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C-Halophosphaalkenes: probing the range of stability and reactivity towards bromine [a]

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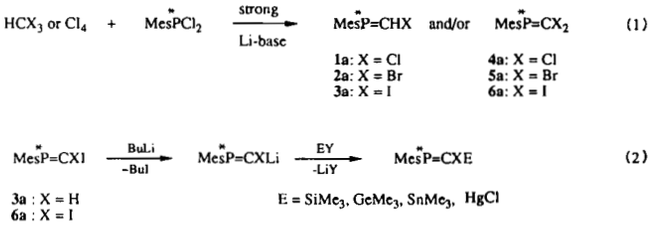
Abstract. The importance of steric protection for the stability of phosphaalkenes $RP{=}CI_2$ (**6**) was investigated by varying the size of group R. The phosphaalkene $IsP{=}CI_2$ (**6b**) (Is = 2,4,6-triisopropylphenyl) could be prepared in 15% isolated yield by reaction of $IsPCl_2$ and HCI_3 with two equivalents of lithium diisopropylamide, in analogy to the synthesis of the stable, sterically more protected, $Mes^*P = CI_2$ (**6a**) (Mes* = 2,4,6-tri-*tert*-butylphenyl). If the steric protection on the phosphorus was decreased further (R = Es = 2,4,6-triethylphenyl, R = Mes = 2,4,6-trimethylphenyl), the substitution products $RP(Cl)N(Pr^i)_2$ (R = Es (**9c**) or Mes (**9d**)) were formed as main products, in addition to thermally unstable phosphaalkenes $EsP{=}CI_2$ (**6c**) and $MesP{=}CI_2$ (**6d**). The structures of **9c-d** were corroborated by independent synthesis from $RPCl_2$ and two equivalents of diisopropylamine.
The reaction of **6a** with bromine gave an *E/Z* mixture of the *C*-bromo-*C*-iodophosphaalkene (*EZ*)-$Mes^*P = CBrI$ (*E/Z*-**10**). Further reaction with bromine proceeded via $Mes^*P{=}CBr_2$ (**5a**) and finally led to $Mes^*P(Br)(CHBr_2)$ (**12**).

Introduction

Phosphaalkenes (methylenephosphanes, RP=CXY) contain a phosphorus–carbon double bond and were therefore, until not so long ago, believed to be incapable of existence[1]. In recent years, an increasing number of examples have shown them to be stable compounds if properly substituted[2]. Kinetic protection of the P=C bond by bulky substituents is an important manner of stabilisation[3].
As the range of functionalities X and Y in phosphaalkenes has been rather limited up to now[2], we decided to try to increase this range. One way to do so is to synthesise phosphaalkenes where X and Y are halogens[4] as, in principle, these may be readily replaced by other groups. Our contribution to this field of chemistry has been a high-yield, one-pot synthesis of *C*-halo-phosphaalkenes **3a**, **4a**, **5a** and **6a** from HCX_3 (X = Cl, Br, I) or CI_4 and Mes^*PCl_2 (Mes* = supermesityl = 2,4,6-tri-*tert*-butylphenyl) (Eqn. 1); depending on the halomethane, *n*-butyllithium or lithium diisopropylamide (LDA) was used as a metallation/halogen–metal exchange reagent[5,6]. Indeed, it has been found that in **3a** and **6a**, iodine could be easily replaced at low temperatures by a reaction with *n*-butyllithium followed by attack of a suitable electrophile (Eqn. 2)[5,6].



(1)

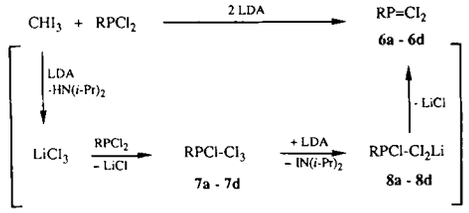
(2)

It would be attractive if this approach were also applicable to a broader range of phosphaalkenes with substituents other than Mes* on phosphorus. For this reason, we investigated its scope and limitations, especially when the steric protection is lowered in the series Mes* > Is(= 2,4,6-triisopropylphenyl) > Es(= 2,4,6-triethylphenyl) > Mes(= 2,4,6-trimethylphenyl).
In the course of this work it turned out that the stability of the less hindered phosphaalkenes **6b-d** is greatly diminished. Therefore, we had to restrict our exploration of the reactivity of phosphaalkenes to **6a**.

Synthesis

For the synthesis of phosphaalkenes **6b-d** with less steric hindrance, the method described for **6a**[6] seemed to be the most promising; it consists of adding two equivalents of lithium diisopropylamide (LDA) to a mixture of one molar equivalent of $RPCl_2$ and HCl_3 in THF at −100°C.

