDCl$_3$, δ, ppm): 5.0. Mass spectrum (Fab$^+$, 3-nitrobenzylalcohol): 281 (M$^+$). Anal. Found: C, 53.44; H, 4.40; I, 31.03; O, 3.85; P, 7.85. C$_{18}$H$_{18}$IOP. Calc.: C, 52.78; H, 4.50; I, 31.09; O, 3.92; P, 7.59%.

3.2.9. (Z)-MeOCH=CHC≡C–P(O)Ph$_2$ 7

The oxidation was performed according to the procedure of Charrier et al. [8]. A solution of H$_2$O$_2$, 3.8 mmol (0.34 ml of a 35 wt.% solution) in water (50 ml) was added dropwise to a solution of (Z)-MeOCH=CHC≡C–PPh$_2$, **2**, 1.013 g (3.8 mmol) in 35 ml of diethyl ether maintained at 0 °C and the mixture was stirred at room temperature for 5 h. After extraction with diethyl ether, the organic phase was washed first with a 0.1 N solution of Na$_2$S$_2$O$_3$ and then water. The mixture was extracted with diethyl ether and chloroform and the organic phase dried over MgSO$_4$. Volatiles were removed under vacuum to leave a yellow-orange oil of the title compound **7** in 95% yield. B.p.$_{0.05}$: 200 °C. IR (CHCl$_3$, cm^{-1}): ν(C≡C) 2160 (s); ν(C=C) 1623 (vs); ν(P=O) 1186 (s). ^{1}H NMR (CDCl$_3$, δ, ppm): 3.76 (s, 3H, CH_3O), 4.63 (dd, 1H, J_{HH} = 6.5 Hz, $^4J_{HP}$ = 3.1 Hz, =CH–C≡), 6.49 (dd, 1H, J_{HH} = 6.6 Hz, $^5J_{HP}$ = 0.6 Hz, MeOCH=), 7.4–7.9 (m, 10H, Ph). ^{13}C NMR (CDCl$_3$, δ, ppm): 61.27 (s, CH_3O), 82.6 (d, $^3J_{CP}$ = 4.3 Hz, =CH–C≡), 85.65 (d, $^1J_{CP}$ = 177 Hz, ≡C–P), 102.26 (d, $^2J_{CP}$ = 32.4 Hz, C≡C–P), 128.51 (d, $^2J_{CP}$ = 13.5 Hz, $C^{2,6}$), 130.9 (d, $^3J_{CP}$ = 11.4 Hz, $C^{3,6}$), 131.98 (d, $^4J_{CP}$ = 3 Hz, C^4), 133.44 (d, $^1J_{CP}$ = 122 Hz, C^{ipso}), 162.0 (s, OCH). ^{31}P NMR (CDCl$_3$, δ, ppm): 8.37. Mass spectrum (Fab$^+$, 3-nitrobenzylalcohol): 283 (M$^+$ + 1). Anal. Found: C, 71.1; H, 5.53; O, 12.26. C$_{17}$H$_{15}$O$_2$P. Calc.: C, 72.34; H, 5.36; O, 11.33%.

3.2.10. Ph$_2$P–C≡C–C≡C–PPh$_2$ 8

The dilithio derivative, C$_4$Li$_2$, was prepared from 1,4-bis(trimethylsilyl)buta-1,3-diyne (1.94 g, 10 mmol) and MeLi–LiBr (22.5 mmol) and the slurry obtained was added to a solution of chlorodiphenylphosphine

