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Identification of a four-center intermediate in a Grignard addition reaction to a P–S bond

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Abstract—The reaction between *tert*-butylmagnesium chloride (or *tert*-pentylmagnesium chloride) and the particular phosphorus–sulfur bond of a benzothiadiphospholic system showed, for the first time, evidence of formation of intermediates with a four-center structure. The possibility, for the phosphorus atom, to have very stable hypervalent coordinations makes it possible to observe its hypervalent states during the course of a reaction. The benzothiadiphosphole, with its bicyclic folded structure, further stabilizes the hypervalent coordinations thus making the intermediates sufficiently stable to be detected during the course of the reaction by ^{31}P NMR spectroscopy, which revealed the nature and the stability of the species involved in this reaction, carried out also using other Grignard reagents.

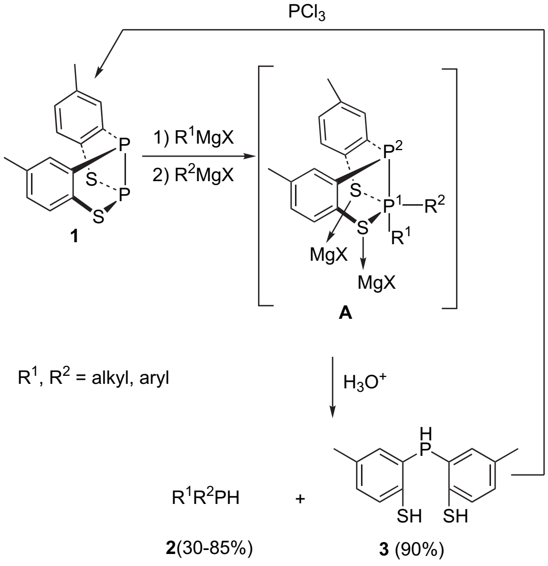
1. Introduction

The nature of the mechanism by which a Grignard reagent reacts with electrophiles is still an open question. This probably means that different intermediates can be accounted for this process depending on the reaction conditions and the electrophilic system used. There are two possible reaction routes: the polar concerted mechanism, which is hypothesized to proceed via a four-center transition state, and the stepwise electron-transfer mechanism.[1] The above two mechanisms may compete and the products from the two processes will often be the same. However, the problem with this reaction is that it is not known precisely what happens during the initial step of this addition reaction. It should be noted that the phosphorus atom can have very stable hypervalent coordinations[2] making it possible to observe hypervalent states during the course of a reaction. In the case of the carbon atom, by contrast, these hypervalent states are possible but very difficult to be identified.[3]

Herein we report for the first time the firm evidence for possible intermediates formed during the initial stage of a Grignard addition reaction between *t*-BuMgCl or *t*-PentMgCl and a P–S bond. These intermediates have been identified by ^{31}P NMR spectroscopy and have a four-center structure, in agreement with that of the classic four-center transition state that has been hypothesized for this type of reaction, and they are assumed to present a carbon atom in a hypervalent state. The reaction course was monitored by ^{31}P NMR spectroscopy for other Grignard reagents.

2. Results and discussion

Recently, we reported[4] a simple, efficient, and atom-economic new method for the preparation of symmetric and asymmetric secondary phosphines. The sequential addition, at room temperature, of equivalent amounts of the Grignard reagents R^1MgX and R^2MgX to a solution of benzothiadiphosphole (**1**) gave phosphines **2** and compound **3**, the residue of starting reagent **1**, which can be regenerated simply by reacting **3** with PCl_3 (Scheme 1). The intermediate of this



Scheme 1. Synthesis of secondary phosphines with recycle of starting reagent **1**.

Keywords: Hypervalent phosphorus intermediates; Phosphines; Grignard addition reactions.

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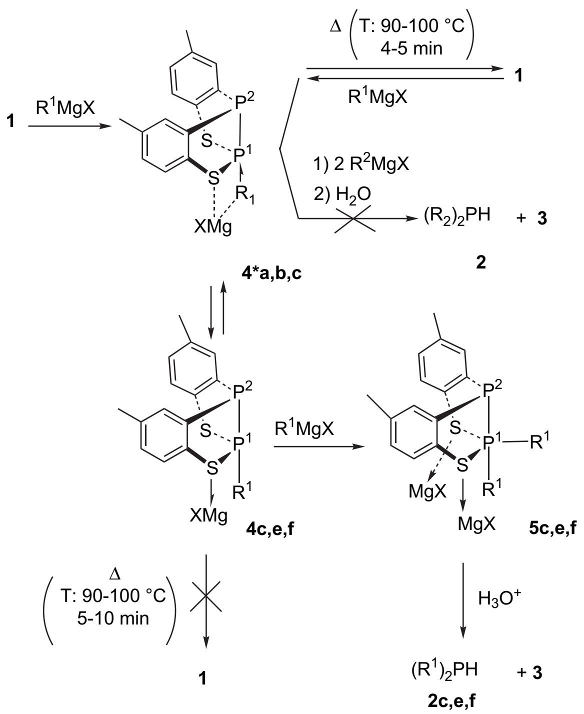
reaction was hypothesized to be a pentacoordinate phosphorus species such as **A**.

