# Syntheses and reactions of mono- and polyelementorganic compounds

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*Abstract*
The synthesis and structure of elementorganic-substituted phosphonium ylides are reported and the use of such polyelementorganic compounds in preparative organic chemistry demonstrated. A concept for the complexation of $C_1$, $C_2$, $C_3$ and $C_4$ is presented which has also been put into practice in the meanwhile.

Theoretical calculations on the model ylide **1**, which carries substituents of the first period of the periodic system at the ylidic C-atom, demonstrate that σ-donors and π-acceptors X stabilize phosphonium ylides, whereas σ-acceptors and π-donors cause a destabilisation (1). It follows, that lithium should show a stabilizing effect, so that phosphorus in such ylides may more or less stabilize two negative charges.
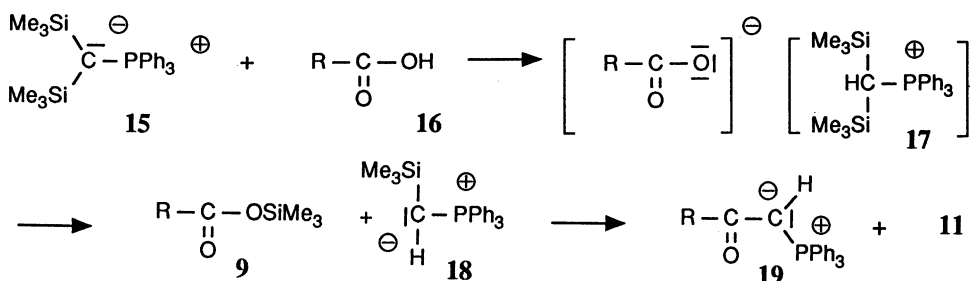


X = Li, Be, B, C, N, O, F
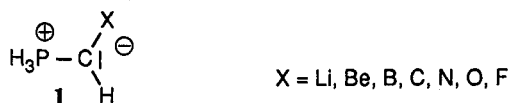
In agreement with the theoretical calculations, ylide **2** can be transformed into the sodium compound **4** with sodium silazid **3** and used for different reactions (2). Thus, **4** reacts with the halogen compound **5** to yield **6**, the acetal group of which can be cleaved with acids. Using bases an ylide is released again. This reacts via intramolecular Wittig reaction to give cyclic α,β-unsaturated nitriles **7**.
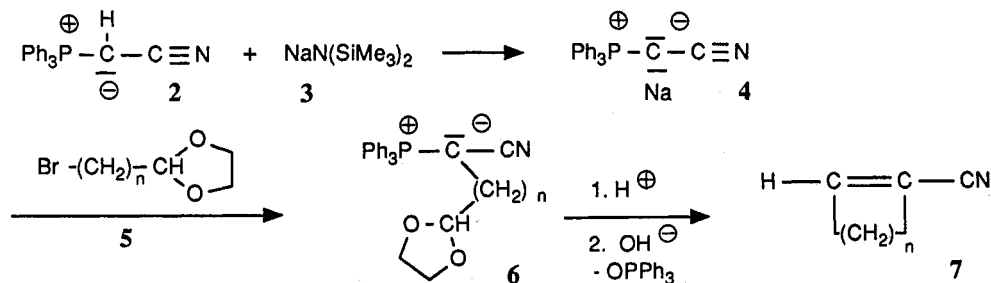


The σ-donor character of the trimethylsilyl group effects a stabilization of the sylilated ylides **8** (3,4,5). They react with carboxylic acid trimethylsilyl ester **9** by formation of the acyl ylides **10** and siloxane **11** (5). With cyclic anhydrides **12** the bis-acyl ylides **13** (5) are obtained with 2 mols of **8**. These can undergo different ring-closure reactions. Thus, from **13** the cyclic α,β-unsaturated ketones **14** are obtained by hydrolysis (6).
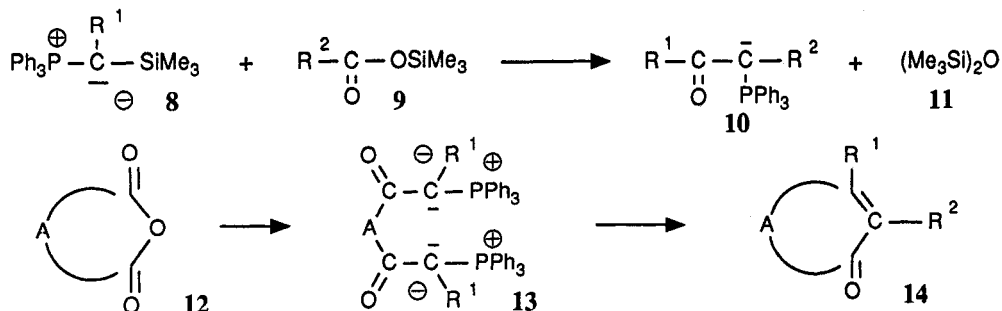