(5 ml, 28 mmol) in 50 ml THF maintained at − 40 °C. The reaction mixture was stirred up to room temperature, hydrolyzed with a saturated solution of NH$_4$Cl and extracted from pentane. The organic phase was dried over MgSO$_4$ and the volatiles removed under vacuum to leave a greenish residue. The latter was washed with boiling MeOH to give a pale beige powder (3.14 g, 75%). M.p. 109 °C (105 °C Ref. [8]). IR (CCl$_4$, cm^{-1}): ν(C≡C) 2072; 3059, 1586, 1480. ^{1}H NMR (CCl$_4$, δ, ppm): 7.08–7.80 (m). ^{13}C NMR (CDCl$_3$, δ, ppm): 81.3 (d, $^1J_{CP}$ = 12.5 Hz, PC), 91.77 (dd, $^2J_{CP}$ = 5.2 Hz, $^3J_{CP}$ = 2.2 Hz, P–C≡C), 129.20 (d, $^3J_{CP}$ = 7.9 Hz, C$^{3.5}$), 129.83 (s, C^4), 133.25 (d, $^2J_{CP}$ = 24.7 Hz, C^{2,6}), 134.92 (d, $^1J_{CP}$ = 5.7 Hz, C^{ipso}). ^{31}P NMR (CDCl$_3$, δ, ppm): − 29.52. Mass spectrum (EI, m/e, relative intensities): 418 (M$^+$; 94), 341 (M$^+$ − Ph; 9), 233 (M$^+$ − PPh$_2$; 100), 209 (M$^+$ − C$_2$PPh$_2$; 38). Anal. Found: C, 80.29; H, 5.15; P, 14.57. C$_{28}$H$_{20}$P$_2$. Calc.: C, 80.38; H, 4.82; P, 14.80%.

3.2.11. Ph$_2$P(O)–C≡C–C≡C–(O)PPh$_2$ 9

The oxidation was performed according to the procedure of Charrier et al. [8]. A solution of H$_2$O$_2$ (1.22 ml of a 35 wt.% solution) in 15 ml of H$_2$O was added to a solution of 2.1 g (5 mmol) Ph$_2$P–C≡C–C≡C–PPh$_2$ dissolved in 40 ml of diethyl ether and maintained at − 40 °C. After stirring for 15 h at room temperature, the mixture was extracted from CHCl$_3$ and the organic phase washed with a 0.1 N solution of Na$_2$S$_2$O$_3$. Standard work-up gave a solid which was recrystallized from MeOH to give **9**. M.p. 191 °C. IR (CHCl$_3$, cm^{-1}): ν(C≡C) 2097; ν(P=O) 1194. ^{1}H NMR (CDCl$_3$, δ, ppm): 7.40–7.87 (m, Ph). ^{13}C NMR (CDCl$_3$, δ, ppm): 79.37 (d, $^1J_{CP}$ = 150 Hz, P–C≡), 85.9 (dd, $^2J_{CP}$ = 34.1 Hz, $^3J_{CP}$ = 21.53 Hz, P–C≡C), 129.35 (d, $^3J_{CP}$ = 14.1 Hz, C$^{3.5}$), 131.46 (d, $^2J_{CP}$ = 11.6 Hz, C^{2,6}), 131.40 (d, $^1J_{CP}$ = 123 Hz, C^{ipso}), 133.46 (s, C^4). ^{31}P NMR (CDCl$_3$, δ, ppm): 9.73. Mass spectrum (Fab$^+$, 3-nitrobenzylalcohol): 451 (M$^+$ + 1). Anal. Found: C, 74.59; H, 4.34; O, 7.07; P, 14.55. C$_{28}$H$_{20}$O$_2$P. Calc.: C, 74.67; H, 4.48; O, 7.10; P, 13.75%.

3.2.12. Oxidation reactions of Ph$_2$P–C≡C–C≡C–SiMe$_3$ 3a with H$_2$O$_2$

A solution of H$_2$O$_2$, 3.6 mmol (0.31 ml of a 35 wt.% solution) in water (10 ml) was added dropwise to 1.0 g (3.26 mmol) Ph$_2$P–C≡C–C≡C–SiMe$_3$, **3a**, dissolved in diethyl ether (30 ml) and cooled to 0 °C. After stirring overnight, the organic phase was washed twice with 5 ml of a 0.1 N solution of Na$_2$S$_2$O$_3$. Standard work-up gave a brown oil. ^{31}P NMR (CDCl$_3$, δ, ppm): 8.85 ppm. IR (CHCl$_3$, cm^{-1}): ν(≡C–H) 3296; ν(C≡C) 2204, 2081; ν(P=O) 1194. ^{1}H NMR (CDCl$_3$, δ, ppm): 2.55 (d, $^5J_{HP}$ = 1.7 Hz, ≡C–H), 7.3–7.9 (2 m, broad, Ph), 0.17, 0.03, 0.02, 0.01 (ratios: 18:3.5:1.6:1; SiMe$_3$). Integration gave 43% ≡C–H compound. The ^{31}P NMR spectrum indicated that no Ph$_2$P(O)–C≡C–C≡C–H