[a] These results have been presented in part in preliminary form: *F. Bickelhaupt*, Pure&Appl. Chem. **65**, 621 (1993).



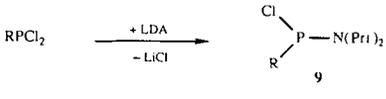
a: R = Mes*, b: R = Is, c: R = Es, d: R = Mes

Scheme 1.

In this procedure, it is conceivable that two reactions can compete. The first and desired reaction leads to **6**. It starts with the metallation of iodoform giving the carbenoid triiodomethyllithium[7] which subsequently substitutes a chlorine at phosphorus to give **7** (Scheme 1). The following step in this sequence was postulated to be a halogen–metal exchange of **7** with LDA at −100°C to furnish **8**, followed by LiCl elimination which finally results in the formation of phosphaalkenes **6**. It should be pointed out that to our knowledge, only a few quite recent reports imply that LDA may function as a halogen–metal exchange reagent[8].

The second and undesired reaction could be the direct substitution of $RPCl_2$ by LDA which would result in **9** (Eqn. 3); this mode of reaction has not been observed in the Mes* (= **a**) series.

The results of the reactions are presented in Table I. Previously, we had found[5] the isolated yield for R = Mes* to be 93%. The analogous reaction of $IsPCl_2$ with LDA and iodoform gave $IsP{=}CI_2$ (**6b**) as the only phosphorus-containing product, according to the ^{31}P-NMR spectrum; however, the isolated yield was much lower (15%, after crystallisation from acetonitrile). This may be caused by the working-up procedure which was much more difficult in the case of R = Is (see Experimental). Another factor is undoubtedly the reduced thermal stability of **6b**. While **6a** is stable indefinitely at room temperature when air is excluded, half of the **6b** had decomposed in C_6D_6 at −20°C in two weeks: a large number of signals was observed in the ^{31}P-NMR spectrum which could not be assigned. This is presumably due to insufficient steric hindrance around the P=C bond. Nevertheless, the bulkiness of the Is group is still considerable; this may be derived from the observation that, as in the Mes* series, the ^{31}P-NMR spectrum gives no indication of direct substitution by LDA at phosphorus under formation of **9b**.



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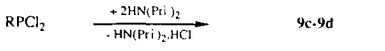


(4)

The trend of increasing instability continues for R = Es and Mes, which offer even less steric protection. Although the formation of the phosphaalkenes **6c** [EsP=CI_2, δ ^{31}P(THF) 340 ppm] and **6d** [MesP=CI_2, δ ^{31}P(THF) 345 ppm] was clearly indicated by the characteristic ^{31}P-NMR signals, isolation was not possible due to their instability. Furthermore, and in contrast to **6a** and **6b**, **6c** and **6d** were not the only products; they were accompanied by **9c** (δ ^{31}P 128 ppm) and **9d** (δ ^{31}P 133 ppm). The identity of **9c** and **9d** was established by independent synthesis from $RPCl_2$ and diisopropylamine (Eqn. 4).

It thus appears that the synthesis of 2,2-diiodophosphaalkenes $RP{=}CI_2$ (**6**) by the reaction of $RPCl_2$ and HCI_3 with two equivalents of LDA is of preparative value only for compounds with highly sterically demanding substituents on phosphorus (R = Mes*, Is). If the substituent is less bulky, attack of lithium diisopropylamide on phosphorus becomes increasingly competitive, and the phosphaalkenes show insufficient thermal stability.

*Table I Yields and ^{31}P-NMR data of phosphaalkenes $RP = CI_2$ (**6**) and $RP(Cl)N(Pr^i)_2$ (**9**) (from $RPCl_2$, CHI_3 and LDA; cf. Scheme 1).*

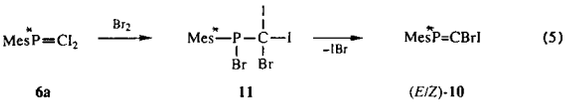
	R	6			9	
		Yield (%)		δ(^{31}P) (ppm)	Yield (%)	δ(^{31}P) (ppm)
a	Mes*	100 [a]	93 [b,c]	340	–	
b	Is	100 [a]	15 [b]	350	–	
c	Es	85 [a]	[d]	340	15 [a]	128
d	Mes	75 [a]	[d]	345	25 [a]	133

[a] Relative yield as determined from the intensities of the ^{31}P-NMR signals. [b] Isolated yield. [c] From ref. 6. [d] Not isolable.

