Synthesis and Reactions of *P*-Supermesityl-*C*-halophosphaalkenes

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C-Halophosphaalkenes (**1**, **2**) were prepared in high yield by a one-pot synthesis from HCX_3 or CI_4 and Mes^*PCl_2 (Mes* = supermesityl = 2,4,6-tri-*tert*-butylphenyl). The *C*-iodophosphaalkenes $Mes^*P{=}CI_2$ (**1c**) and $Mes^*P{=}CHI$ (**2c**) undergo halogen-metal exchange with *n*-BuLi at low temperatures. The resulting carbenoids $Mes^*P{=}CILi$ (**11c**) and $Mes^*P{=}CHLi$ (**6**) reacted with $ClMMe_3$ (M = Si, Ge, Sn) to give $Mes^*P{=}ClMMe_3$ [(*Z*)-**13**: M = Ge; (*Z*)-**14**: M = Sn] or $Mes^*P{=}CHMMe_3$ (**8**–**10**), respectively. Further reaction of (*Z*)-**13** and (*Z*)-**14** with *n*BuLi and $ClMMe_3$ gave $Mes^*P{=}C(MMe_3)_2$ (**18**: M = Ge; **19**: M = Sn). The carbenoid (*Z*)-**11c** decomposed at −85°C; instead of the expected "phospha-isonitrile" $Mes^*P{=}C{:}$ (**21**), only $Mes^*C{\equiv}P$ (**15**) was obtained which lends experimental support to the theoretically predicted instability of **21**.

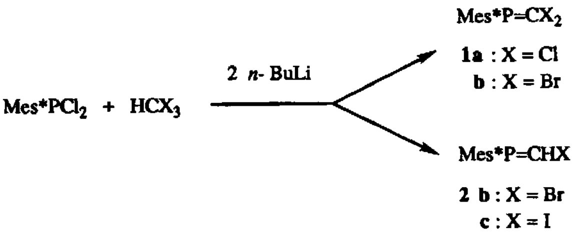
Phosphaalkenes halogenated at the alkene carbon atom are of interest because, potentially, substitution of the halogens by other groups opens an access to new functionalized phosphaalkenes. The first representative of this class was described in 1981[1], and a variety of synthetic approaches has been developed since[2–4]. We now report on a one-pot synthesis of *C*-halogenated phosphaalkenes, the essential feature of which is the reaction of supermesityldichlorophosphane (Mes^*PCl_2; supermesityl = Mes* = 2,4,6-tri-*tert*-butylphenyl) with a lithium carbenoid[5] followed by *n*-butyllithium-induced elimination. In particular, iodo-substituted phosphaalkenes are easily accessible by this route, and a preliminary investigation of their reactivity is presented.

Synthesis of *C*-Halophosphaalkenes

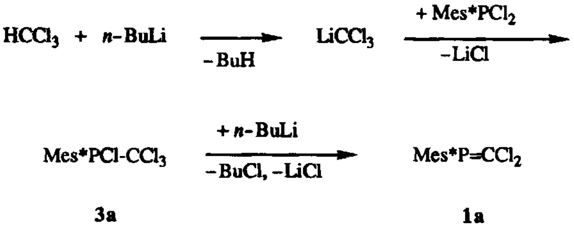
In our approach, two equivalents of *n*-butyllithium are added at −100°C to a solution of supermesityldichlorophosphane and a haloform CHX_3; the reaction mixture is then slowly warmed to room temperature. Depending on the halogen, either a dihalophosphaalkene **1** (**1a**: X = Cl; 73% yield), a monohalophosphaalkene **2** [(*E*/*Z*)-**2c**: X = I; 90% yield], or a mixture of both [**1b**, (*E*/*Z*)-**2b**, X = Br; ratio **1b**:(*E*)-**2b**:(*Z*)-**2b** = 5:1:4] is obtained (Scheme 1).

The formation of **1a** is easily explained as shown in Scheme 2. Metallation of chloroform by *n*-butyllithium gives the well-known carbenoid trichloromethyllithium[5a] which reacts with supermesityldichlorophosphane to give **3a**; it should be pointed out that so far we have in none of our reactions detected intermediates such as **3** (or **4**, vide infra) directly by ^{31}P-NMR spectroscopy. Apparently, **3** undergoes rapid halogen-metal exchange with a second molecule of *n*-butyllithium; this leads to **1a**, presumably in a more or less concerted fashion.

Scheme 1



Scheme 2



$$HCCl_3 + n\text{-}BuLi \xrightarrow[-BuH]{} LiCCl_3 \xrightarrow[-LiCl]{+\,Mes^*PCl_2}$$

$$\underset{\mathbf{3a}}{Mes^*PCl\text{-}CCl_3} \xrightarrow[-BuCl,\ -LiCl]{+\,n\text{-}BuLi} \underset{\mathbf{1a}}{Mes^*P{=}CCl_2}$$

In contrast, iodoform reacts predominantly by halogen-metal exchange to furnish diiodomethyllithium[5b], which reacts further to give intermediate **4c** (Scheme 3). Like iodoform, **4c** is not metallated, but preferentially reacts by a second halogen-metal exchange, concomitant with elimination of lithium chloride, leading to an *E*/*Z* mixture (80:20) of **2c** (90%). The preferential formation of the sterically less hindered *E* stereoisomer of **2c** is probably not so much a consequence of its higher thermodynamic stability (= less steric hindrance), but rather of *trans* elimination from the most stable conformer **4c′** as shown in Scheme 3. It cannot be excluded that to a minor extent (*Z*)-**2c** originates from small amounts of **1c** which was detected at intermediate stages of the reaction by ^{31}P-NMR spectroscopy [cf. the formation of **1b** and (*Z*)-**2b**, vide infra).

At first sight, the explanation of the formation of *both* **1b** and **2b** in the bromoform reaction seems straightforward:

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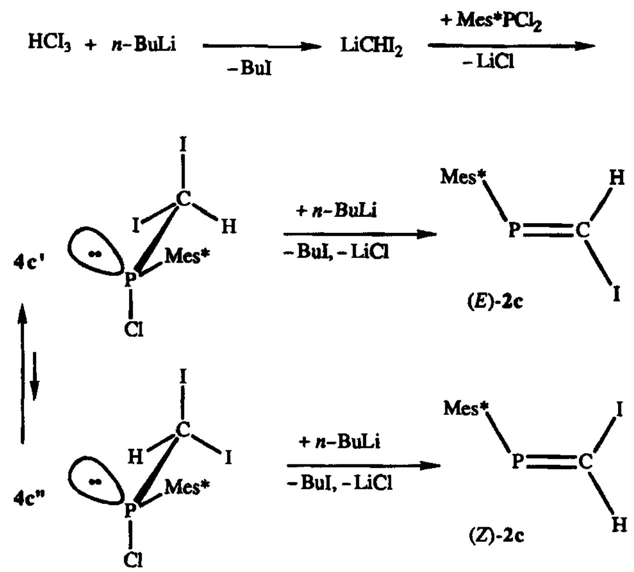
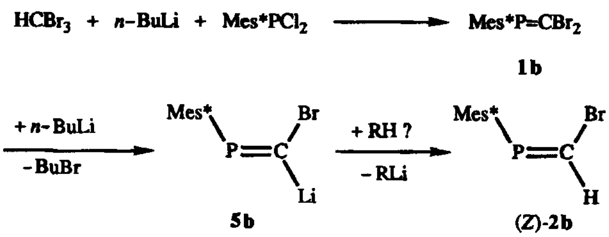
Scheme 3



as bromine has properties intermediate between those of chlorine and iodine, metallation of bromoform via $LiCBr_3$ leading to $Mes^*P(Cl)CBr_3$ (**3b**), or halogen-metal exchange leading via $LiCHBr_2$ to $Mes^*P(Cl)CHBr_2$ (**4b**) might occur to a comparable extent[5c]; these intermediates react further as discussed above for **3a** and **4c**, respectively, to give **1b** and **2b**. However, the following observations cast doubt on this simple rationalization. In the first place, the *E*/*Z* ratio of **2b** (20:80) is opposite to that of **2c**, i.e. the more crowded stereoisomer is formed preferentially; this suggests a different genesis. Secondly, and more importantly, when the reaction of Scheme 1 is stopped half way, i.e. after addition of *one* equivalent of *n*-butyllithium, a ^{31}P-NMR spectrum of the reaction mixture showed the complete absence of **2b** at this stage; instead, the starting material supermesityldichlorophosphane and product **1b** were present in a 1:1 ratio.