was present when the spectrum was run; this may be due to its polymerization giving insoluble material.

3.2.13. Oxidation reactions of $Ph_2P-C\equiv C-C\equiv C-SiPh_3$ 3b with H_2O_2

The same procedure as for $Ph_2P-C\equiv C-C\equiv C-SiMe_3$ was used with 0.96 g (1.95 mmol) of $Ph_2P-C\equiv C-C\equiv C-SiPh_3$, 3b, and 1.9 mmol H_2O_2 (0.16 ml of a 35 wt.% solution) in water (5 ml) and the reaction was stirred for 5 h. Extraction from chloroform followed by the standard work-up gave a brown residue. IR ($CHCl_3$, cm^{-1}): $\nu(SiOH)$ 3680; $\nu(\equiv C-H)$ 3296; $\nu(C\equiv C)$ 2204, 2080; $\nu(P=O)$ 1191. ^1H NMR ($CDCl_3$, δ, ppm): 2.56 (d, $^5J_{HP} = 1.7$ Hz, $\equiv C-H$), 7.3–7.9 (3 m, Ph). Integration gave 28% $\equiv C-H$ compound. ^{31}P NMR ($CDCl_3$, δ, ppm) 9.4, 9.5 (ratio: 1:2; i.e., δ $Ph_2P(O)-C\equiv C-C\equiv C-H$: 9.4 ppm). ^{29}Si NMR ($CHCl_3$, δ, ppm): -14.0 (Ph_3SiOH), -21.8, -27.8.

3.2.14. Oxidation reactions of $Ph_2P-C\equiv C-SiMe_3$ with H_2O_2

The same procedure as for $Ph_2P-C\equiv C-C\equiv C-SiMe_3$ was used with 3.12 g (11.06 mmol) of $Ph_2P-C\equiv C-SiMe_3$ in Et_2O (80 ml) maintained at 0 °C and 11.6 mmol H_2O_2 (0.98 ml of a 35 wt.% solution) in water (20 ml). Standard work-up gave 2.6 g of an off-white solid corresponding to a 48:52 mixture of $Ph_2P(O)-C\equiv C-SiMe_3$ and $Ph_2P(O)-C\equiv C-H$. IR ($CHCl_3$, cm^{-1}): $\nu(\equiv C-H)$ 3289; $\nu(C\equiv C)$ 2264, 2125; $\nu(P=O)$ 1190. ^1H NMR ($CDCl_3$, δ, ppm): 7.86–7.78 (m, 4H, Ph), 7.54–7.43 (m, 6H, Ph), 3.34 (d, $^3J_{HP} = 9.88$ Hz, $\equiv CH$, 52%), 0.27 (s, $SiMe_3$, 48%). ^{31}P NMR ($CDCl_3$, δ, ppm): 8.76 ($Ph_2P(O)-C\equiv C-H$), 7.58 ($Ph_2P(O)-C\equiv C-SiMe_3$). ^{13}C NMR ($CDCl_3$, δ, ppm): ^{13}C values of $Ph_2P(O)-C\equiv C-H$ (vide infra) and: -0.39 (d, $^4J_{CP} = 0.6$ Hz, CH_3), 99.2 (d, $^1J_{CP} = 151$ Hz, $P-C\equiv$), 116.34 (d, $^2J_{CP} = 19.2$ Hz, $C\equiv C-Si$), 129.0 (d, $^3J_{CP} = 13.4$ Hz, $C^{3,5}$), 131.34 (d, $^2J_{CP} = 11.2$ Hz, $C^{2,6}$), 132.62 (d, $^4J_{CP} = 3.0$ Hz, C^4), 133.25 (d, $^1J_{CP} = 121$ Hz, C^{ipso}).