To evaluate whether secondary phosphines are also formed using Grignard reagents bearing bulky groups, we attempted to react **1** with *tert*-butylmagnesium chloride (Scheme 2).



a : R^1 = *t*-Bu; **b** : R^1 = *t*-Pent
c : R^1 = *i*-Pr ; **d** : R^1 = Ph_3C
e : R^1 = *n*-Bu; **f** : R^1 = Ph
R^2: *n*-Bu, Ph; X = Br, Cl

Scheme 2.

GC–MS analysis of the reaction mixture showed only starting reagent **1**, indicating that the reaction between **1** and *tert*-butylmagnesium chloride does not proceed even in the presence of an excess of Grignard reagent. Surprisingly, however, when we subsequently added a less hindered Grignard reagent, R^2MgX (Scheme 2) to the reaction mixture containing **1** and *tert*-butylmagnesium chloride, GC–MS analysis of the reaction mixture again showed only compound **1**, indicating that **1** also does not react with this new Grignard reagent. Given that, in the absence of *tert*-butylmagnesium chloride, R^2MgX easily reacts[4] with **1** to afford the corresponding secondary symmetrical phosphine R^2_2PH, our finding of no apparent reaction between **1** and R^2MgX was unexpected. A plausible explanation would be that in the reaction mixture, **1** reacts with the *tert*-butyl Grignard to form an unstable intermediate, and that this intermediate decomposes in the GC injector such that the GC–MS analysis indicates that only compound **1** is present. Thus, we conjectured that the *tert*-butylmagnesium chloride may have complexed with the S–P bond of **1**, thus hindering the subsequent attack of the less hindered Grignard reagent.

To gain more information about the hypothesized interaction between reagent **1** and *tert*-butylmagnesium chloride, we recorded a ^{31}P NMR spectrum of the final crude reaction mixture. As expected, no signals characteristic of reagent **1** were observed in the spectrum, but two new sets of doublets [δ=38.1 (d, $^1J_{P-P}$=275 Hz), 9.6 (d, $^1J_{P-P}$=275 Hz)] strongly upfield with respect to those of **1** [δ=86.8 (d, $^1J_{P-P}$=208 Hz), 66.7 (d, $^1J_{P-P}$=208 Hz)] were observed, suggesting the presence of a new species containing a P–P bond. In addition, these latter signals remained for several hours indicating the good stability of this intermediate. The ^1H NMR spectrum of the crude reaction mixture in THF-d_8 contains signals characteristic of the presence of two non-equivalent aromatic rings as well as a doublet with a coupling constant of 14 Hz in the region of *tert*-butylic protons, which is ascribed to a $^3J_{P-H}$ coupling. This was confirmed by examination of the ^{13}C NMR spectrum, which contained two doublets of doublets, centered at 37.2 and 29.9 ppm, which can be assigned, respectively, to the tertiary and methylic carbon atoms of the *tert*-butyl group each coupled with two phosphorus atoms linked in a P–P bond. Furthermore, to determine which phosphorus is adjacent to the *tert*-butyl moiety, we carried out a ^1H, ^{31}P heteronuclear multiple bond correlation experiments (HMBC, Fig. 1) optimized for coupling constant of 12.5 Hz (close to the observed three bond $^3J_{P-H}$ coupling constant of the methyl signal of the *tert*-butyl moiety). The HMBC spectrum showed a cross peak indicating a correlation between the proton resonance of the methyl doublet at 1.14 ppm and that of the ^{31}P doublet at 38.1 ppm.