Reactions

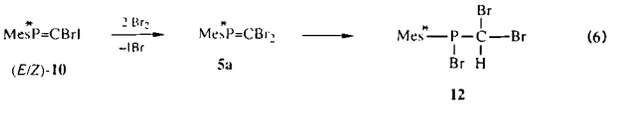
Relatively few investigations have been concerned with the behaviour of phosphaalkenes towards electrophiles[2]. Several different products have been reported in the reactions of phosphaalkenes with bromine; they range from 1,1 addition to phosphorus or 1,2 addition to the P=C bond, and sometimes consecutive reactions such as P–C bond cleavage occur[9]. We report here an interesting and surprising reaction of **6a** with bromine.

When **6a** was reacted with slightly less than one molar equivalent of bromine at −60°C (Eqn. 5) a mixture of (*E*/*Z*)-Mes*P=CBrI (*E*/*Z*-**10**) was formed. This was concluded from the ^{31}P-NMR spectrum of the crude reaction mixture [δ ^{31}P(THF) 304, 310 ppm]. However, some **5a** was also formed, while unreacted **6a** remained in the reaction mixture [ratio **6a**/(*E*/*Z*)-**10**/**5a** = 1 : 6 : 1, ratio (*E*)-**10**/(*Z*)-**10** = 1 : 1]. It was not possible to separate the two isomers *E*-**10** and *Z*-**10**, but they were positively identified by high-resolution mass spectra (HRMS) and ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy after crystallisation from pentane (see Experimental).



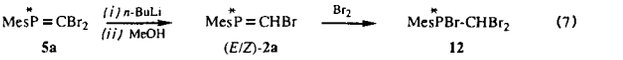
(5)

On addition of more bromine to the THF solution, the signals of **10** (and **6a**) disappeared at the expense of those of **5a** [δ ^{31}P(THF) 271 ppm]. Finally, when a total amount of three molar equivalents of bromine had been added, compound **12** was formed [δ ^{31}P(THF) 63 ppm] (Eqn. 6).



(6)

It was not possible to isolate **12** from the crude reaction mixture. Therefore, **12** was synthesised independently by the reaction of **5a** with *n*-butyllithium followed by treatment with methanol to give *E*/*Z*-**2a**; subsequent reaction of **2a** with bromine gave **12** (Eqn. 7). The spectral data (^{1}H-, ^{31}P-NMR spectra and HRMS) of both samples were identical.



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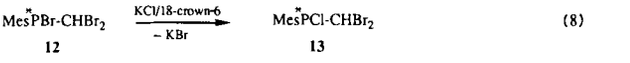
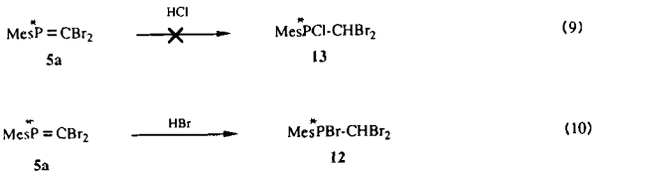


(8)

The bromine at phosphorus in compound **12** can be replaced by chlorine by reaction with KCl/18-crown-6 in THF to give **13** (Eqn. 8). This may seem a rather complicated route to synthesise **13**; however, the more simple addition of hydrogen chloride to the P=C bond of **5a** was attempted but, to our surprise, no reaction occurred (^{31}P NMR, Eqn. 9). By contrast, the reaction of **5a** with hydrogen bromide proceeded readily (Eqn. 10). Even though the product was not isolated, it could unambiguously be identified as **12** by its typical ^{1}H-, ^{13}C- and ^{31}P-NMR chemical shifts and corresponding coupling constants. However, due to the excess of hydrogen bromide, the reaction did not stop at this stage but proceeded to give other unidentified products.

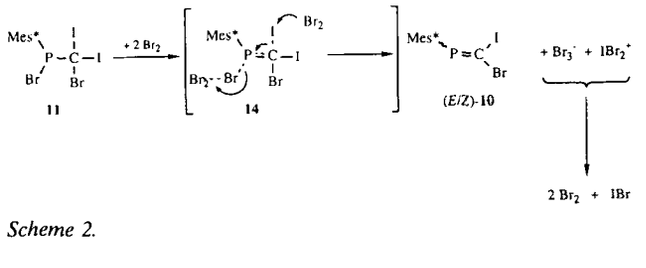


The proton NMR signals of the *ortho-tert*-butyl groups of **12** and **13** were very broad at room temperature, indicating hindered rotation round the P–C_{Ar} bond. The coalescence temperature of **12** and **13** were 290 K ($\Delta\nu$ = 61.1 Hz at 200 K) and 293 K ($\Delta\nu$ > 77.1 Hz at 200 K), corresponding to a free enthalpy of activation $\Delta G^{\neq} = 12.8$ and $\Delta G^{\neq} > 14$ kcal/mol, respectively.