Scheme 4



We therefore propose the course of events as illustrated in Scheme 4. The reaction of *n*-butyllithium with bromoform proceeds (most likely via **4b**[5d]) to furnish **1b**. In a subsequent reaction, **1b** undergoes halogen-metal exchange by bromophilic attack of *n*-butyllithium. This attack occurs from the least hindered side, i.e. at the *E* bromine atom, to give the carbenoid intermediate **5b** which is protonated to furnish (*Z*)-**2b**. Several aspects of this interesting mechanism, such as the intermediacy of either **3b** or more likely **4b**, or the source of protons in the last step, are under investigation.

While **1a** and **2c** are conveniently accessible by this procedure, **1b** and **1c** are not. Fortunately, both compounds could be obtained in high yield by slight variations which were inspired by the mechanistic considerations presented above.

The second equivalent of *n*-butyllithium (see Scheme 1) is required for the final elimination step. As, according to Scheme 4, butyllithium also tends to destroy **1b**, it was first converted into a base which is sufficiently strong to effect elimination, but less prone to halogen-metal exchange. To this end, supermesityldichlorophosphane was added to a solution of two equivalents of dibromomethyllithium prepared from bromoform and *n*-butyllithium in THF at −100°C (Scheme 5); the carbenoid acts both as a nucleophile, presumably to furnish **4b**, and subsequently as a base to give **1b** in 52% yield.

Scheme 5

$$2\,HCBr_3 + 2\,n\text{-}BuLi \longrightarrow 2\,LiCHBr_2$$

$$LiCHBr_2 + Mes^*PCl_2 \longrightarrow \underset{\mathbf{4b}}{Mes^*PCl\text{-}CHBr_2}$$

$$\mathbf{4b} \xrightarrow[-\,CH_2Br_2,\ -\,LiCl]{+\,LiCHBr_2} \underset{\mathbf{1b}}{Mes^*P{=}CBr_2}$$

Compound **1c** was synthesized by a route analogous to that of Scheme 2 using the carbenoid triiodomethyllithium. As the latter is not accessible from iodoform and *n*-butyllithium (vide supra), it was prepared from tetraiodomethane and *n*-butyllithium (two equivalents) in the presence of supermesityldichlorophosphane (Scheme 6); **1c** was obtained in 93% yield, presumably via $Mes^*P(Cl)CI_3$ (**4c**).

Scheme 6

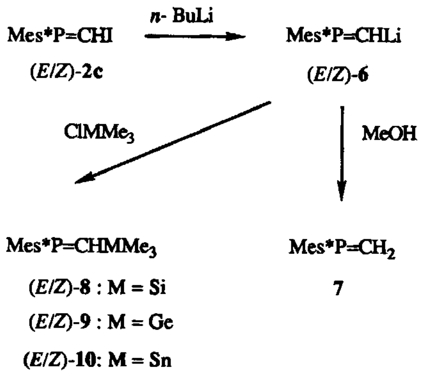
$$CI_4 + Mes^*PCl_2 \xrightarrow{2\,n\text{-}BuLi} \underset{\mathbf{1c}}{Mes^*P{=}CI_2}$$

Reactivity of the Iodophosphaalkenes 1c and 2c

Appel et al.[2b,c] have described the halogen-metal exchange and subsequent derivatization of **1a** and **1b**. Similar investigations on iodophosphaalkenes have not been reported, but are of interest in view of the different, and usually higher, reactivity of organic iodides.

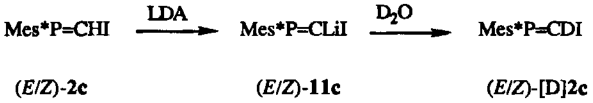
The reaction of (*E*/*Z*)-**2c** (80:20 mixture, vide supra) with *n*-butyllithium proceeded readily at −80°C by halogen-metal exchange to give (*E*/*Z*)-**6c**, which was converted to **7**−**10** with methanol or with trimethylelement halides Me_3MCl (M = Si, Ge, Sn), respectively (Scheme 7). The stereochemistry of the (*E*/*Z*)-**2c** mixture is apparently retained in both consecutive reactions as evidenced by the same 80:20 ratio of (*E*/*Z*)-**9**−**10**. (*E*/*Z*)-**8** could not be obtained in pure form. The reaction gave a mixture of **8** and **7** in a ratio of 80:20 (according to ^{31}P-NMR spectroscopy); the *E*/*Z* ratio of **8** was 80:20. In the case of (*Z*)-**10**, the assignment is confirmed by its synthesis from **1c** (see following paragraph).

Scheme 7



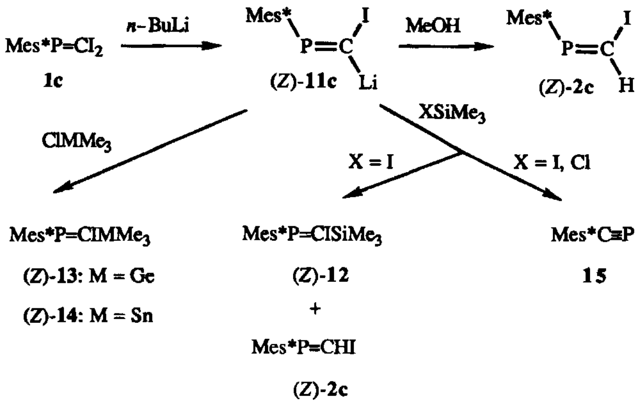
An alternative derivatization of (*E*/*Z*)-**2c** was achieved by metallation with lithium diisopropylamide (LDA) at $-100\,^{\circ}$C to furnish the carbenoid lithium reagent (*E*/*Z*)-**11c** (Scheme 8), which was characterized by deuterolysis to (*E*/*Z*)-[D]**2c** (*E*:*Z* = 80:20).

Scheme 8



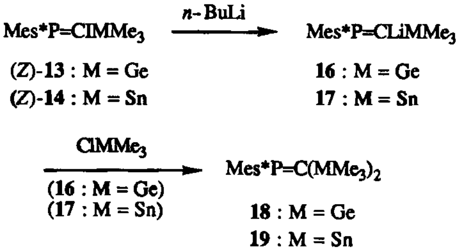
Compound **1c** shows high reactivity towards *n*-butyllithium and undergoes halogen-metal exchange even at $-120\,^{\circ}$C to furnish (*Z*)-**11c** exclusively; this follows from methanolysis to (*Z*)-**2c** (Scheme 9). As in the case of **1b** (vide supra), the stereospecificity must be due to steric factors which determine the attack of *n*-butyllithium from the (least hindered!) *E* side. Similarly, (*Z*)-**11c** reacted stereospecifically with chlorotrimethylgermane and chlorotrimethylstannane to furnish (*Z*)-**13** and (*Z*)-**14**, respectively; in the ^{31}P-NMR spectra, signals of the other stereoisomer were not observed. With chlorotrimethylsilane, the phosphaalkyne **15** was the only product observed; apparently, thermal elimination of lithium iodide from **11c** is easier and occurs at a temperature lower than that required for silylation (vide infra). The more reactive iodotrimethylsilane was converted into a mixture of (*Z*)-**12** and **15** and (*Z*)-**2c** (in a ratio of 3:2:5; the latter was probably formed from some HI which was present in the iodotrimethylsilane).