The spectrum additionally showed cross couplings in the aromatic region indicating connections with the phosphorus atom signal at 9.6 ppm (Fig. 1). The NMR spectroscopic data are consistent with a structure such as **4*a**, which contains a P–P–C(CH)$_3$ structure and is characterized by non-symmetric aromatic rings. Such a configuration could form if one of the sulfur atoms in **1** coordinates with the magnesium atom of *tert*-butylmagnesium chloride. To verify the thermal instability of this intermediate, as indicated by the GC–MS data, after removal of the solvent, the crude reaction mixture containing only **4*a** was heated to 90–100 °C, then re-dissolved in THF and analyzed by ^{31}P NMR spectroscopy. After about 4–5 min at this temperature, we observed the disappearance of the signals corresponding to **4*a** and the concomitant appearance of signals related to starting compound **1** (see Fig. 2).

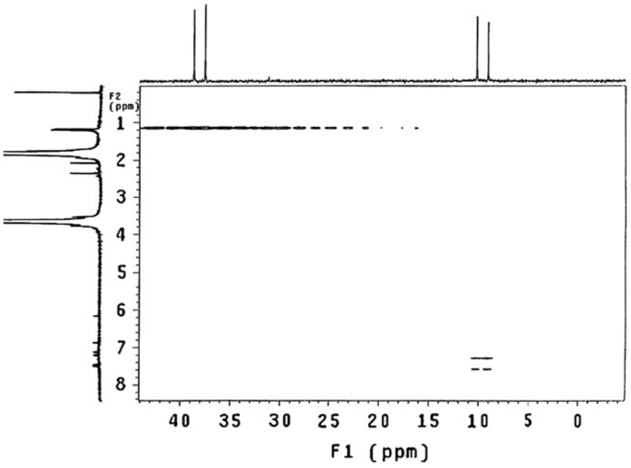


Figure 1. ^1H and ^{31}P HMBC spectrum of intermediate **4*a** in THF-d_8.

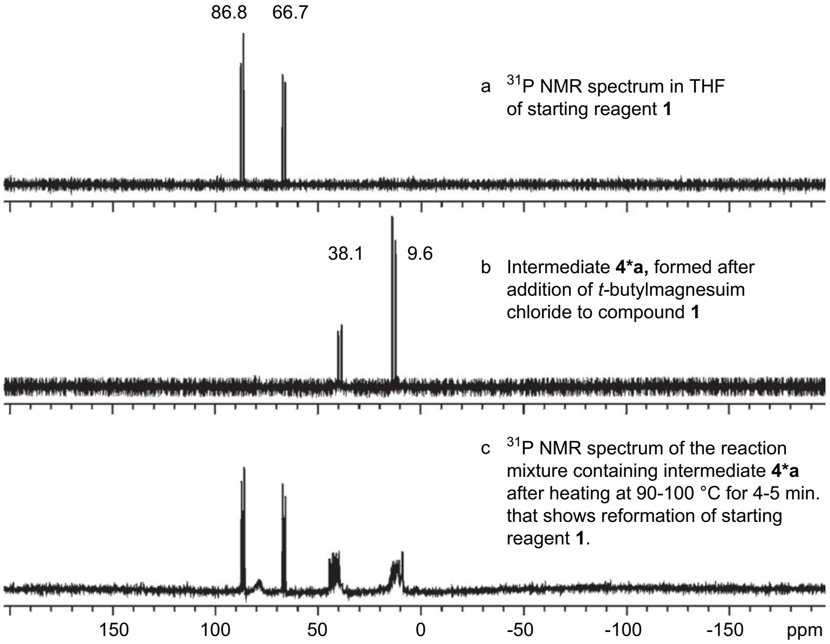


Figure 2. ^{31}P NMR spectra in THF of the reaction between benzothiadiphosphole **1** and *tert*-butylmagnesium chloride.

The fact that simple heating at 90–100 °C is sufficient to break the phosphorus–carbon bond, which is typically a very strong bond, with reformation of starting reagent **1**, supports the hypothesis that the intermediate has a structure like that of **4*a** (Scheme 2), in which the magnesium atom is coordinated both with the sulfur atom and, with a labile interaction, with the carbon atom of the *tert*-butyl group. In addition, this behavior, together with spectroscopic information, supports the proposed structure bearing two phosphorus–sulfur bonds. In fact, if **4*a** contains only one P–S bond, the reformation of **1** by simple heating seems to be very improbable.