Formally, the formation of (*E*/*Z*)-**10** by the reaction of bromine with **6a** comes down to substitution of a bromine atom in **6a** by an iodine atom. Obviously, this cannot occur in a simple one-step process; we suggest that this reaction proceeds as follows:

It is likely that in the first step of the sequence of reactions, bromine adds to the phosphorus–carbon double bond of **6a** with formation of the intermediate **11** (Eqn. 5). Evidence for **11** comes from ^{31}P-NMR spectra taken during the course of the reaction which showed a signal at δ ^{31}P(THF) 78 ppm; this chemical shift is compatible with the assigned structure of a secondary bromophosphine [*cf.* for instance δ ^{31}P(THF) 63 ppm for **12** (Eqn. 10)]. At the end of the reaction, this signal had disappeared. Next, iodine bromide is eliminated from **11** to give (*E*/*Z*)-**10**. This step was unexpected and is unlikely to occur spontaneously. Rather, we imagine it to proceed with the catalytic assistance of bromine as illustrated in the transition state **14** (Scheme 2); in particular, the extrusion of bromide anion will be facilitated by the bromine molecule acting as a Lewis acid.

The unexpected formation of **12** (via **5a**; Eqn. 6) may be rationalised by the assumption that, in THF, hydrogen bromide is formed which, instead of bromine, adds to the phosphorus–carbon double bond in **5a**. It is known that hydrogen bromide has a higher reactivity towards P=C bonds than hydrogen chloride[11]; in fact, hydrogen bromide does react with **5a** giving **12** (Eqn. 10) The occurrence of hydrogen bromide in the reaction mixture must be due to the reaction of THF with bromine. We checked this assumption by letting a solution of bromine in THF



Scheme 2.

stand at room temperature under the same conditions as those applied for the reaction of **6a** with bromine; hydrogen bromide was indeed identified by mass-spectroscopic analysis of the reaction mixture, together with products derived from THF by bromination. Analogous formation of hydrogen chloride has been reported for the reaction of THF with thionyl chloride[12] or with chlorine[13].

Experimental

All experiments were performed in flamed-out glassware, under a nitrogen atmosphere and with water-free solvents. NMR spectra were recorded on a Bruker AC 200 spectrometer (^{1}H, ^{13}C: 50.12 MHz) and on a Bruker WM 250 spectrometer (^{13}C: 62.9 MHz, ^{31}P: 101.25 MHz). High-resolution mass spectra (HRMS) were recorded on a Finnigan MAT 5 spectrometer. Elemental analyses were performed by the Microanalytisches Labor Pascher in Remagen (Germany). Compounds $RPCl_2$ were synthesised via a reaction of the aryllithium reagents (R = Mes*), the aryl Grignard reagents (R = Is, Es) or the arylzinc reagent (R = Mes) with PCl_3[14]

Diiodomethylene-(2,4,6-triisopropylphenyl)phosphane (**6b**)

A solution of LDA in THF (20 ml, 0.52 M, 10.3 mmol) was added over a period of 30 minutes at −100°C to a solution of $IsPCl_2$ (1.48 g, 5.26 mmol) and HCl_3 (2.07 g, 5.27 mmol) in 33 ml of THF. The reaction mixture was slowly warmed up to room temperature. The solvent was evaporated *in vacuo* at room temperature. If all THF were evaporated, an undissolvable gum-like residue remained which could not be further extracted or otherwise worked up. In order to avoid this, the reaction mixture was evaporated until only a few ml of THF remained; the resulting concentrated solution was extracted with two 150-ml portions of pentane. The pentane extract was evaporated *in vacuo* at room temperature. The red residue was crystallised from acetonitrile to give **6b** (red crystals, yield 0.41 g, 0.8 mmol, 15%). ^{1}H NMR (C_6D_6): 7.07 (d, 2H, Ar-*H*, ^{4}J(HP) 1.4 Hz), 3.25 (m, 2H, *o*-C*H*(CH_3)$_2$), 2.72 (sept, 1H, *p*-C*H*(CH_3)$_2$, ^{3}J(HH) 6.9 Hz), 1.28 (d, 6H, *o*-CH(CH_3CH$_3$), ^{3}J(HH) 6.7 Hz), 1.17 (d, 6H, *o*-CH(CH$_3$CH_3), ^{3}J(HH) 6.9 Hz), 1.06 (d, 6H, *p*-CH(CH_3)$_2$, ^{3}J(HH) 6.8 Hz). ^{13}C NMR (C_6D_6): 152.0 (s, *p*-Ar), 149.8 (d, *o*-Ar, ^{2}J(CP) 3 Hz), 148.2 (d, *ipso*-Ar, ^{1}J(CP) 50 Hz), 122.3 (dd, *m*-Ar, ^{1}J(CH) 150 Hz, ^{3}J(CH) 4 Hz), 64.5 (d, P = *C*, ^{1}J(CP) 80 Hz), 34.9 (d, *p*-*C*H(CH$_3$)$_2$, ^{1}J(CH) 125 Hz), 33.5 (dd, *o*-*C*H(CH$_3$)$_2$, ^{3}J(CP) 8 Hz, ^{1}J(CH) 125 Hz), 24.4 (dq, *o*-CH(*C*H$_3$CH$_3$), ^{4}J(CP) 9 Hz, ^{1}J(CH) 125 Hz), 24.0 (dq, *o*-CH(CH$_3$*C*H$_3$), ^{4}J(CP) 9 Hz, ^{1}J(CH) 125 Hz), 23.9 (q, *p*-C(*C*H$_3$)$_2$, ^{1}J(CH) 125 Hz). ^{31}P NMR (C_6D_6): 350.6. It was not possible to record a mass spectrum of **6b** due to decomposition.