Scheme 9



Compounds (*Z*)-**13** and (*Z*)-**14**, in turn, could be lithiated with *n*-butyllithium at the slightly higher temperature of $-80\,^{\circ}$C to give **16** and **17**, respectively. These compounds were converted to **18** and **19** as shown in Scheme 10.

Scheme 10



Configurations of *C*-Substituted Phosphaalkenes

The assignment of *E* or *Z* configurations to unsymmetrically substituted phosphaalkenes is still a difficult matter. Apart from a few unambiguous assignments by X-ray crystal structure determination[2d,6)], they are usually based on the more or less empirical rule[2a−c,2e,7)] that in a stereoisomeric pair RP=CXY, the nuclei *n* present in the group X *cis* to the phosphorus lone pair have larger couplings than those of the *trans* group Y; this rule not only holds for nuclei *n* of atoms bound directly to the olefinic carbon atom [α-position; $^{2}J(\mathrm{P}n)$], but also for those in the β-position [$^{3}J(\mathrm{P}n)$]. For the convenience of this discussion, we will call this empirical rule the "*cis* rule".

Although Appel et al. do not explicitly state so, they have apparently used the *cis* rule for the *E*/*Z* assignments of **2a**−**c**[2c)]. On the other hand, they pointed out contradictory evidence for the *E*/*Z* pair of **8**[2d)]: (*E*)-**8** has both the larger $^{2}J(\mathrm{PH})$ = 25 Hz (even though lone pair and H are *trans*) and the larger $^{3}J(\mathrm{P{=}C{-}Si{-}}C)$ = 8.3 Hz [(*Z*)-**8**: $^{2}J(\mathrm{PH})$ = 18, $^{3}J(\mathrm{PC})$ = 3.4 Hz] (in accordance with the old rule), so that unambiguous assignment on the basis of the relative magnitude of the coupling constant is not possible in this case. In Tables 1 and 2, relevant NMR spectroscopic data of phosphaalkenes are collected.

We assign the configuration of the *C*-halogen-substituted (*E*)-**2c** (δ^{31}P = 290) on the following grounds:

- it has the smaller $^{2}J(\mathrm{P{=}C}H)$ and thus obeys the *cis* rule, as assumed by Appel et al.[2c,7)];
- it is the isomer formed via intermediate **4c** in large excess (80:20) as expected for the mechanism of its formation (cf. Scheme 3);
- it is the only isomer formed from **1c** on lithiation and subsequent protonation (cf. Scheme 9); as substitution of the (*E*)-iodine in **1c** must be the reason for the observed stereospecificity (vide supra), and as both iodine-lithium exchange and protonation are expected

Table 1. Characteristic NMR data of monosubstituted phosphaalkenes Mes*P = CHX (**8** – **10**)

Compound	X	δ (^{1}H)^a (P=C*H*)	δ (^{13}C)^a (P=*C*)	δ (^{31}P)^a	δ (M)^a	^2J(PH) [Hz]	^1J(P=C) [Hz]	^3J(PC) [Hz]	^2J(PM) [Hz]
(*E*) - **8**^{b}	SiMe$_3$	7.72	178.5	329.2	– 6.6^c	25	66	8.3	32.0^e
(*E*) - **9**	GeMe$_3$	8.00	180.2	313.5	-	23	67	8.2	
(*E*) - **10**	SnMe$_3$	8.20	178.6	323.0	– 34^d	26	75	9.0	280^f
(*Z*) - **8**^{b}	SiMe$_3$	7.89	173.3	337.3	– 8.8^c	18	54	3.4	21.5^e
(*Z*) - **9**	GeMe$_3$	7.96	174.3	331.1	-	23	56	2.7	
(*Z*) - **10**	SnMe$_3$	8.47	175.6	353.9	- 51^d	23	58	0	181^f

[a] δ relative to TMS (^{1}H, ^{13}C, ^{29}Si), 85% H_3PO_4 (^{31}P), $SnMe_4$ (^{119}Sn). – [b] Not purified; see also refs.[2d,8c]. – [c] ^{29}Si NMR. – [d] ^{119}Sn NMR. – [e] ^2J(P^{29}Si). – [f] ^2J(P^{119}Sn).

Table 2. Characteristic NMR data of disubstituted phosphaalkenes Mes*P = CIX (**12** – **14**) and Mes*P = CX_2 (**18** – **20**)

Compound	X	δ (^{13}C)^a (P=*C*)	δ (^{31}P)^a	δ (M)^a	^1J(P=C) [Hz]	^3J(PC) [Hz]	^2J(PM) [Hz]
(Z) - **12**^{b}	SiMe$_3$		338				
(Z) - **13**	GeMe$_3$	144	328		57	8.9	
(Z) - **14**	SnMe$_3$	146	335	8^d	77	5.9	268^f
20^c	SiMe$_3$	187.8	393	-4.5 (*E*)^e		14.7 (*E*)	39 (*E*)^g
				-9.8 (Z)^e	90	3.2 (Z)	11 (Z)^g
18	GeMe$_3$	194.0	364		88	13.5 (*E*) 2.8 (Z)	
19	SnMe$_3$	198.3	386	- 16 (*E*)^d		10.8 (*E*)	322 (*E*)^f
				- 43 (Z)^d	93	0	150 (Z)^f

[a] δ relative to TMS (^{1}H, ^{13}C, ^{29}Si), 85% H_3PO_4 (^{31}P), $SnMe_4$ (^{119}Sn). – [b] In THF, directly from the reaction mixture. – [c] Ref.[8]. – [d] ^{119}Sn NMR. – [e] ^{29}Si NMR. – [f] ^2J(P^{119}Sn). – [g] ^2J(P^{29}Si).

to proceed with retention of configuration, certainly at the low temperature of this reaction (– 120 °C)[9], this presents strong support for the assignment;

- while each of the three previous arguments alone may not seem compelling, their combination is consistent and convincing.

The *E*/*Z* configuration of the other halogen-phosphaalkenes **2** follows by analogy with the relative magnitude of ^2J(P = C*H*).

We next turn our attention to the Group 14-substituted phosphaalkenes (*E*/*Z*)-**8** – **10**. They are formed from (*E*/*Z*)-**2c** (80:20) in the identical ratio of 80:20. This strongly suggests that the *E*/*Z* configuration is retained in both electrophilic substitution steps involved, in line with expectation[9]. If this conclusion is accepted, one is confronted with the difficulty that ^2J(P – H) is *larger* for the *E* isomers in violation of the *cis* rule. On the other hand, ^2J(P – ^{29}Si) of (*E*)-**8** (32 Hz) and ^2J(P – ^{119}Sn) of (*E*)-**10** (280 Hz) are larger than those for (*Z*)-**8** (21 Hz) and (*Z*)-**10** (181 Hz). This is in accord with the *cis* rule [note that analogously the same conclusion can be drawn for (*E*/*Z*)-**8** from ^3J(P = C – Si – C)[2d], vide supra].

We draw the conclusion that the old *cis* rule cannot be valid in its original form and has to be modified as follows: In phosphaalkenes RP = CXY, the coupling between phosphorus and nuclei *n* in X [^nJ(P*n*)] is larger than that of corresponding nuclei in Y if two conditions are simultaneously fulfilled (or simultaneously *not* fulfilled):

1) X has the same or lower electronegativity than Y.
2) X has the *cis* configuration relative to the phosphorus lone pair.