In order to check whether the behavior showed by the reaction between compound **1** and *tert*-butylmagnesium chloride could be observed in other cases, we carried out the reaction with Grignard reagents characterized by different steric hindrance (Scheme 2). We found that the reaction between compound **1** and *tert*-pentylmagnesium chloride produces intermediate **4*b**, which, when heated, went back to starting reagents, as previously observed for **4*a**. It is interesting to note that, in the case **b** (see related spectra in Supplementary data), after partial reformation of starting reagent **1** by heating **4*b** for 1–2 min at 90–100 °C, we added a further amount of *tert*-pentylmagnesium chloride obtaining again disappearance of signals of **1** and enhancement of those of **4*b**. This latter reaction mixture, after further heating, again reverted to **1**, clearly indicating the reversibility of the process.

A different behavior was observed with *iso*-propylmagnesium chloride, less sterically hindered than the cases **a** and **b**. In the case **c**, immediately after the addition of 1 equiv of *iso*-propylmagnesium chloride to reagent **1** we observed, at ^{31}P NMR, two couples of doublets, ascribed to intermediates **4*c** [δ=30.1 (d, $^{1}J_{\mathrm{P-P}}$=262 Hz), 10.4 (d, $^{1}J_{\mathrm{P-P}}$=262 Hz)] and **4c** [δ=28.5 (d, $^{1}J_{\mathrm{P-P}}$=266 Hz), 15.1 (d, $^{1}J_{\mathrm{P-P}}$=266 Hz)]. The reaction mixture, after removal of the solvent under a positive flow of argon, was heated at 90–100 °C for 4–5 min and, after dissolution in THF, showed, at ^{31}P NMR analysis, complete disappearance of signals related to **4*c** and concomitant appearance of those of starting reagent **1**. Addition of a further amount of *iso*-propylmagnesium chloride to this reaction mixture produced disappearance of signals of starting reagent **1** and appearance of signals of **4*c**. Furthermore, after about 24 h from the addition of a large excess (>5 equiv) of *iso*-propylmagnesium chloride to **1**, the ^{31}P NMR spectrum of the reaction mixture showed disappearance of signals related to intermediates **4*c** and **4c** and appearance of a new couple of doublet [(δ=14.3 (d, $^{1}J_{\mathrm{P-P}}$=177 Hz), −53.9 (d, $^{1}J_{\mathrm{P-P}}$=177 Hz)] ascribed to the pentacoordinate intermediate **5c**. After addition of acidic water, signals of **5c** disappeared and concomitantly signals of diisopropylphosphine **2c** and compound **3** appeared. The reaction does not occur with tritylmagnesium chloride (case **d**), probably too hindered and consequently not able to form coordination intermediates with reagent **1**.

In contrast, when we carried out the reaction between **1** and 1 equiv of *n*-butylmagnesium bromide (case **e**, Fig. 3) or phenylmagnesium bromide (case **f**), we observed in the ^{31}P NMR spectrum the presence of starting material **1** together with two couples of doublets ascribed to intermediate **4e** [δ=15.8 and 12.2 ($^{1}J_{\mathrm{P-P}}$=258 Hz)] or **4f** [δ=27.6 and 14.0 ($^{1}J_{\mathrm{P-P}}$=265 Hz)] and to pentacoordinate intermediate **5e** (or **5f**).

When a further equivalent of Grignard reagent was added to the above solution the ^{31}P NMR spectrum showed complete conversion of starting reagent **1** and only presence of one couple of doublets, which is in accord with stable pentacoordinate phosphorus species such as **5e** [δ=−31.6 and −43.3 ($^{1}J_{\mathrm{P-P}}$=169 Hz)] or **5f** [δ=−8.3 and −45.3 ($^{1}J_{\mathrm{P-P}}$=179 Hz)], respectively. In fact, after addition of water to these reaction mixtures we observed the immediate disappearance of signals of **5e** (or **5f**) and the concomitant