The bis-trimethylsilylated ylide **15** (5,7) reacts with carboxylic acid **16** first to the salt **17**, the carboxylate anion of which attacks a trimethylsilyl group by formation of a trimethylsilyl ester **9** and the silylated ylide **18**. Both react together, as already mentioned, to give the acyl ylide **19** and siloxane **11**. With this method it is possible to substitute the OH-group in free carboxylic acids by the ylide function in a one-pot reaction.

$$Me_3Si\text{-}\underset{Me_3Si}{\overset{\ominus}{C}}\text{-}PPh_3^{\oplus} \quad + \quad R\text{-}\underset{O}{\overset{||}{C}}\text{-}OH \quad \longrightarrow \quad \left[ R\text{-}\underset{O}{\overset{||}{C}}\text{-}\underline{O}| \right]^{\ominus} \left[ Me_3Si\text{-}\underset{Me_3Si}{HC}\text{-}PPh_3^{\oplus} \right]$$

$$\mathbf{15} \qquad\qquad \mathbf{16} \qquad\qquad\qquad\qquad\qquad\qquad \mathbf{17}$$

$$\longrightarrow \quad R\text{-}\underset{O}{\overset{||}{C}}\text{-}OSiMe_3 \quad + \quad \underset{H}{\overset{Me_3Si}{|\overset{\oplus}{C}}}\text{-}PPh_3 \quad \longrightarrow \quad R\text{-}\underset{O}{\overset{\ominus}{C}}\text{-}\overset{H}{\underset{PPh_3}{C}}^{\oplus} \quad + \quad \mathbf{11}$$

$$\mathbf{9} \qquad\qquad\qquad \mathbf{18} \qquad\qquad\qquad\qquad \mathbf{19}$$

The oxidation of the ylide **15** with the adduct from ozone and triphenyl phosphite **20** gives rise to the formation of the bis-trimethylsilyl ketone **21**, beside triphenyl phosphane oxide **22** and triphenyl phosphate **23** (9). **21** possesses highly interesting spectroscopic properties and reacts in various ways. With isonitriles **24**, it gives e. g. ketene imines of type **26**. Intermediate **25**, which is converted subsequently by Brook-rearrangement (10) to **26**, is postulated (11).

$$Me_3Si\text{-}\underset{Me_3Si}{\overset{\ominus}{\overset{\oplus}{C}}}\text{-}PPh_3 \quad + \quad O_3 \cdot P(OPh)_3 \quad \longrightarrow \quad \underset{Me_3Si}{\overset{Me_3Si}{C}}{=}O \quad + \quad \begin{matrix} OPPh_3 & \mathbf{22} \\ OP(OPh)_3 & \mathbf{23} \end{matrix}$$

$$\mathbf{15} \qquad\qquad\qquad \mathbf{20} \qquad\qquad\qquad \mathbf{21}$$

$$\mathbf{17} \quad + \quad R\text{-}N{\equiv}C \quad \longrightarrow \quad R\text{-}N{\equiv}\overset{\oplus}{C}\text{-}\underset{Me_3Si}{\overset{Me_3Si}{C}}\text{-}\underline{O}|^{\ominus} \quad \longrightarrow \quad R\text{-}N{=}C{=}C\underset{OSiMe_3}{\overset{SiMe_3}{}}$$

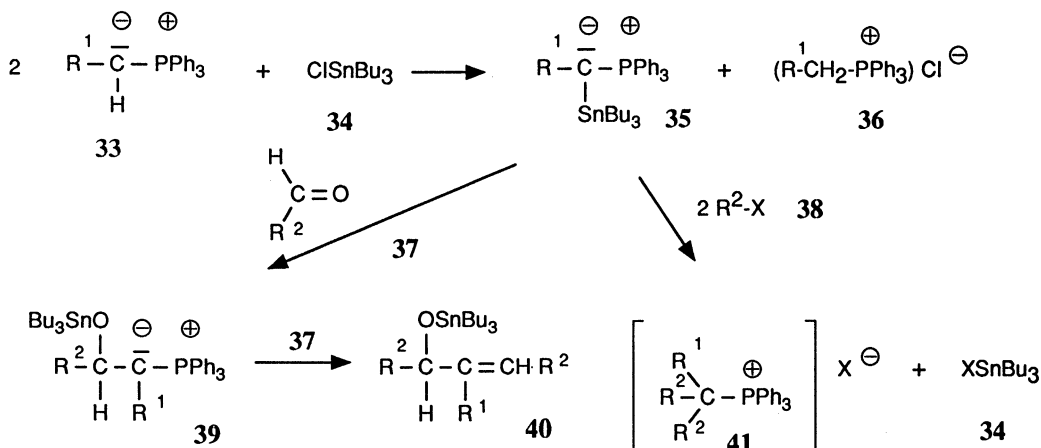$$\mathbf{24} \qquad\qquad\qquad \mathbf{25} \qquad\qquad\qquad\qquad \mathbf{26}$$
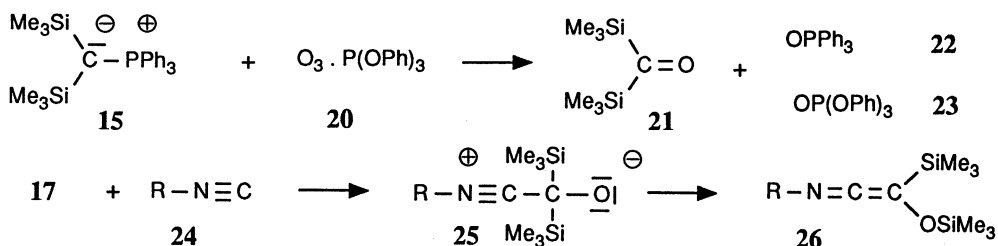
As shown in the introduction, one may expect that the silylated ylide **18** can be converted with sodium (sand) to the sodium compound **27**. This reacts with many halogen compounds, among others also with the titanium compound **28** to **29**. This tris-elementorganic compound **29** does not react with benzoyl chloride **30** at the ylidic C-atom any more, but at titanium. **31** is obtained besides the ester **32**. An X-ray structure analysis of **31** exists which shows unequivocally that the compound is monomeric (12).