It is evident that the "old" *cis* rule was applicable in the light of the revised form because the phosphaalkenes to which it was applied originally were monohalophosphaalkenes (X = H, Y = halogen) or carried two organic groups on the olefinic carbon, so that the first condition was fulfilled; in this case, the magnitude of the coupling depends (implicitly) on condition 2 only. On the contrary, the old rule breaks down for combinations like X = H and Y = M (M = Si, Sn).

At present, it is difficult to identify the factors which are responsible for this new *cis* rule. The phenomenon that for equal nuclei *n*, ^2J(P*n*) is greater if *n* and the phosphorus lone pair are *cis*, seems to be general and holds not only for phosphaalkenes[6], but also for saturated phosphanes[10] and for other nuclei having lone pairs in general[11]. In the present case, however, this phenomenon is dominated by the electronegativity of X and Y (condition 1). Possibly, electronegativity is acting through its influence on hybridization; high s-character will tend to increase coupling via the Fermi contact term.

In this context, it should be pointed out that as far as available the coupling constants of *E*/*Z* pairs show remarkable differences of ^1J(= C – X). For instance, in (*Z*)-**9** and (*Z*)-**10** we find ^1J(= C – H) = 132 Hz, while for the *E* isomers ^1J(= C – H) = 148 Hz, in line with ^2J(PH) being larger in the *E* (= lone pair to H *trans*) series; concomitantly, ^1J(= C – ^{119}Sn) is smaller in (*E*)-**10** than in (*Z*)-**10** (257 and 310 Hz, respectively). It is obvious that more experimental material is required to test the generality of this modified rule; moreover, a thorough theoretical analysis would be highly desirable.

Nevertheless, the modified rule is consistent with other NMR data. From the genesis of (*Z*)-**14** (Scheme 9) one may confidently assign the *Z* configuration (cf. the steric arguments for **2c** and **8** – **10**) and, indeed, its ^2J(P – ^{119}Sn) = 268 Hz is "large" (note that tin is *cis* to the phosphorus lone pair!). Similarly, **19** has both a *cis*-tin (=*E*!) with a large coupling of 323 Hz and a *trans*-tin (=*Z*) with a typical "small" coupling of 156 Hz. In addition, the modified *cis* rule holds for the $^3J(^{31}P=CM^{13}CH_{3-})$, too, the couplings of the carbon *cis* to the lone pair being larger (J = 5.9–13.5 Hz) than those of the *trans* carbon (J = 0–3.5 Hz) [cf. **8**[2d], **9**, **10**, (*Z*)-**13**, (*Z*)-**14**, **18**, and **19**][12].

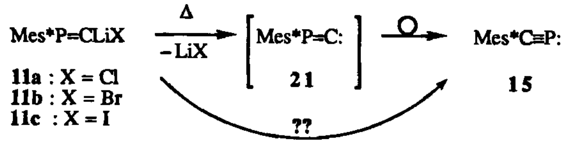
The other data of Tables 1 and 2 did not reveal general and useful trends; in particular, the chemical shifts seem to be determined by a complex interplay of factors which do not yield to a straightforward analysis[12].

Are "Phospha-isonitriles" Capable of Existence?

The chemistry of nitrogen includes the well-known couple nitrile/isonitrile ($RC{\equiv}N$:/$RN^+{\equiv}C:^-$). In the phosphorus series, only the phosphaalkynes $RC{\equiv}P$ are known[13], even though the so-called "phospha-isonitriles"[14] have been the goal of both experimental[2c,6a,15,16] and theoretical[17] investigations.

An obvious synthetic approach to the phospha-isonitrile **21** is the elimination of lithium halide from carbenoids such as **11** (Scheme 11). The groups of Appel[2c] and of Yoshifuji[15a] reported that **11a** reacted (at an unknown temperature between −80°C and room temperature[15a]) to form the isomeric **15** instead; a similar experiment with **11b** apparently did not lead to clear-cut results[2b].

Scheme 11



Carbenoid (*Z*)-**11c** appears to be even less stable than **11a** and **11b**, as we experienced in the attempted reaction with chlorotrimethylsilane (see Scheme 9). The stability of (*Z*)-**11c** was therefore monitored by ^{31}P-NMR spectroscopy. From −120 to −100°C it was stable as evidenced by its signal at $\delta(^{31}P)$ = 288, but at −85°C reaction to **15** occurred with a half-life of roughly four hours, corresponding to an activation barrier of about ΔG^{+} = 13 kcal/mol (55 kJ/mol). Phosphorus signals other than those of **11c** and **15** were not observed, not even of short-lived intermediates; the observed activation barrier is probably that for carbenoid decomposition, i.e. for the reaction (*Z*)-**11c** ⟶ **21**, and the rearrangement of **21** *at this low temperature* must be extremely rapid or even concomitant with lithium iodide elimination. The latter case, if true, would be in accordance with theoretical calculations which predict **21** to be a transition state rather than a short-lived intermediate[17a].

Experimental

All experiments were performed in flamed out glassware and in a nitrogen atmosphere. – NMR: Bruker WM 90 (^{1}H), Bruker WM 250 (^{31}P: 101.25 MHz, ^{13}C: 62.9 MHz, ^{29}Si: 49.49 MHz, ^{119}Sn: 93.27 MHz). – High-resolution mass spectra (HRMS): Finnigan MAT 5. – Oily compounds which were not 100% pure and could not be purified due to their instability, have not been subjected to elemental analysis (**9**, **10**, **18**, **19**); however, in these cases a high resolution mass spectrum confirmed the elemental composition.

Tetraiodomethane was purchased from Aldrich, and prior to use I_2 was sublimed off in vacuo. All solvents were dried prior to use.

(Dichloromethylene)(2,4,6-tri-tert-butylphenyl)phosphane (**1a**): A solution of 25 ml of *n*-butyllithium (*n*BuLi) in hexane (1.6 M; 40 mmol) was added during 30 min at −100°C to a solution of Mes*PCl_2 (6.94 g, 20 mmol) and $HCCl_3$ (2.38 g, 20 mmol = 1.6 ml) in 150 ml of THF. The reaction mixture was slowly warmed to room temp. The solvent was evaporated in vacuo at room temp. and the residue extracted with 200 ml of pentane. **1a** crystallized from pentane in colorless crystals (yield: 5.2 g, 29.2 mmol, 73%), m.p. 148°C (ref.[4b] 145–146°C). – ^{1}H NMR (C_6D_6): δ = 1.28 (s, 9H, *p*-*t*Bu), 1.51 [d, 18H, *o*-*t*Bu, *J*(HP) = 0.6 Hz], 7.55 [d, 2H, Ar*H*, *J*(HP) = 1.7 Hz]. – ^{13}C NMR (C_6D_6): δ = 155.7 [d, P=C, *J*(CP) = 76.0 Hz], 154.3 [d, *o*-Ar, *J*(CP) = 2.4 Hz], 152.0 (s, *p*-Ar), 134.1 [d, *ipso*-Ar, *J*(CP) = 52.7 Hz], 122.6 (s, *m*-Ar), 38.0 [s, *o*-$C(CH_3)_3$], 35.2 [s, *p*-$C(CH_3)_3$], 32.8 [d, *o*-$C(CH_3)_3$, *J*(CP) = 6.8 Hz], 31.4 [9 s, *p*-$C(CH_3)_3$]. – ^{31}P NMR ($CDCl_3$): δ = 233. See also ref.[2b,4b].