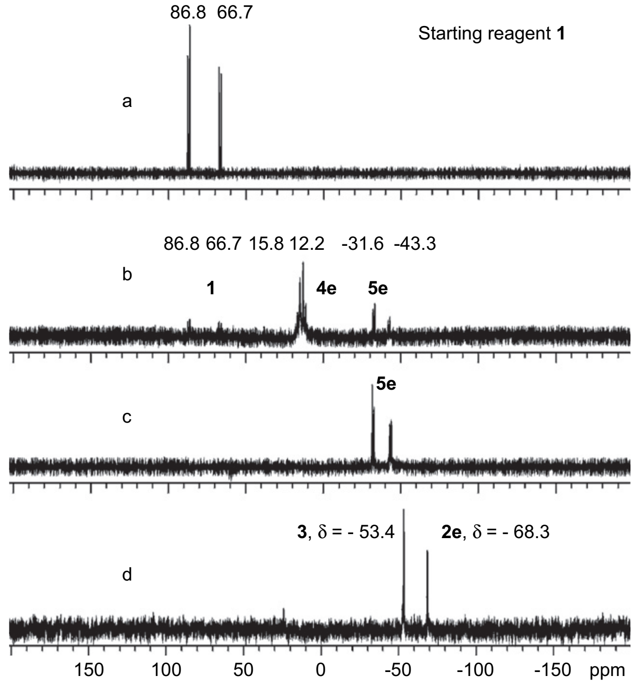


Figure 3. ^{31}P NMR spectra of the reaction between benzothiadiphosphole **1** and *n*-butylmagnesium bromide carried out in the NMR tube in THF. (**a**) Spectrum of the starting reagent **1**. (**b**) After addition of 1 equiv of the Grignard reagent with respect to **1** (presence of intermediate **4e** and traces of **5e** and starting material **1**). (**c**) After addition of a further equivalent of Grignard reagent (only presence of **5e**). (**d**) Spectrum obtained after addition of acidic water of the previous reaction mixture **c**, showing formation of dibutylphosphine (**2e**) and compound **3**.

appearance of signals of the corresponding secondary phosphine **2e** (or **2f**) and of the compound **3**, residue of reagent **1** (Fig. 3).

It has to be noted that a simple heating at 90–100 °C of a mixture of intermediates **4e**,**f** and **5e**,**f** was not able to give **1** in appreciable amounts. This might indicate a different strength of the phosphorus–carbon bond both for **4e**,**f** and **5e**,**f** with respect to **4*a**,**b**, in agreement with the observed trend, toward upfields, of the corresponding ^{31}P NMR chemical shifts. Then, in **4e**,**f** (Scheme 2) the C–Mg bond is completely broken and, consequently, a total coordination (only partial in the case of **4*a**,**b**) between sulfur and MgX group occurs.

In agreement with this proposed mechanism and with the two different structures **4*** and **4**, it is observed that the attack of the second equivalent of RMgX (R=*n*-butyl, phenyl) to **4** is favored with respect to that of the first equivalent of the same Grignard to **1**. In fact, as reported above, the addition of only 1 equiv (or less) of *n*-butylmagnesium bromide (or phenylmagnesium bromide) to compound **1** produces always ^{31}P NMR signals of both **4e** and **5e** (or **4f** and **5f**) together, obviously, with those of unreacted **1** (see Fig. 3 and Fig. 3, Supplementary data for case **f**). This behavior can be due to the complete coordination between sulfur and magnesium atoms in intermediates **4e**,**f** that makes the adjacent phosphorus atom more active to undergo the second attack of the Grignard reagent with respect to the first one.

Table 1. ^{31}P NMR signals, in THF, of intermediates **4*a**,**b**,**d**, **4d**–**f**, and **5d**–**f**

Intermediate	δ_P^1 (ppm)	δ_P^2 (ppm)
4*a	38.1 ($J_{P\text{–}P}$=275 Hz)	9.6 ($J_{P\text{–}P}$=275 Hz)
4*b	40.4 ($J_{P\text{–}P}$=281 Hz)	12.1 ($J_{P\text{–}P}$=281 Hz)
4*c	30.1 ($J_{P\text{–}P}$=262 Hz)	10.4 ($J_{P\text{–}P}$=262 Hz)
4c	28.5 ($J_{P\text{–}P}$=266 Hz)	15.1 ($J_{P\text{–}P}$=266 Hz)
4e	15.8 ($J_{P\text{–}P}$=258 Hz)	12.2 ($J_{P\text{–}P}$=258 Hz)
4f	27.6 ($J_{P\text{–}P}$=265 Hz)	14.0 ($J_{P\text{–}P}$=265 Hz)
5c	14.3 ($J_{P\text{–}P}$=177 Hz)	−53.9 ($J_{P\text{–}P}$=177 Hz)
5e	−31.6 ($J_{P\text{–}P}$=169 Hz)	−43.3 ($J_{P\text{–}P}$=169 Hz)
5f	−8.3 ($J_{P\text{–}P}$=179 Hz)	−45.3 ($J_{P\text{–}P}$=179 Hz)