Column chromatography (silica gel, Et_2O) of 1.05 g of the $Ph_2P(O)-C\equiv C-SiMe_3$ and $Ph_2P(O)-C\equiv C-H$ mixture gave 0.900 g of nearly pure $Ph_2P(O)-C\equiv C-H$, i.e. complete transformation of $Ph_2P(O)-C\equiv C-SiMe_3$ into $Ph_2P(O)-C\equiv C-H$. The same transformation was observed using florisil instead of silica gel. Recrystallization from toluene–pentane (10:90) gave pure $Ph_2P(O)-C\equiv C-H$. M.p. 57–58 °C (Ref. [23]: 68 °C); IR ($CHCl_3$, cm^{-1}): $\nu(\equiv C-H)$ 3289; $\nu(C-H)$ 3063; $\nu(C\equiv C)$ 2064; $\nu(P=O)$ 1194. ^1H NMR ($CDCl_3$, δ, ppm): (identical to Ref. [23]): 7.94–7.83 (m, 4H, Ph), 7.59–7.48 (m, 6H, Ph), 3.37 (d, 1H, $^3J_{HP} = 9.7$ Hz, $\equiv C-H$). ^{13}C NMR ($CDCl_3$, δ, ppm): 79.09 (d, $^1J_{CP} = 160.5$ Hz, $P(O)-C\equiv$), 95.0 (d, $^2J_{CP} = 27.4$ Hz, $P(O)-C\equiv C$), 129.12 (d, $^3J_{CP} = 13.6$ Hz, $C^{3,5}$), 131.29 (d, $^2J_{CP} = 11.32$ Hz, $C^{2,6}$), 132.5 (d, $^1J_{CP} = 122$ Hz, C^{ipso}), 132.94 (d, $^4J_{CP} = 3$ Hz, C^4). Mass spectrum (Fab$^+$,

3-nitrobenzylalcohol): 227 ([$M^+ + 1$]; linked molecular ion: 149 ($M^+ - Ph$).

3.2.15. $W(CO)_5Ph_2P-C\equiv C-C\equiv C-SiMe_3$ 10a

A solution of $W(CO)_5THF$, prepared by irradiation of a solution of $W(CO)_6$ (1.40 g, 3.98 mmol) in 400 ml of THF for 2 h, was added to a solution of $Ph_2P-C\equiv C-C\equiv C-SiMe_3$, 3a, (1.22 g, 3.98 mmol) and the mixture was stirred for 36 h. Evaporation of the solvent under vacuum left a residue which was crystallized from toluene–pentane (2:1) to give the title compound 10a as a beige-colored powder in 44% yield. M.p. 123.5–124.7 °C. IR ($CHCl_3$, cm^{-1}): $\nu(C\equiv C)$ 2074; $\nu(CO)$ 1978, 1945. ^1H NMR ($CDCl_3$, δ, ppm): 0.26 (s, 9H, CH_3), 7.45–7.72 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$, δ, ppm): -0.25 (CH_3), 71.57 (d, $^1J_{CP} = 76.6$ Hz, $P-C\equiv$), 86.58 (d, $^3J_{CP} = 4.3$ Hz, $Si-C\equiv C$), 93.42 (d, $^2J_{CP} = 15.2$ Hz, $P-C\equiv C$), 95.54 ($Si-C$), 129.31 (d, $^3J_{CP} = 10.9$ Hz, $C^{3,5}$), 131.18 (d, $^4J_{CP} = 2.1$ Hz, C^4), 131.77 (d, $^2J_{CP} = 14.0$ Hz, $C^{2,6}$), 134.41 (d, $^1J_{CP} = 49.3$ Hz, C^{ipso}), 196.64 (d, $^2J_{CP} = 6.8$ Hz, CO cis with ^{183}W satellites, $^1J_{CW} = 127$ Hz), 199.43 (d, $^2J_{CP} = 22.7$ Hz, CO trans, ^{183}W satellites not observed). ^{31}P NMR ($CDCl_3$, δ, ppm): -3.72 with ^{183}W satellites, $^1J_{PW} = 246$ Hz. ^{29}Si NMR ($CHCl_3$, δ, ppm): -14.79. Mass spectrum (EI; m/e (relative intensity)): 630 (M^+; 5), 574 (M^+-2CO; 27), 490 ($M^+ - 5CO$; 74), 475 ($M^+ - 5CO - Me$; 10), 306 ($M^+ - W(CO)_5$; 14), 233 ($M^+ - W(CO)_5 - SiMe_3$; 7). Anal. Found: C, 45.99; H, 3.05; P, 5.07; Si, 4.85; W, 29.86. $C_{24}H_{19}O_5PSiW$. Calc.: C, 45.73; H, 3.04; P, 4.91; Si, 4.46; W, 29.17%.