(Dibromomethylene)(2,4,6-tri-tert-butylphenyl)phosphane (**1b**): A solution of 12.5 ml of *n*BuLi in hexane (1.6 M; 20 mmol) was added during 30 min at −100°C to a solution of $HCBr_3$ (5.06 g, 20 mmol) in 100 ml of THF. The reaction mixture was stirred for 1 h at −100°C (the color turned yellow). Mes*PCl_2 (3.47 g, 10 mmol) in THF was slowly added to this solution. The reaction mixture was slowly warmed to room temp. The solvent was evaporated in vacuo at room temp. and the residue extracted with 150 ml of pentane. **1b** crystallized from pentane in colorless crystals (yield: 2.46 g, 5.5 mmol, 55%); m.p. 157–158°C (ref.[2b] 158–159°C). – ^{1}H NMR (C_6D_6): δ = 1.28 (s, 9H, *p*-*t*Bu), 1.49 (s, 18H, *o*-*t*Bu), 7.52 [d, 2H, ArH, *J*(HP) = 1.6 Hz]. – ^{13}C NMR (C_6D_6): δ = 153.5 [d, *o*-Ar, *J*(CP) = 2.5 Hz], 152.1 (s, *p*-Ar), 139.7 [d, *ipso*-Ar, *J*(CP) = 57.0 Hz], 128.0 [d, P=C, *J*(CP) = 86.8 Hz], 122.8 (s, *m*-Ar), 38.0 [s, *o*-$C(CH_3)_3$], 35.2 [s, *p*-$C(CH_3)_3$], 32.9 [d, *o*-$C(CH_3)_3$, *J*(CP) = 7.0 Hz], 31.4 [s, *p*-$C(CH_3)_3$]. – ^{31}P NMR (C_6D_6). δ = 271. See also ref.[2b,4b].

(Diiodomethylene)(2,4,6-tri-tert-butylphenyl)phosphane (**1c**): A solution of 5.6 ml of *n*BuLi in hexane (1.6 M; 9 mmol) was added during 15 min at −110°C to a solution of Mes*PCl_2 (1.6 g, 4.5 mmol) and CI_4 (2.6 g, 5.0 mmol) in 50 ml of THF. The reaction mixture was slowly warmed to room temp. (the color slowly changed from purple to green and finally to orange). The solvent was evaporated in vacuo at room temp., and the residue was extracted with 100 ml of pentane. The pentane was evaporated in vacuo at room temp., yielding orange crystals (2.3 g, 4.2 mmol, 93%). – ^{1}H-, ^{13}C-, ^{31}P-NMR spectra were identical with those of ref.[2c,4b].

Reaction of Dichloro(2,4,6-tri-tert-butylphenyl)phosphane and Bromoform with nBuLi: A solution of 0.62 *n*BuLi in hexane (1.6 M; 1 mmol) was added during 1 min at −100°C to a solution of Mes*PCl_2 (347 mg, 1 mmol) and $HCBr_3$ (253 mg, 1 mmol) in 10 ml of THF. The reaction mixture was slowly warmed to room temp. The products (**2b** and Mes*PCl_2) were identified by their ^{31}P-NMR chemical shifts [δ (THF) = 270 and 153, respectively]. Another 0.62 ml of *n*BuLi solution in hexane (1.6 M; 1 mmol) was added during 1 min at −100°C to this solution. The reaction mixture was slowly warmed to room temp. The products were analyzed by ^{31}P-NMR spectroscopy. Only **1b** and (*E*/*Z*)-**2b** (20:80 ratio) in a 1:1 ratio could be observed; yields were not determined.

(Iodomethylene)(2,4,6-tri-tert-butylphenyl)phosphane (**2c**): A solution of 8 ml of *n*BuLi in hexane (1.6 M; 12.8 mmol) was added during 15 min at −100°C to a solution of Mes*PCl_2 (2.2 g, 6.3 mmol) and HCI_3 (2.5 g, 6.3 mmol) in 20 ml of THF. The temp. was slowly raised to room temp. The solvent was evaporated in vacuo at room temp. and the residue extracted with 100 ml of pentane. **2c** was further purified over a silicagel column with pentane as eluent (the silicagel was dried in an oven for 4 d at 140°C) yielding a brownish-red oil (2.37 g, 5.7 mmol, 90%). According to the ^{31}P-NMR spectrum, the *E*/*Z* ratio was 80:20. – (*E*)-**2c** ^{1}H NMR (C_6D_6): δ = 1.30 (s, 9H, *p*-*t*Bu), 1.46 (s. 18H, *o*-*t*Bu), 7.45 [d, 2H, ArH, *J*(HP) = 1.1 Hz], 7.69 [d, 1H, P=CH, *J*(HP) = 25.8 Hz]. – (*Z*)-**2c** ^{1}H NMR (C_6D_6): δ = 1.35 (s, 9H, *p*-*t*Bu), 1.50 (s, 18H, *o*-*t*Bu), 7.53 [d, 2H, ArH, *J*(HP) = 1.5 Hz], 7.62 [d, 1H, P=CH,*J*(HP) = 40.0 Hz]; ref.[2c].

General Procedure for the Preparation of **8**–**10**: A solution of 0.62 ml of *n*BuLi in hexane (1.6 M; 1 mmol) was added during 1 min at −100°C to a solution of **2c** (*E*/*Z* ratio of 80:20) (0.42 g, 1.0 mmol) in 10 ml of Et_2O. The reaction mixture was stirred at −80°C for 30 min, then cooled to −120°C; 1.5 eq. of $ClMMe_3$ (0.16 g $ClSiMe_3$, 0.23 g $ClGeMe_3$, 0.29 g $ClSnMe_3$) in 10 ml of Et_2O were added during a period of 5 min. The reaction mixture was warmed up to room temp. All the volatile products were then evaporated in vacuo (10^{-2} mbar) at room temp. The residue was extracted with 25 ml of pentane. The pentane was evaporated in vacuo, yielding yellowish oils. **8** could not be obtained in pure form; it contained 20% 7. The *E*/*Z* ratio of **9** and **10** was 80:20. (Yields: **8** not determined; **9** 400 mg, 0.98 mmol, 98%; **10** 353 mg, 0.8 mmol, 80%).

(E)-(2,4,6-Tri-tert-butylphenyl)[(trimethylsilyl)methylene]phosphane [(*E*)-**8**]: Only those ^{13}C nuclei which couple with the ^{31}P nucleus could be clearly identified by selective decoupling of ^{31}P. – ^{13}C NMR (C_6D_6): δ = 178.5 [d, P=C, *J*(CP) = 66.4 Hz] 146.0 [d, *ipso*-Ar, *J*(CP) = 69.2 Hz], 34.2 [d, *o*-C(CH_3)$_3$, *J*(CP) = 8 Hz], −0.1 [d, $SiMe_3$, *J*(CP) = 9 Hz]. – ^{29}Si NMR (C_6D_6): δ = −6.6 [d, *J*(^{29}SiP) = 32 Hz]. – ^{31}P NMR (C_6D_6); δ = 328.1 [d, *J*(PH) = 24.7, *J*(P^{29}Si) = 31 Hz].

(Z)-(2,4,6-Tri-tert-butylphenyl)[(trimethylsilyl)methylene]phosphane [(*Z*)-**8**]: Only those ^{13}C nuclei which couple with the ^{31}P nucleus could be clearly identified by selective decoupling of ^{31}P. – ^{13}C NMR (C_6D_6): δ = 173.3 [d, P=C, *J*(CP) = 54.4 Hz], 33.9 [d, *o*-C(CH_3)$_3$, *J*(CP) = 8.2 Hz], −0.8 [d, $SiMe_3$, *J*(CP) = 3.2 Hz]. – ^{29}Si NMR (C_6D_6): δ = −8.8 [d, *J*(^{29}SiP) = 21 Hz]. – ^{31}P NMR (C_6D_6); δ = 337.2 [d, *J*(PH) = 18, *J*(P^{29}Si) = 21 Hz].