The observation of intermediates such as **4e**,**f** clearly implies that the reaction proceeds through the formation of the corresponding **4*** precursors; and the fact that we did not observe signals related to intermediates **4***,**e**,**f** might be due to the limited steric hindrance of the Grignard reagents used that makes these intermediates not detectable, which being transformed, immediately after their formation, into **4e**,**f**. In line with this is the fact that when *iso*-propylmagnesium chloride with a steric hindrance between that of cases **a**,**b** and that of *n*-butylmagnesium bromide, both intermediates, **4*c** and **4c** were observed. These findings confirm that the behavior of *iso*-propyl Grignard reagent falls in a ‘border line’ situation between that of cases **a**,**b** and **e**,**f**. The contemporaneous presence of the two intermediates **4*c** and **4c** suggest the presence of an equilibrium between the two intermediates, which in cases **a**,**b** is completely shifted toward **4*a**,**b** whereas in cases **e**,**f** is shifted in opposite sense.

In order to make an easy comparison, ^{31}P NMR chemical shifts of intermediates **4*a**,**b**,**c**, **4c**,**e**,**f**, and **5c**,**e**,**f** are collected in Table 1.

As it can be seen, the chemical shift of the signal related to the P^1 phosphorus atom linked to the carbon atom of the *tert*-butyl and the *tert*-pentyl moieties, at 38.1 and 40.4 ppm for intermediates **4*a** and **4*b**, respectively, is significantly different from that of intermediates **4c**,**e**,**f**, whereas, as expected, chemical shifts related to the P^2 phosphorus atom fall in the same region of the spectrum for both intermediates **4*** and **4**. In addition, on going from intermediates **4c**,**e**,**f** toward pentacoordinated **5c**,**e**,**f**, both signals related to the P^1 and P^2 phosphorus atoms are strongly upfield, as expected as a consequence of a coordination change from a tetra to a pentacoordinated phosphorus intermediate.[5]

In other words, we observed a different behavior depending on the steric hindrance of the Grignard reagent. Actually, with bulky reagents, such as *tert*-butyl- and *tert*-pentylmagnesium chloride, the reaction only gave formation of the four-center intermediates **4*a**,**b**, which can be reverted to starting reagent **1** by simple heating, whereas with *iso*-propylmagnesium chloride both intermediates **4*c** and **4c** were observed and, in the other cases (**e**,**f**), only **4e** and **4f** were detected. Finally, once formed intermediate **4**, the reaction can proceed also toward intermediates **5**.

3. Conclusion

In conclusion, here we have reported the first experimental evidence of an intermediate formed during the initial stage of a Grignard addition reaction. This intermediate has a four-center structure and derives from the reaction between sterically hindered Grignard reagents (*tert*-butylmagnesium chloride, *tert*-pentylmagnesium chloride, or *iso*-propylmagnesium chloride) and a particular phosphorus–sulfur bond of compound **1**, which, with its bicyclic folded structure, stabilizes the hypervalent intermediates involved in this Grignard addition. This feature made the intermediates sufficiently stable to monitor the reaction course by ^{31}P NMR spectroscopy, thereby revealing the nature and stability of all the species involved in this reaction, carried out also using other Grignard reagents.

4. Experimental

4.1. General procedures

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 600 (or 400), 150.82, and 242.77 (or 161.89) MHz, respectively. Chemical shifts are referenced to solvent (THF-d_8, 1.8 and 26.7 ppm for ^{1}H and ^{13}C NMR, respectively) and to H_3PO_4 (ext. std) for ^{31}P NMR spectra. J values are given in hertz. THF was distilled from sodium benzophenone ketyl. All Grignard reagents used, except tritylmagnesium chloride (Ph_3CMgCl), which was prepared according to Gilman,[6] are commercially available. Air and moisture sensitive solutions and reagents were handled in a dried apparatus under an atmosphere of argon.

4.2. Formation of intermediates 4*a and 4*b: general procedure

To a solution of compound **1** (0.030 g, 0.098 mmol), dissolved in 3 mL of THF-d_8, a solution of Grignard reagent (*tert*-butyl- or *tert*-pentylmagnesium chloride, 1.5 equiv) was added. After about 5–10 min the reaction mixture, analyzed by GC–MS analysis, showed only the presence of the starting reagent **1**. A sample of the same crude reaction mixture, analyzed by ^{31}P NMR spectroscopy, showed the presence of signals of **4***, which was characterized also by ^{1}H NMR, ^{13}C NMR, and, in the case of **4*a**, also by ^{1}H–^{31}P HMBC NMR. The remaining reaction mixture, after removal of the solvent under a positive flow of argon, was heated at 90–100 °C for 4–5 min and, after dissolution in THF-d_8, showed, at ^{31}P NMR analysis, complete disappearance of signals related to **4*** and concomitant appearance of those of starting reagent **1** (Fig. 1). If the reaction is carried out with equimolar amount of reagents, a longer reaction time is required to have complete conversion of the starting reagent **1** into intermediate **4***. Addition of other Grignard reagents to this intermediate did not give changes in the spectrum. All attempts of crystallization of **4*** did not lead to the formation of crystals suitable for X-ray diffraction analysis.