General procedure for the synthesis of (**9c**) *and* (**9d**) *according to Eqn. 4*

A solution of diisopropylamine (200 mg, 2 mmol) in 2 ml of THF was added over a period of 10 min at 0°C to a solution of $RPCl_2$ (R = Mes, 221 mg, 1 mmol; R = Es, 286 mg, 1 mmol) in 5 ml of THF. The reaction mixture was stirred at room temperature for 2 h. The solvent was evaporated *in vacuo* at room temperature. The residue was extracted with pentane. Compounds **9c** and **9d** were crystallised from pentane to yield colourless crystals (yield **9c** 177 mg, 0.54 mmol, 54%; **9d** 168 mg, 0.58 mmol, 58%).

Chloro(diisopropylamino)(2,4,6-triethylphenyl)phosphane (**9c**) M.p. 64–65°C. ^{1}H NMR (C_6D_6): 0.95 (d, 6H, CH_3CHC*H*$_3$, ^{3}J(HH) 6.6 Hz), 1.11 (t, 3H, *p*-CH_2C*H*$_3$, ^{3}J(HH) 7.6 Hz), 1.33 (t, 6H, *o*-CH_2C*H*$_3$, ^{3}J(HH) 7.4 Hz), 1.36 (d, 6H, C*H*$_3$CHCH$_3$, ^{3}J(HH) 5.9 Hz), 2.44 (q, 2H, *p*-C*H*$_2$CH$_3$, ^{3}J(HH) 7.6 Hz), 2.96 (m, 2H, *o*-C*H*HCH$_3$, ^{3}J(HH) 7.2 Hz, ^{2}J(HH) 14 Hz), 3.37 (m, *o*-C*H*HCH$_3$, ^{3}J(HH) 7.2 Hz, ^{2}J(HH) 14 Hz), 3.55 (m, 2H, C*H*(CH$_3$)$_2$), 6.91 (d, 2H, Ar*H*, ^{4}J(HP) 3.4 Hz). ^{13}C NMR (C_6D_6): 149.3 (d, *o*-Ar, ^{2}J(CP) 20.9 Hz), 146.7 (t, *p*-Ar, ^{2}J(CH) 5.1 Hz), 130.4 (d, *ipso*-Ar, ^{1}J(CP) 44.3 Hz), 128.2 (dd, *m*-Ar, ^{3}J(CP) 11.1 Hz, ^{1}J(CH) 154.5 Hz), 49.4 (dd, *C*H(CH$_3$)$_2$, ^{2}J(CP) 4.4 Hz, ^{1}J(CH) 136.2 Hz), 28.9 (dt, *o*-*C*H$_2$CH$_3$, ^{3}J(CP) 22 Hz, ^{1}J(CH) 126.8), 28.8 (t, *p*-*C*H$_2$CH$_3$, ^{1}J(CH) 126.2 Hz), 23.5 (q, CHC(*C*H$_3$)$_2$, ^{1}J(CH) 124.1 Hz), 16.9 (q, *o*-CH_2*C*H$_3$, ^{1}J(CH) 126.7 Hz), 15.4 (q, *p*-CH_2*C*H$_3$, ^{1}J(CH) 126.2 Hz). ^{31}P NMR (C_6D_6): 129.7 ppm (t, ^{3}J(PH) 9.6 Hz). HRMS calcd. for $C_{18}H_{31}PN^{35}Cl$: 327.1883; found; 327.189. Anal. calcd. for $C_{18}H_{31}PNCl$ (327.92): C 65.94, H 9.53, N 4.27, Cl 10.8, P 9.45; found: C 65.81, H 9.59, N 4.28, Cl 10.4, P 9.37%.