3.2.16. $W(CO)_5Ph_2P-C\equiv C-C\equiv C-SnMe_3$ 10b

A solution of $W(CO)_5THF$, prepared by irradiation of a solution of $W(CO)_6$ (0.7 g, 2.0 mmol) in 400 ml of THF for 2 h, was added to a solution of $Ph_2P-C\equiv C-C\equiv C-SnMe_3$, 3c, (0.79 g, 2.0 mmol) and the mixture was stirred for 36 h. Evaporation of the solvent under vacuum left a residue which was crystallized from toluene–pentane (2:1) to give the title compound 10b as a beige-colored powder in 28% yield. M.p. 140.0–141.5 °C. IR ($CHCl_3$, cm^{-1}): $\nu(C\equiv C)$ 2075; $\nu(CO)$ 1988, 1945. ^1H NMR ($CDCl_3$, δ, ppm): 0.39 (s, 9H, CH_3; tin satellites: $^2J_{H^{119}Sn} = 61$ Hz; $^2J_{H^{117}Sn} = 58.5$ Hz), 7.26–7.72 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$, δ, ppm): -7.17 (CH_3, tin satellites: $^1J_{C^{117}Sn} = 387.1$ Hz, $^1J_{C^{119}Sn} = 405.5$ Hz), 72.25 (d, $^1J_{CP} = 370.0$ Hz, $P-C\equiv$), 90.05 (d, $^3J_{CP} = 4.3$ Hz, $P-C\equiv C-C\equiv$), 93.8 (d, $^2J_{CP} = 15.7$ Hz, $P-C\equiv C-$), 98.36 ($C\equiv C-Sn$), 129.3 (d, $^3J_{CP} = 10.9$ Hz, $C^{3,5}$), 131.10 (d, $^4J_{CP} = 2$ Hz, C^4), 131.75 (d, $^2J_{CP} = 13.9$ Hz, $C^{2,6}$), 134.67 (d, $^1J_{CP} = 49.25$ Hz, C^{ipso}), 196.74 (d, $^2J_{CP} = 6.8$ Hz, CO cis, ^{183}W satellites: $^1J_{CW} = 127$ Hz), 199.59 (d, $^2J_{CP} = 22.6$ Hz, CO trans, ^{183}W satellites: $^1J_{CW} = 179$ Hz). ^{31}P NMR ($CDCl_3$, δ, ppm): -4.19, ^{183}W satellites: $^1J_{PW} = 2.45$ Hz. ^{119}Sn NMR ($CDCl_3$, δ, ppm): -53.43 (d, $^5J_{SnP} = 3.3$ Hz).

Mass spectrum (EI; m/e (relative intensity)): 720 (M^+; 9), 664 ($M^+ - 2CO$; 48), 580 ($M^+ - 5CO$; 100), 535 ($M^+ - 5CO - 3CH_3$; 16), 233 ($Ph_2PC_4^+$; 54). Anal. Found: C, 40.42; H, 2.56. $C_{24}H_{19}O_5PSnW$. Calc.: C, 39.98; H, 2.66%.