(E)-(2,4,6-Tri-tert-butylphenyl)[(trimethylgermyl)methylene]phosphane [(*E*)-**9**]: ^{1}H NMR (C_6D_6): δ = 0.29 (s, 9H, $GeMe_3$), 1.36 (s, 9H, *p*-*t*Bu), 1.59 (s, 18H, *o*-*t*Bu), 7.57 [d, 2H, *m*-Ar, *J*(HP) = 0.6 Hz], 8.00 [d, 1H, P=CH, *J*(HP) = 26.4 Hz]. – ^{13}C NMR (C_6D_6): δ = 180.2 [dd, P=C, *J*(CP) = 67.4, *J*(CH) = 147.8 Hz], 152.9 (d, *o*-Ar, *J*(CP) = 1.4 Hz,) 150.3 (s, *p*-Ar), 146.0 [d, *ipso*-Ar, *J*(CP) = 69.7 Hz], 121.9 [dd, *m*-Ar, *J*(CH) = 153.1, ^{3}*J*(CH) = 6 Hz], 38.4 [s, *o*-C(CH_3)$_3$], 35.1 [s, *p*-C(CH_3)$_3$], 34.2 [d, *o*-C(CH_3)$_3$, *J*(CP) = 7.8 Hz], 31.6 [s, *p*-C(CH_3)$_3$], −0.5 [d, $GeMe_3$, *J*(CP) = 8.2 Hz]. – ^{31}P NMR (C_6D_6): δ = 313.5 [d, *J*(PH) = 23.2 Hz]. – MS (70 eV): *m*/*z* (%) = 408 (4) [M$^+$], 393 (16) [M$^+$ − Me], 289 (41) [M$^+$ −$GeMe_3$]. – HRMS calcd. for $C_{22}H_{39}{}^{70}GeP$ 404.2032, found 404.2073.

(Z)-(2,4,6-Tri-tert-butylphenyl)[(trimethylgermyl)methylene]phosphane [(*Z*)-**9**]: ^{1}H NMR (C_6D_6): δ = 0.34 (s, 9H, $GeMe_3$), 1.36 (s, 9H, *p*-*t*Bu), 1.59 (s, 18H, *o*-*t*Bu), 7.47 [d, 2H, *m*-Ar, *J*(HP) = 1.0 Hz], 7.96 [d, 1H, P=CH, *J*(HP) = 23.5 Hz]. – ^{13}C NMR (C_6D_6): δ = 174.3 [dd, P=C, *J*(CP) = 56.0, *J*(CH) = 131.7 Hz], 153.9 [d, *o*-Ar, *J*(CP) = 1.4 Hz], 149.5 (s, *p*-Ar), 141.5 [d, *ipso*-Ar, *J*(CP) = 65.9 Hz], 119.7 [dd, *m*-Ar, *J*(CH) = 151.8, ^{3}*J*(CH) = 6.5 Hz], 38.4 [s, *p*-C(CH_3)$_3$], 35.0 [s, *o*-C(CH_3)$_3$], 33.8 [d, *o*-C(CH_3)$_3$, *J*(CP) = 8.2 Hz], 31.5 [s, *p*-C(CH_3)$_3$], −1.0 [d, $GeMe_3$, *J*(CP) = 2.7 Hz]. – ^{31}P NMR (C_6D_6): δ = 331.1 [d, *J*(PH) = 22.7 Hz]. – MS/HRMS see (*E*)-**9**.

(E)-(2,4,6-Tri-tert-butylphenyl)[(trimethylstannyl)methylene]phosphane [(*E*)-**10**]: ^{1}H NMR (C_6D_6): δ = 0.25 [s, 9H, $SnMe_3$, *J*(H^{119}Sn) = 54.4, *J*(H^{117}Sn) = 51.7 Hz], 1.37 (s, 9H, *p*-*t*Bu), 1.61 (s, 18H, *o*-*t*Bu), 7.55 [d, 2H, *m*-Ar, *J*(HP) = 0.6 Hz], 8.20 [d, 1H, P=CH, *J*(HP) = 26.1 Hz]. – ^{13}C NMR (C_6D_6): δ = 178.6 [dd, P=C, *J*(CP) = 75, *(J*(CH) = 148, *J*(C^{119}Sn) = 257, *J*(C^{117}Sn) = 240 Hz], 152.7 [d, *o*-Ar, *J*(CP) = 1.5 Hz], 149.4 (s, *p*-Ar), 147.5 [d, *ipso*-Ar, *J*(CP) = 75 Hz], 121.9 [dd, *m*-Ar, *J*(CH) = 153, ^{3}*J*(CH) = 5.8 Hz], 38.4 [s, *o*-C(CH_3)$_3$], 35.0 [s, *p*-C(CH_3)$_3$], 34.4 [qd, *o*-C(CH_3)$_3$, *J*(CP) = 7.5, *J*(CH) = 130 Hz], 31.6 [q, *p*-C(CH_3)$_3$, *J*(CH) = 129 Hz], −8.4 [qd, $SnMe_3$, *J*(CP) = 9.0, *J*(CH) = 128 Hz]. – ^{31}P NMR (C_6D_6): δ = 323.0 [d, *J*(PH) = 25.8, *J*(P^{119}Sn) = 279.9, *J*(P^{117}Sn) = 268.7 Hz]. – ^{119}Sn NMR (C_6D_6): δ = −34.1 [d, *J*(SnP) = 280.1 Hz]. – MS (70 eV): *m*/*z* (%) = 454 (1) [M$^+$], 439 (7) [M$^+$ −Me], 289 (100) [M$^+$ − $SnMe_3$]. – HRMS calcd. for $C_{21}H_{36}{}^{120}SnP$ [M$^+$ − Me] 439.1576, found 439.1536.

(Z)-(2,4,6-Tri-tert-butylphenyl)[(trimethylstannyl)methylene]phosphane [(*Z*)-**10**]: ^{1}H NMR (C_6D_6): δ = −0.20 [s, 9H, $SnMe_3$, *J*(H^{119}Sn) = 57.1, *J*(H^{117}Sn) = 52.9 Hz], 1.37 (s, 9H, *p*-*t*Bu), 1.58 (s, 18H, *o*-*t*Bu), 7.47 [d, 2H, *m*-Ar, *J*(HP) = 1.1 Hz], 8.47 [d, 1H, P=CH, *J*(HP) = 23.5 Hz]. – ^{13}C NMR (C_6D_6: δ = 175.6 [dd, P=C, *J*(CP) = 57.7, *J*(CH) = 132, *J*(C^{119}Sn) = 310, *J*(C^{117}Sn) = 296 Hz], 153.6 [d, *o*-Ar, *J*(CP) = 1.9 Hz], 149.9 (s, *p*-Ar), 122.2 [dd, *m*-Ar, *J*(CH) = 155, ^{3}*J*(CH) = 6 Hz], 38.6 [s, *o*-C(CH_3)$_3$], 35.1 [s, *p*-C(CH_3)$_3$], 34.0 [dq, *o*-C(CH_3)$_3$, *J*(CP) = 7.8, *J*(CH) = 130 Hz], 31.5 [q, *p*-C(CH_3)$_3$, *J*(CH) = 129 Hz], −8.5 [qd, $SnMe_3$, *J*(CH) = 128, *J*(C^{119}Sn) = 347, *J*(C^{117}Sn) = 332 Hz]. – ^{31}P NMR (C_6D_6): δ = 353.9 [d, *J*(PH) = 23.5, *J*(P^{119}Sn) = 181.2, *J*(P^{117}Sn) = 172.6 Hz]. – ^{119}Sn NMR (C_6D_6): δ = −51.5 [d, *J*(SnP) = 181.1 Hz]. – MS/HRMS see (*E*)-**10**.