Chloro(diisopropylamino)(2,4,6-trimethylphenyl)phosphane (**9d**) M.p. 95–98°C. ^{1}H NMR (C_6D_6): 0.90 (d, 6H, CH_3CHCH_3, ^3J(HH) 6.6 Hz), 1.34 (d, 6H, CH_3CHCH_3, ^3J(HH) 6.8 Hz), 2.05 (s, 6H, *p*-CH_3), 2.68 (d, 6H, *o*-CH_3, ^3J(HP) 2.6 Hz), 3.45 (m, 2H, $CH(CH_3)_2$, ^3J(HH) 6.7 Hz, ^3J(HP) 10.3 Hz), 6.71 (d, 2H, Ar*H*, ^4J(HP) 3.3 Hz). ^{13}C NMR (C_6D_6): 142.5 (dd, *o*-Ar, ^2J(CP) 21.5 Hz, ^2J(CH) 5.7 Hz), 139.8 (t, *p*-Ar, ^2J(CH) 5.9 Hz), 130.9 (dd, *m*-Ar, ^3J(CP) 2.9 Hz, ^1J(CH) 156 Hz), 130.6 (d, *ipso*-Ar, ^1J(CP) 42.8 Hz), 49.4 (dd, $CH(CH_3)_2$, ^2J(CP) 5.1 Hz, ^1J(CH) 135.4 Hz), 23.5 (dq, *o*-CH_3, ^3J(CP) 14.2 Hz, ^1J(CH) 130.1 Hz), 23.4 (dq, *p*-CH_3, ^5J(CP) 13 Hz, ^1J(CH) 127.1 Hz), 20.8 (q, $CH(CH_3)_2$, ^1J(CH) 126.4 Hz). ^{31}P NMR (C_6D_6): 129.0 (t, ^3J(PH) 10.3 Hz). HRMS calcd. for $C_{15}H_{25}PN^{35}Cl$: 285.1413; found: 285.142.

*(Bromoiodomethylene)(2,4,6-tri-*tert*-butylphenyl)phosphane* (*E* / *Z*-**10**)

A solution of 2.0 ml of bromine (0.4 M, 0.8 mmol) in THF was added over a period of 10 min at −70°C to a solution of **6a** (0.545 g, 1.01 mmol) in 15 ml of diethyl ether. The reaction mixture was stirred at −70°C for 1 h, and slowly warmed up to room temperature. All volatile products were evaporated *in vacuo* at room temperature. The residue was extracted four times with 5-ml portions of pentane. The combined pentane extracts were evaporated to dryness. The residue was crystallised from pentane to yield red crystals (yield 65 mg; ratio **6a**/(*E*/*Z*)-**10**/**5a** = 1:6:1; ratio (*E*)-**10**/(*Z*)-**10** = 1:1, according to ^{31}P-NMR spectroscopy; these ratios were analogous to those of the unpurified reaction mixture). By selective decoupling of one of the ^{31}P nuclei of (*E* or *Z*)-**10** the carbon nuclei of that isomer could be assigned; it was not possible to assign the *E* or *Z* configuration. A similar assignment of the proton signals was not possible. ^{1}H-NMR (C_6D_6): 7.53, 7.51 (2H, *m*-Ar), 1.49, 1.47 (18H, *o-tert*-butyl), 1.30, 1.28 (9H, *p-tert*-butyl).
Isomer I ^{31}P NMR (C_6D_6): 307.4. ^{13}C NMR (C_6D_6) 152.3 (s, *p*-Ar), 152.2 (s, *o*-Ar), 145.3 (d, *ipso*-Ar, ^1J(CP) 58.7 Hz), 123.1 (dd, *m*-Ar, ^3J(CP) 1 Hz, ^1J(CH) 154 Hz), 95.9 (d, P = *C*, ^1J(CP) 77 Hz), 37.7 (d, *o*-$C(CH_3)_3$, ^3J(CP) 0.6 Hz), 35.1 (s, *p*-$C(CH_3)_3$), 32.9 (dq, *o*-$C(CH_3)_3$, ^4J(CP) 6.9 Hz, ^1J(CH) 126 Hz), 31.3 (q, *p*-$C(CH_3)_3$, ^1J(CH) 125.5 Hz).
Isomer II ^{31}P NMR (C_6D_6): 302.0. ^{13}C NMR (C_6D_6) 152.3 (s, *o*-Ar), 152.1 (s, *p*-Ar), 143.4 (d, *ipso*-Ar, ^1J(CP) 61.6 Hz), 122.3 (dd, *m*-Ar, ^3J(CP) 1 Hz, ^1J(CH) 148.6 Hz), 92.1 (d, P = *C*, ^1J(CP) 91.1 Hz), 37.6 (d, *o*-$C(CH_3)_3$, ^3J(CP) 0.6 Hz), 34.8 (s, *p*-$C(CH_3)_3$), 32.7 (dq, *o*-$C(CH_3)_3$, ^4J(CP) 6.9 Hz, ^1J(CH) 125.9 Hz), 31.1 (q, *p*-$C(CH_3)_3$, ^1J(CH) 125.8 Hz). HRMS calcd. for $C_{19}H_{29}PI^{81}Br$: 496.0214; found: 496.021.