4.2.1. Intermediate 4*a. ^{1}H NMR (600 MHz, THF-d_8, 25 °C): δ (ppm)=7.58 (d, J=10.7 Hz, 1H), 7.53 (d, J=7.9 Hz, 1H), 7.29 (d, J=6.5 Hz, 1H), 7.20 (d, J=8.4 Hz, 1H), 6.94 (d, J=8.3 Hz, 1H), 6.21 (br d, J=3 Hz, 1H), 2.34 (s, 3H), 2.04 (s, 3H), 1.14 (d, $^{3}J_{P-H}$=14 Hz, 9H); ^{13}C NMR (150.82 MHz, THF-d_8, 25 °C): δ (ppm)=152.5 (dd, J=4, 1 Hz), 149.7 (d, J=25 Hz), 143.6 (dd, J=26, 2 Hz), 137.8, 136.4, 136.0 (d, J=9 Hz), 135.3 (d, J=33 Hz), 133.4 (d, J=4 Hz), 132.4, 131.7, 130.3, 126.7 (d, J=6 Hz), 37.2 (dd, $^{1}J_{P-C}$=31 Hz, $^{2}J_{P-C}$=18 Hz, $\mathit{C}(\mathrm{CH_3})_3$), 29.3 (dd, $^{2}J_{P-C}$=14 Hz, $^{3}J_{P-C}$=6 Hz, $\mathrm{C}(\mathit{C}\mathrm{H_3})_3$), 22.5 (s, CH_3), 22.3 (s, CH_3); ^{31}P NMR (242.77 MHz, THF-d_8, 25 °C, H_3PO_4 ext. std): δ (ppm)=38.1 (d, $^{1}J_{P-P}$=275 Hz), 9.6 (d, $^{1}J_{P-P}$=275 Hz).

4.2.2. Intermediate 4*b. ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ (ppm)=7.54 (d, J=8.5 Hz, 1H), 7.46 (d, J=8.0 Hz, 2H), 7.12 (d, J=8.0 Hz, 1H), 6.74 (d, J=7.8 Hz, 1H), 6.07 (br d, J=2 Hz, 1H), 2.38 (s, 3H), 2.02 (s, 3H), 1.60–1.45 (m, 2H), 1.10 (d, J_{P-H}=11 Hz, 6H), 1.06–0.97 (m, 3H); ^{13}C NMR (100.56 MHz, THF-d_8, 25 °C): δ (ppm)=151.3 (d, J=4 Hz), 148.2 (d, J=26 Hz), 142.4 (d, J=27 Hz), 136.5, 135.0, 134.5 (d, J=10 Hz), 133.8 (d, J=33 Hz), 132.1, 130.9, 130.2, 128.9, 125.2 (d, J=6 Hz), 39.0 (dd, $^{1}J_{P-C}$=37 Hz, $^{2}J_{P-C}$=11 Hz, $C(CH_3)_2$), 32.9 (d, J=6 Hz), 23.6 (dd, $^{2}J_{P-C}$=12 Hz, $^{3}J_{P-C}$=6 Hz, $C(CH_3)_2$), 23.0 (dd, $^{2}J_{P-C}$=12 Hz, $^{3}J_{P-C}$=7 Hz, $C(CH_3)_2$), 20.3 (s, CH_3), 20.1 (s, CH_3), 8.3 (d, J=12 Hz, CH_3); ^{31}P NMR (242.77 MHz, THF-d_8, 25 °C, H_3PO_4 ext. std): δ (ppm)=40.4 (d, $^{1}J_{P-P}$=281 Hz), 12.1 (d, $^{1}J_{P-P}$=281 Hz).