*Reaction of (E/Z)-***2c** *with Lithium Diisopropylamide (LDA)*: A solution of 1.5 ml of LDA in THF (0.57 M; 0.85 mmol) was added at −100°C to a solution of **2c** (*E*/*Z* ratio was 80:20) (370 mg, 0.9 mmol) in 10 ml of THF. This reaction mixture was stirred at −100°C for 2 h; then 30 µl of D_2O (1.5 mmol) was added. The reaction mixture was warmed to room temp. The products were characterized by ^{31}P-NMR spectroscopy. The chemical shifts of (*E*/*Z*)-[D]**2c** were nearly the same as for (*E*/*Z*)-**2c**, only the typical ^{2}*J*(PH) couplings were missing. – ^{31}P NMR (THF): δ = 309 (*Z*) 20%, 290 (*E*) 80%.

General Procedure of the Preparation of (*Z*)-**13** *and* (*Z*)-**14**: A solution of 0.62 ml of *n*BuLi in hexane (1.6 M; 1 mmol) was added during 5 min at −120°C to a solution of **1c** (0.54 g, 1.0 mmol) in 10 ml of Et_2O. The reaction mixture was stirred for 15 min, while the temp. was kept below −100°C. The reaction mixture was cooled to −120°C, and 1.5 eq. of $ClMMe_3$ (0.23 g $ClGeMe_3$, 0.29 g $ClSnMe_3$) in 10 ml of Et_2O were added during a period of 5 min. The reaction mixture was warmed to room temp. All the volatile products were evaporated in vacuo (10^{-2} mbar) at room temp. The residue was extracted with 50 ml of pentane. The pentane was evaporated in vacuo yielding yellowish crystals. (*Z*)-**13** 428 mg, 0.8 mmol, 80%; (*Z*)-**14** 493 mg, 0.85 mmol, 85%. (*Z*)-**13** and (*Z*)-**14** were crystallized from pentane.

[Iodo(trimethylgermyl)methylene](2,4,6-tri-tert-butylphenyl)phosphane [(*Z*)-**13**]: M.p. 117–117.5°C. – ^{1}H NMR (C_6D_6): δ = 0.49 (s, 9H, $GeMe_3$), 1.36 (s, 9H, *p*-*t*Bu), 1.56 (s, 18H, *o*-*t*Bu), 7.56 [d, 2H, *m*-Ar, *J*(HP) = 1.2 Hz]. – ^{13}C NMR (C_6D_6): δ = 152.1 [d, *o*-Ar, *J*(CP) = 1.9 Hz], 150.9 (s, *p*-Ar), 149.1 [dt, *ipso*-Ar, *J*(CP) =

67.6, *J*(CH) = 7.0 Hz], 144.0 [d, P=C, *J*(CP) = 56.6 Hz], 122.8 [dd, *m*-Ar, *J*(CH) = 153.4, ^3J(CH) = 6.1 Hz], 38.0 [s, *o*-*C*(CH_3)$_3$], 35.2 [s, *p*-*C*(CH_3)$_3$], 33.4 [dq, *o*-C(*C*H_3)$_3$, *J*(CP) = 7.2, *J*(CH) = 120 Hz], 31.6 [q, *p*-C(*C*H_3)$_3$, *J*(CH) = 125 Hz], 0.5 [dq, $GeMe_3$, *J*(CP) = 8.9, *J*(CH) = 126.6 Hz]. – ^{31}P NMR (C_6D_6): δ = 327.6. – MS (70 eV): *m/z* (%) = 534 (1) [M^+], 407 (8) [M^+ – I]. – HRMS calcd. for $C_{22}H_{38}{}^{70}GePI$ 530.0997, found 530.1010.

$C_{22}H_{38}GePI$ (530.1)					
Calcd.	C 49.58	H 7.17	Ge 13.6	I 23.8	P 5.81
Found	C 49.72	H 7.22	Ge 13.6	I 23.2	P 5.85

[Iodo(trimethylstannyl)methylene](2,4,6-tri-tert-butylphenyl)-phosphane [(Z)-**14**]: M.p. 102.0–103.5°C. – ^{1}H NMR (C_6D_6): δ = 0.37 [s, 9H, $SnMe_3$, *J*($H^{119}Sn$) = 55.9, *J*($H^{117}Sn$) = 53.5 Hz], 1.37 (s, 9H, *p*-*t*Bu), 1.58 (s, 18H, *o*-*t*Bu), 7.56 [d, 2H, *m*-Ar, *J*(HP) = 0.5 Hz]. – ^{13}C NMR (C_6D_6: δ = 151.8 [d, *o*-Ar, *J*(CP) = 1.8 Hz], 150.7 (s, *p*-Ar), 150.3 [dt, *ipso*-Ar, *J*(CP) = 72.6, *J*(CH) = 7.0 Hz], 146.0 [d, P=C, *J*(CP) = 77.3 Hz], 122.7 [dd, *m*-Ar, *J*(CH) = 153.5, ^3J(CH) = 6.3 Hz], 38.0 [s, *o*-*C*(CH_3)$_3$], 35.2 [s, *p*-*C*(CH_3)$_3$], 33.4 [dq, *o*-C(*C*H_3)$_3$, *J*(CP) = 6.0, *J*(CH) = 119 Hz], 31.5 [q, *p*-C(*C*H_3)$_3$, *J*(CH) = 128 Hz], –6.6 [dq, $SnMe_3$, *J*(CP) = 5.9, *J*(CH) = 130.3, *J*($C^{119}Sn$) = 208, *J*($C^{117}Sn$) = 197 Hz]. – ^{31}P NMR (C_6D_6): δ = 335.5 [*J*($P^{119}Sn$) = 268, *J*($P^{117}Sn$) = 257 Hz]. – ^{119}Sn NMR(C_6D_6): δ = 8.0 [d, *J*(SnP) = 262.6 Hz]. – MS (70 eV): *m/z* (%) = 580 (4) [M^+], 457 (12), [M^+ – I]. – HRMS calcd. for $C_{22}H_{38}P^{120}SnI$ 580.0776, found 580.0851.

$C_{22}H_{38}PSnI$ (580.1)					
Calcd.	C 45.63	H 6.61	I 21.9	P 5.35	Sn 20.5
Found	C 46.48	H 6.85	I 21.1	P 5.35	Sn 18.9

(Iodomethylene)(2,4,6-tri-tert-butylphenyl)phosphane [(*Z*)-**2c**]: A solution of 1.25 ml of *n*BuLi in hexane (1.6 M; 2 mmol) was added during 5 min at –120°C to a solution of **1c** (1.08 g, 2 mmol) in 20 ml of Et_2O. The reaction mixture was stirred while the temp. was kept below –100°C. MeOH (156 mg, 3 mmol) was added, and the reaction mixture was slowly warmed to room temp. The solvent was evaporated in vacuo and the residue extracted with 50 ml of pentane. The pentane was evaporated in vacuo yielding a yellow oil (624 mg, 1.5 mmol, 75%). – ^{1}H, ^{13}C, ^{31}P NMR: *vide supra.*

General Procedure for the Preparation of **18** and **19**: A solution of 0.62 ml of *n*BuLi in hexane (1.6 M; 1 mmol) was added during 1 min at –100°C to a solution of (*Z*)-**13** (0.53 g, 1.0 mmol) or (*Z*)-**14** (0.58 g, 1.0 mmol), respectively, in 10 ml of Et_2O. The reaction mixture was stirred for 60 min, maintaining the temp. below –75°C. The reaction mixture was cooled to –120°C and 1.5 eq. of $ClMMe_3$ (0.23 g $ClGeMe_3$, 0.29 g $ClSnMe_3$, respectively) in 10 ml of Et_2O were added during a period of 5 min. The reaction mixture was warmed to room temp. The volatile products were evaporated in vacuo (10^{-2} mbar) at room temp. The residue was extracted with 50 ml of pentane. The pentane was evaporated in vacuo yielding yellowish oils, yields **18**: 500 mg (0.96 mmol, 96%); **19**: 550 mg (0.89 mmol, 89%).