*(Bromomethylene)-(2,4,6-tri-*tert*-butylphenyl)phosphane* (**2a**)

A solution of 2 ml of *n*-butyllithium in hexane (1.6 M, 3.2 mmol) was added over a period of 10 min at −100°C to a solution of **5a**[5] (1.41 g, 3.15 mmol) in 25 ml of THF. This reaction mixture was stirred at −90°C for 1 h. At this temperature, MeOH (0.13 ml, 3.2 mmol) was added to this reaction mixture. The reaction mixture was slowly warmed to room temperature. The solvent was evaporated *in vacuo* at room temperature. The residue was extracted with pentane. According to the ^{31}P-NMR spectrum of the unpurified reaction mixture the *E*/*Z* ratio of **2a** was 10:90. **2a** crystallised from pentane as colourless crystals (yield 0.84 g, 2.2 mmol, 72%). M.p. 74–76°C.
(*Z*)-**2a** ^{1}H NMR (C_6D_6): 7.58 (d, 2H, Ar-*H*, ^4J(HP) 1.5 Hz), 7.11 (d, 1H, P = C*H*Br, ^2J(HP) 44.2 Hz), 1.55 (s, 18H, *o-tert*-butyl), 1.34 (s, 9 H, *p-tert*-butyl). ^{13}C NMR (C_6D_6): 153.8 (d, *o*-Ar, ^2J(CP) 2.1 Hz), 151.0 (s, *p*-Ar), 138.6 (dd, P = *C*HBr, ^1J(CP) 56.7 Hz, ^1J(CH) 181.1 Hz), 128.3 (d, *ipso*-Ar, ^1J(CP) 58.2 Hz), 122.3 (dd, *m*-Ar, ^1J(CH) 153 Hz, ^3J(CP) 6.5 Hz), 38.0 (s, *o*-$C(CH_3)_3$), 35.1 (s, *p*-$C(CH_3)_3$), 33.0 (q, *o*-$C(CH_3)_3$, ^1J(CH) 126 Hz), 31.5 (q, *p*-$C(CH_3)_3$, ^1J(CH) = 126 Hz). ^{31}P NMR (C_6D_6): 269.2 (d, ^2J(PH) 44.1 Hz).
(*E*)-**2a** ^{1}H NMR (C_6D_6): 7.52 (d, 2H, Ar-*H*, ^4J(HP) 1.3 Hz), 7.49 (d, 1H, P = C*H*Br, ^2J(HP) 19.8 Hz), 1.47 (s, 18 H, *o-tert*-butyl), 1.30 (s, 9H, *p-tert*-butyl). ^{13}C NMR see Ref. 4d. ^{31}P NMR (C_6D_6): 261.8 (d, ^2J(PH) 24.0 Hz). HRMS calcd. for $C_{19}H_{30}P^{79}Br$: 368.1269; found: 368.126.

*Bromo(dibromomethyl)-(2,4,6-tri-*tert*-butylphenyl)phosphane* (**12**)

A solution of 4.9 ml of bromine in CCl_4 (0.41 M, 2.0 mmol) was added over a period of 30 min at −20°C to a solution of **2a** (0.73 g, 2.0 mmol, *E*/*Z* mixture, *vide supra*) in 20 ml of CCl_4. The reaction mixture was slowly warmed to room temperature. The solvent was evaporated *in vacuo* at room temperature and the residue was extracted with pentane. The pentane was evaporated *in vacuo* at room temperature. Compound **12** crystallised from pentane as colourless crystals (yield 0.63 g, 1.2 mmol, 61%). ^{1}H NMR (C_6D_6): 7.42 (d, 2H, *m*-Ar, ^4J(HP) 2.4 Hz), 6.28 (d, 1 H, C*H*Br_2, ^2J(HP) 1.6 Hz), 1.38 (s, 18H, *o-tert*-butyl), 1.23 (s, 9H, *p-tert*-butyl). ^{13}C NMR (C_6D_6): 154.9 (d, *o*-Ar, ^2J(CP) 2.5 Hz), 150.3 (t, *p*-Ar, ^2J(CH) 3.6 Hz), 129.7 (d, *ipso*-Ar, ^1J(CP) 77.5 Hz), 128.3 (d, *m*-Ar, ^1J(CH) 158 Hz), 45.3 (dd, *C*HBr_2, ^1J(CP) 89.3 Hz, ^1J(CH) 181 Hz), 39.8 (s, *o*-$C(CH_3)_3$), 34.2 (s, *p*-$C(CH_3)_3$) 31.8 (q, *o*-$C(CH_3)_3$, ^1J(CH) 129 Hz), 31.0 (q, *p*-$C(CH_3)_3$, ^1J(CH) 126 Hz). ^{31}P NMR (C_6D_6): 63.4. HRMS calcd. for $C_{19}H^{81}_{29}Br^{79}Br_2$ [M-H]$^+$: 526.9537; found: 526.953.