3.2.17. Reaction of $W(CO)_5Ph_2P-C\equiv C-C\equiv C-SiMe_3$, 10a, with $^nBu_4NF$

A solution of $^nBu_4NF$ (1 M in THF), 0.72 ml (0.72 mmol), was added dropwise to a solution of 0.370 g (0.6 mmol) of $W(CO)_5Ph_2P-C\equiv C-C\equiv C-SiMe_3$, 10a, in 20 ml of THF maintained at 0 °C. The solution turned immediately violet; after stirring for 2 h, the reaction mixture was hydrolyzed with 15 ml of a saturated solution of NH_4Cl at 0 °C. Standard work-up led to a brown oil. IR ($CHCl_3$, cm^{-1}): $\nu(\equiv C-H)$ 3308 (very weak); $\nu(C\equiv O)$ 2075, 1952, 1989. ^1H NMR ($CDCl_3$, δ, ppm) 2.16 ($\equiv C-H$, traces); several Me groups: 0.10, 0.11, 0.14, (ratios 1:0.2:0.2), 7.0–7.9 (m, broad, Ph). ^{31}P NMR ($CDCl_3$, δ, ppm): -6.0 (very broad peak), 34.19 (small and sharp), 83.6 (broad).

3.2.18. $Ph_2P-C\equiv C-C\equiv C-(\eta^5-C_5H_4)Mn(CO)_3$ 11

A solution of 1.31 g (3.3 mmol) of $Ph_2P-C\equiv C-C\equiv C-SnMe_3$, 3c, in 20 ml of DMF was added dropwise to the mixture of 1.03 g (3 mmol) of $(\eta^5-IC_5H_4)Mn(CO)_3$ (impurity: 3.8% $CpMn(CO)_3$), and 0.043 g (5 mol%) $(CH_3CN)_2PdCl_2$ dissolved in 50 ml of DMF and the reaction mixture was stirred overnight. Diethyl ether (50 ml) was added, and the reaction mixture was hydrolyzed with 25 ml of a 50% KF solution and argon was bubbled through the solution for 30 min. Standard work-up led to a black viscous wax of 11. IR ($CHCl_3$, cm^{-1}): $\nu(C\equiv O)$ 2028, 1948. ^{31}P NMR ($CDCl_3$, δ, ppm): -29.81 (traces at 23.1, 22.0 and 7.9). ^1H NMR ($CDCl_3$, δ, ppm): 5.0 (t, 4H, $J = 2.1$ Hz), 4.66 (t, 4H, $J = 2.1$ Hz), 7.3–7.7 (2m, 10 H, Ph). Traces of DMF and $CpMn(CO)_3$.

The same reaction was tried in THF as solvent; ^{31}P NMR indicated a major peak at -29.65 ppm but other impurities at -30.2, -31.8, 14.5, 18.8, 21.4 and 23.25 ppm.

3.2.19. Reaction of 3c, $Ph_2P-C\equiv C-C\equiv C-SnMe_3$ with $(\eta^5-IC_5H_4)Mo(CO)_3CH_3$

The same procedure as for $(\eta^5-IC_5H_4)Mn(CO)_3$ was used with 0.99 g (2.4 mmol) $Ph_2P-C\equiv C-C\equiv C-SnMe_3$, 3c, 0.93 g (2.3 mmol) $(\eta^5-IC_5H_4)Mo(CO)_3CH_3$ and 0.030 g (5 mol%) $(CH_3CN)_2PdCl_2$. A brown-black sticky residue was obtained. ^{31}P NMR ($CDCl_3$, δ, ppm): very broad peaks at 63, 48 and 30 ppm; other peaks at 110, 23, 20 and 8 ppm.