[Bis(trimethylgermyl)methylene](2,4,6-tri-tert-butylphenyl)-phosphane (**18**): ^{1}H NMR (C_6D_6): δ = 0.27 (s, 9H, $GeMe_3$), 0.58 (s, 9H, $GeMe_3$), 1.35 (s, 9H, *p*-*t*Bu), 1.57 (s, 18H, *o*-*t*Bu), 7.45 [d, 2H, *m*-Ar, *J*(HP) = 0.9 Hz]. – ^{13}C NMR (C_6D_6): δ = 194.0 [d, P=C, *J*(CP) = 88.2 Hz], 153.3 [d, *o*-Ar, *J*(CP) = 2.5 Hz], 150.4 (s, *p*-Ar), 144.2 [dt, *ipso*-Ar, *J*(CP) = 81.7, *J*(CH) = 6.5 Hz], 122.2 [dd, *m*-Ar, *J*(CH) = 153.0, ^3J(CH) = 6.5 Hz], 38.5 [s, *o*-*C*(CH_3)$_3$], 35.1 [s, *p*-*C*(CH_3)$_3$], 33.8 [dq, *o*-C(*C*H_3)$_3$, *J*(CP) = 8.6, *J*(CH) = 125 Hz], 31.6 [q, *p*-C(*C*H_3)$_3$, *J*(CH) = 130 Hz], 2.6 [dq, $GeMe_3$, *J*(CP) = 13.5, *J*(CH) = 125.6 Hz], 1.1 [dq, Z-$GeMe_3$, *J*(CP) = 2.8, *J*(CH) = 124.1 Hz]. – ^{31}P NMR (C_6D_6): δ = 363.8. – MS (70 eV): *m/z* (%) = MS (70 eV): *m/z* (%) = 524 (9) [M^+], 509 (21) [M^+ – Me], 407 (49) [M^+ – $GeMe_3$]. – HRMS calcd. for $C_{25}H_{47}{}^{70}Ge_2P$ 518.1901, found 518.1930.

[Bis(trimethylstannyl)methylene](2,4,6-tri-tert-butylphenyl)-phosphane (**19**): ^{1}H NMR (C_6D_6): δ = –0.15 [s, 9H, $SnMe_3$, *J*($H^{119}Sn$) = 53.3, *J*($H^{117}Sn$) = 50.8 Hz], 0.44 [s, 9H, (*E*)-$SnMe_3$, *J*($H^{119}Sn$) = 54.0, *J*($H^{117}Sn$) = 51.8 Hz], 1.36 (s, 9H, *p*-*t*Bu), 1.57 (s, 18H, *o*-*t*Bu), 7.47 [d, 2H, *m*-Ar, *J*(HP) = 0.8 Hz]. – ^{13}C NMR (C_6D_6): δ = 198.3 [d, P=C, *J*(CP) = 93.0 Hz], 152.6 [d, *o*-Ar, *J*(CP) = 1.3 Hz], 150.0 (s, *p*-Ar), 148.6 [dt, *ipso*-Ar, *J*(CP) = 87.3, *J*(CH) = 6.0 Hz], 122.4 [dd, *m*-Ar, *J*(CH) = 153.0, ^3J(CH) = 5.7 Hz], 38.6 [s, *o*-*C*(CH_3)$_3$], 35.1 [s, *p*-*C*(CH_3)$_3$], 34.1 [dq, *o*-C(*C*H_3)$_3$, *J*(CP) = 8.7, *J*(CH) = 128 Hz], 31.6 [q, *p*-C(*C*H_3)$_3$, *J*(CH) = 126 Hz], –6.1 [dq, (*E*)-$SnMe_3$, *J*(CP) = 10.8, *J*(CH) = 128.7, *J*($C^{119}Sn$) = 339, *J*($C^{117}Sn$) = 322 Hz], –6.7 [q, (*Z*)-$SnMe_3$, *J*(CH) = 128.4, *J*($C^{119}Sn$) = 333, *J*($C^{117}Sn$) = 318 Hz]. – ^{31}P NMR (C_6D_6): δ = 386.7 [*J*($P^{119}Sn$(*E*)) = 321.3, *J*($P^{117}Sn$(*E*)) = 307.2, *J*($P^{119}Sn$(*Z*)) = 156.4, *J*($P^{117}Sn$(*Z*)) = 150.0 Hz.] – ^{119}Sn NMR (C_6D_6): δ = –16.0 [d, (*E*)-$SnMe_3$, *J*(^{119}SnP) = 322.7 Hz], –43.1 [d, (*Z*)-$SnMe_3$, *J*(^{119}SnP) = 155.7 Hz]. – MS (70 eV): *m/z* (%) = 618 (2) [M^+], 603 (2) [M^+ – Me], 453 (7) [M^+ – $SnMe_3$]. – HRMS calcd. for $C_{25}H_{47}{}^{118}Sn^{120}Sn$ 616.145, found 616.151.

CAS Registry Numbers

1a: 100281-24-1 / **1b**: 100281-23-0 / **1c**: 118281-77-9 / (*E*)-**2b**: 92957-46-5 / (*Z*)-**2b**: 92957-43-2 / (*E*)-**2c**: 118281-72-4 / (*Z*)-**2c**: 118281-73-5 / (*E*)-[D]**2c**: 136409-18-2 / (*Z*)-[D]**2c**: 136409-19-3 / **7**: 84114-18-1 / (*E*)-**8**: 105890-78-6 / (*Z*)-**8**: 105890-79-7 / (*E*)-**9**: 136409-14-8 / (*Z*)-**9**: 136409-15-9 / (*E*)-**10**: 136409-16-0 / (*Z*)-**10**: 136409-17-1 / (*Z*)-**13**: 136409-20-6 / (*Z*)-**14**: 136409-21-7 / **15**: 100938-86-1 / **18**: 136409-22-8 / **19**: 136409-23-9 / **21**: 136409-24-0 / Mes*PCl_2: 79074-00-3 / $HCCl_3$: 67-66-3 / CI_4: 507-25-5 / $HCBr_3$: 75-25-2 / HCI_3: 75-47-8 / $ClSiMe_3$: 75-77-4 / $ClGeMe_3$: 1529-47-1 / $ClSnMe_3$: 1066-45-1

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[12] We attempted to further confirm the modified *cis*-rule by a comparison of the chemical shifts of the coupling nuclei at the (P=)C carbon. One may expect the nuclei *cis* to the supermesityl group to be more shielded than the corresponding *trans* nuclei because the former will reside in the shielding cone of the supermesityl ring which is more or less perpendicular to the P=C plane. However, while this expectation is born out in most cases (**8**–**10**; Sn in **10** and **19**), there are exceptions (e.g. P=CH in **9** are nearly identical; in Mes*P=C*H*Ph, they are even reversed[2d]), so that this criterion is not absolutely reliable.

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