4.3. Formation of the intermediates 4*c, 4c, and 5c

To a solution of compound **1** (0.306 g, 1.0 mmol), dissolved in 10 mL of THF, 1.0 equiv of *iso*-propylmagnesium chloride (2.0 M in THF) was added. After 1 min the ^{31}P NMR spectrum of the crude reaction mixture showed the presence of compounds **4*c** and **4c**. This reaction mixture treated with a further amount of *iso*-propylmagnesium chloride (2.0 equiv) showed again the presence of signals related to **4*c** and **4c**, but with time signals corresponding to compound **5c** appeared. After 24 h, the conversion from **4c** to **5c** was almost complete. Addition of acidic water to this reaction mixture produced disappearance of signals of **5c**, and appearance of those of diisopropylphosphine (**2c**) [^{31}P NMR (THF): δ=−15.2 ppm (br d, $^{1}J_{P-H}$=199 Hz)] and of compound **3** [^{31}P NMR (THF): δ=−53.4 ppm (br d, $^{1}J_{P-H}$=228 Hz)]. In another experiment, ^{31}P NMR spectrum of a solution containing intermediate **4*c**, after removal of the solvent under a positive flow of argon was heated at 90–100 °C for 4–5 min and after dissolution in THF, showed, at ^{31}P NMR analysis, complete disappearance of signals related to **4*c** and concomitant appearance of those of starting reagent **1**. Addition of a further amount of *iso*-propylmagnesium chloride to this reaction mixture produced again disappearance of signals of starting reagent **1** and appearance of signals of **4*c**.

4.3.1. Intermediate 4*c. ^{31}P NMR (161.89 MHz, THF, 25 °C, H_3PO_4 ext. std): δ (ppm)=30.1 (d, $^{1}J_{P-P}$=262 Hz), 10.4 (d, $^{1}J_{P-P}$=262 Hz).

4.3.2. Intermediate 4c. ^{31}P NMR (161.89 MHz, THF, 25 °C, H_3PO_4 ext. std): δ (ppm)=28.5 (d, $^{1}J_{P-P}$=266 Hz), 15.1 (d, $^{1}J_{P-P}$=266 Hz).

4.3.3. Intermediate 5c. ^{31}P NMR (161.89 MHz, THF, 25 °C, H_3PO_4 ext. std): δ (ppm)=14.3 (d, $^{1}J_{P-P}$=177 Hz), −53.9 (d, $^{1}J_{P-P}$=177 Hz).

4.4. Formation of intermediates 4e,f and 5e,f: general procedure

To a solution of compound **1** (0.306 g, 1.0 mmol), dissolved in 10 mL of THF, 1.0 equiv of *n*-butylmagnesium bromide (or phenylmagnesium bromide) was added. After 1 min the ^{31}P NMR spectrum of the crude reaction mixture showed presence of starting material **1** together with compounds **4e** (or **4f**) and **5e** (or **5f**). When a further equivalent of Grignard reagent was added to the above solution containing intermediate **4e** (or **4f**), the corresponding ^{31}P NMR spectrum showed complete conversion of starting reagent **1** and presence of intermediate **5e** (or **5f**). Addition of acidic water to this solutions gave compound **3** together with di(*n*-butyl)phosphine (**2e**) (or diphenylphosphine (**2f**)). ^{31}P NMR spectra of solutions containing intermediates **4** and/or **5**, after heating at 90–100 °C for 5–10 min, resulted unchanged.

4.4.1. Intermediate 4e. ^{31}P NMR (161.89 MHz, THF, 25 °C, H_3PO_4 ext. std): δ (ppm)=15.8 (d, $^1J_{P-P}$=258 Hz), 12.2 (d, $^1J_{P-P}$=258 Hz).

4.4.2. Intermediate 4f. ^{31}P NMR (161.89 MHz, THF, 25 °C, H_3PO_4 ext. std): δ (ppm)=27.6 (d, $^1J_{P-P}$=265 Hz), 14.0 (d, $^1J_{P-P}$=265 Hz).

4.4.3. Intermediate 5e. ^{31}P NMR (161.89 MHz, THF, 25 °C, H_3PO_4 ext. std): δ (ppm)=−31.6 (d, $^1J_{P-P}$=169 Hz), −43.3 (d, $^1J_{P-P}$=169 Hz).

4.4.4. Intermediate 5f. ^{31}P NMR (161.89 MHz, THF, 25 °C, H_3PO_4 ext. std): δ (ppm)=−8.3 (d, $^1J_{P-P}$=179 Hz), −45.3 (d, $^1J_{P-P}$=179 Hz).

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Supplementary data

Experimental procedures, characterization data, behavior, and spectra of intermediates **4*b**, **4*c**, **4c**, **4f**, **5c**, and **5f** are provided. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.10.015.

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