3.2.20. Reaction of 3c, $Ph_2P-C\equiv C-C\equiv C-SnMe_3$ with $CpFe(CO)_2I$

The same procedure as for $(\eta^5-IC_5H_4)Mn(CO)_3$ was used with 0.96 g (2.4 mmol) $Ph_2P-C\equiv C-C\equiv C-SnMe_3$,

3c, 0.61 g (2.0 mmol) $CpFe(CO)_2I$, 0.026 g (5 mol%) $(CH_3CN)_2PdCl_2$. THF (20 ml) was used as solvent and the catalyst was added to the mixture of the two components. After stirring overnight, the solvent was removed under vacuum to give a black powder. ^{31}P NMR($CDCl_3$, δ, ppm) (relative intensities): 19.7 (1), 20.6 (1), 42.0 (1), 42.2 (1), 43.6 (8), 45 (3), 50.3 (2.3), 51.7 (1.1), 61.8 (1.4), 63.1 (2), 107.3 (1.5).

The same reaction was tried using $Pd(PPh_3)_4$ (0.116 g) as catalyst. ^{31}P NMR ($CDCl_3$, δ, ppm) (relative intensities): 42.0 (1.7), 43.6 (5.7), 45 (2), 50.3 (5.7), 51.7 (4), 61.6 (1.9), 61.8 (1.3), 63.1 (1.3), 67.7 (1), 105.5 (1), 107.3 (3).

3.2.21. Reaction of 1, $Ph_2P-C\equiv C-C\equiv CLi$ with $CpFe(CO)_2I$

$Ph_2P-C\equiv C-C\equiv CLi$, 1, was prepared as previously described (vide supra) with 1.03 g (3.86 mmol) of (Z)-$MeOCH=CHC\equiv C-PPh_2$ and the solution was cooled to -50 °C. A solution of 1.17 g (3.86 mmol) $CpFe(CO)_2I$ in 20 ml of THF was added and the mixture was stirred overnight. Evaporation of the volatiles under vacuum led to a brown-black residue. Extraction using dichloromethane, followed by filtration and removal of the solvent gave a black residue. ^{31}P NMR ($CDCl_3$, δ, ppm) (relative intensities): -27.8 (1.7), 11.0 (4), 39.7 (3), 51.0 (1), 51.3 (1).

References

[1] D. Chemla and J. Zyss (eds.), Non-Linear Optical Properties of Organic Molecules and Crystals, Vols. 1 and 2, Academic Press, Orlando, 1987.

[2] (a) J.W. Perry, A.E. Stiegman, S.R. Marder and D.R. Coulter, R. Soc. Chem. Special Publ., Org. Mater. Non-Linear Opt., 69 (1989) 189. (b) J.R. Allan, G.H.W. Milburn, A.J. Shand, J. Tsibouklis and A.R. Werninck, R. Soc. Chem. Special Publ., Org. Mater. Non-Linear Opt., 69 (1989) 196.

[3] (a) M.S. Paley, D.O. Frazier, S.P. McManus, S.E. Zutaut and M. Sanghadasa, Chem. Mater., 5 (1993) 1641. (b) K. Chane-Ching, M. Lequan, R.M. Lequan, A. Grisard and D. Markovitsi, J. Chem. Soc. Faraday Trans., 87 (1991) 2225. (c) K. Chane-Ching, M. Lequan, R.M. Lequan, C. Runser, M. Barzoukas and A. Fort, J. Mater. Chem., 5 (1995) 649.

[4] (a) J. Le Moigne, F. Fajzar and A. Thierry, Macromolecules, 24 (1991) 2622. (b) H.S. Nalva, Adv. Mater., 5 (1993) 341 and references cited therein. (c) M.S. Paley, D.O. Frazier, H. Abdeldayem and S.P. McManus, Chem. Mater., 6 (1994) 2213.

[5] (a) R.J.P. Corriu, C. Guérin, B. Henner, T. Kuhlmann, A. Jean, F. Garnier and A. Yassar, Chem. Mater., 2 (1990) 351. (b) J.L. Bréfort, R.J.P. Corriu, C. Guérin, B.J.L. Henner, A. Jean, T. Kuhlmann, F. Garnier and A. Yassar, Organometallics, 11 (1992) 2500.