Chloro(dibromomethyl)(2,4,6-tri-tert-butylphenyl)phosphane (**13**)

Solid potassium chloride (46 mg, 0.61 mmol) was added to a solution of **12** (0.25 g, 0.47 mmol) and 18-crown-6 (0.19 g, 0.73 mmol) in 5 ml of THF. The reaction mixture was stirred for 40 h at room temperature. More potassium chloride (100 mg, 1.3 mmol) was added to the reaction mixture. After stirring for another hour, the solvent was evaporated *in vacuo*. The residue was extracted with pentane. The combined pentane fractions were evaporated to dryness to yield a colourless oil of **13** (0.17 g, 0.35 mmol, 75%). ^{1}H NMR (C_6D_6): 7.41 (d, 2H, Ar*H*, ^4J(HP) 2.3 Hz), 6.21 (d, 1H, C*H*Br_2, ^2J(HP) 0.7 Hz), 1.53 (bs, 18 H, *o-tert*-butyl), 1.21 (s, 9 H, *p-tert*-butyl). ^{13}C NMR (C_6D_6): 154.75 (s, *p*-Ar), 154.70 (d, *o*-Ar, ^2J(CP) 3.1 Hz), 130.28 (d, *ipso*-Ar, ^1J(CP) 71.5 Hz), 123.60 (bs, *m*-Ar), 47.60 (dd, *C*HBr_2, ^1J(CP) 85.3 Hz, ^1J(CH) 180.0 Hz), 39.55 (s, *p*-$C(CH_3)_3$), 35.07 (s, *o*-$C(CH_3)_3$), 34.18 (q, *p*-$C(CH_3)_3$, ^1J(CH) 129.9 Hz), 31.07 (s, *p*-$C(CH_3)_3$, ^1J(CH) 125.8 Hz). ^{31}P NMR (C_6D_6): 66.28. HRMS calcd. for $C_{19}H_{30}P^{35}Cl^{79}Br^{81}Br$: 484.0121, for $C_{19}H_{30}P^{37}Cl^{79}Br_2$: 484.0111; found: 484.012 (due to the limited resolution, the peaks were not separated and only one molecular ion signal was observed).

Reaction of **6a** *with three molar equivalents of bromine*

Bromine (0.026 ml, 0.5 mmol) was added at −70°C to a solution **6a** (0.273 g, 0.50 mmol) in 10 ml of THF; the reaction mixture was warmed to room temperature and stirred for approximately 2 h. This process was repeated twice. The product formed could only be characterised by its ^{31}P- and ^{1}H-NMR and high-resolution mass spectra which were identical with those of a sample of **12** prepared from **2a** (*vide supra*); it was not possible to isolate the product by crystallisation.

Reaction of THF with bromine

Bromine (3.1 g, 19 mmol) was added under stirring to THF (20 ml). The mixture was stirred for about 16 h at room temperature; during this period, the brownish colour became lighter and more orange. A sample of 5 ml of this reaction mixture was cooled with liquid nitrogen, coupled to the direct inlet of the mass spectrometer and warmed up to room temperature over a period of 3 h. During the first 2 h, only THF was monitored by MS; afterwards, HBr and Br_2 were detected by their mass and isotope pattern, later followed increasingly by two not fully characterised products which are presumably derived from THF by bromination: HRMS calcd. for $C_4H_6^{79}BrO$: 148.9602; found: 148.9601 (tentatively assigned as [M–H]$^+$ of 2-bromotetrahydrofuran); and HRMS calcd. for $C_4H_7^{79}Br$: 133.9731; found 133.972 (tentatively assigned as $M^{+\cdot}$ of 4-bromo-1-butene).

Reaction of **5a** *with hydrogen bromide*

Hydrogen bromide, prepared from tetraline (25 ml) and bromine (1.5 ml)[10], was condensed in a reaction vessel which was cooled with liquid nitrogen (−196°C). A solution of **5a** (0.22 g, 0.5 mmol) in THF (10 ml) was added. The reaction mixture was warmed to room temperature and stirred for 12 h. All volatile products were evaporated *in vacuo* and the residue was extracted with pentane. The combined pentane fractions were evaporated to dryness. The residue was characterised by ^{31}P- and ^{1}H-NMR and by high-resolution mass spectroscopy; the spectra were identical with those of a sample of **12** prepared from **2a** (*vide supra*).

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