[6] (a) R.J.P. Corriu, C. Guérin, B. Henner, A. Jean and H. Mutin, J. Organomet. Chem., 396 (1990) C35. (b) R.J.P. Corriu, Ph. Gerbier, C. Guérin, B.J.L. Henner, A. Jean and P.H. Mutin, Organometallics, 11 (1992) 2507. (c) R. Corriu, C. Guérin, Ph. Gerbier, B. Henner and R. Fourcade, J. Organomet. Chem., 449 (1993) 311.

[7] N. Devylder, *Thesis*, Montpellier, France, 1994.

[8] C. Charrier, W. Chodkiewicz and P. Cadiot, *Bull. Soc. Chim. Fr.*, (1966) 1002.

[9] H.J. Bestmann, D. Hadawi, H. Behl, M. Brewer and F. Hampel, *Angew. Chem. Int. Ed. Engl.*, *32* (1993) 1205.

[10] G. Zweifel and S. Rajagopalan, *J. Am. Chem. Soc.*, *107* (1985) 700.

[11] E.C. Stracker and G. Zweifel, *Tetrahedron*, *31* (1990) 6815.

[12] (a) A.B. Holmes, C.L. Jennings-White, A.H. Schulters, B. Akinde and D.R.M. Walton, *J. Chem. Soc. Chem. Commun.*, (1979) 840. (b) A.B. Holmes and G.E. Jones, *Tetrahedron Lett.*, *21* (1980) 3111.

[13] W. Siebert, W.E. Davidsohn and M.C. Henry, *J. Organomet. Chem.*, *15* (1968) 69.

[14] H. Hartmann, C. Beumann and H. Czempik, *Z. Anorg. Allg. Chem.*, *287* (1956) 261.

[15] O. Orama, *J. Organomet. Chem.*, *314* (1986) 273.

[16] (a) C.J. Adams, M.I. Bruce, E. Horn and E.R.T. Tiekink, *J. Chem. Soc. Dalton Trans.*, (1992) 1157. (b) C.J. Adams, M.I. Bruce, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, *450* (1993) C9. (c) C.J. Adams, M.I. Bruce, E. Horn, B.W. Skelton, E.R.T. Tiekink and A.H. White, *J. Chem. Soc. Dalton Trans.*, (1993) 3299. (d) C.J. Adams, M.I. Bruce, E. Horn, B.W. Skelton, E.R.T. Tiekink and A.H. White, *J. Chem. Soc. Dalton Trans.*, (1993) 3313.

[17] C. Lo Sterzo, M.M. Miller and J.K. Stille, *Organometallics*, *8* (1989) 2331.

[18] (a) C. Lo Sterzo, *J. Chem. Soc. Dalton Trans.*, (1992) 1989. (b) E. Viola, C. Lo Sterzo, R. Crescenzi and G. Frachey, *J. Organomet. Chem.*, *493* (1995) 55. (c) E. Viola, C. Lo Sterzo, R. Crescenzi and G. Frachey, *J. Organomet. Chem.*, *493* (1995) C9.

[19] R. Crescenzi, C. Lo Sterzo, *Organometallics*, *11* (1992) 4301.

[20] Ch. Elschenbroich and A. Salzer (eds.), *Organometallics, A Concise Introduction*, VCH, Weinheim, 1989.

[21] K.W. Barnett and D.W. Slocum, *J. Organomet. Chem.*, *44* (1972) 1 and references cited therein.

[22] E.J. Corey and J.O. Albright, *J. Org. Chem.*, *48* (1983) 2114.

[23] M.P. Simonnin, W. Chodkiiewicz and P. Cadiot, *C.R. Acad. Sci. Paris*, *258* (1964) 1537.

[24] D.W. Aubrey, W. Gerrard and E.F. Mooney, *J. Chem. Soc.*, (1962) 1786.

[25] J.R. Doyle, P.E. Slade and H.B. Jonassen, *Inorg. Synth.*, *6* (1960) 216.

[26] R.B. King and J.J. Eisch (eds.), *Organometallic Synthesis*, Vol. 4, Elsevier, Amsterdam, 1988, p. 84.