$$Ph_3P\text{-}\overset{\oplus}{\underset{H}{C}}\overset{SiMe_3}{|}{}^{\ominus} \quad + \quad Na\,(sand) \quad \longrightarrow \quad Ph_3P\text{-}\overset{SiMe_3}{\underset{Na}{C}|} \quad \xrightarrow{\text{Cl-Ti\,[OCH(CH}_3)_2]_3} $$

$$\mathbf{18} \qquad\qquad\qquad\qquad\qquad\qquad \mathbf{27} \qquad\qquad\qquad\qquad \mathbf{28}$$

$$Ph_3P\text{-}\overset{\oplus}{\underset{Ti[OCH(CH_3)_2]_3}{C}}\overset{SiMe_3}{|}{}^{\ominus} \quad \xrightarrow[\mathbf{30}]{\langle\text{Ph}\rangle\text{-}\overset{O}{\overset{||}{C}}\text{-}Cl} \quad Ph_3P\text{-}\overset{\oplus}{C}{}^{\ominus}\overset{SiMe_3}{\underset{Cl}{\overset{Ti}{\diagup}}}\underset{OCH(CH_3)_2}{\overset{OCH(CH_3)_2}{}} \quad + \quad \langle\text{Ph}\rangle\text{-}\overset{O}{\overset{||}{C}}\text{-}O\text{-}CH(CH_3)_2$$

$$\mathbf{29} \qquad\qquad\qquad\qquad\qquad\qquad \mathbf{31} \qquad\qquad\qquad\qquad\qquad \mathbf{32}$$
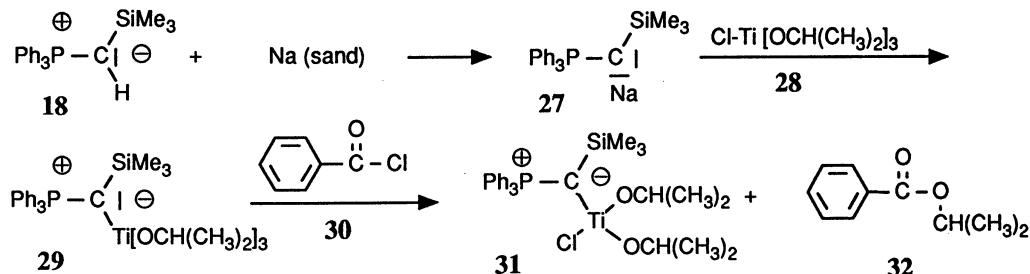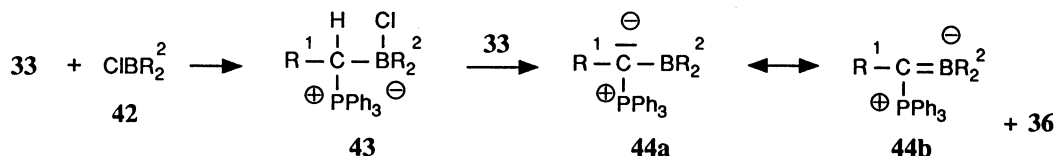
Ylides **35**, which carry a tributylstannyl group, can easily be obtained from 2 mols of ylide **33** and 1 mol tributylstannyl chloride (besides the salt **36**) by trans-ylidation. The bis-elementorganic compound **35** reacts with aldehydes **37** first to **39**, which immediately undergoes a Wittig reaction with a second mol **37** to afford **40**.
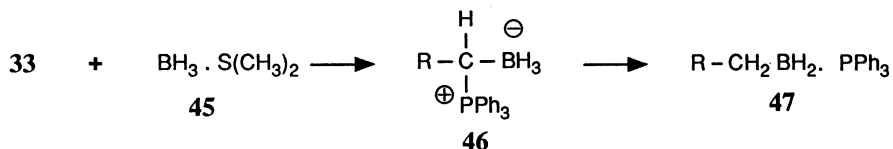
From **35** and alkyl halogenides the phosphonium salts **41** arise. Monoalkylation products could not yet be isolated (13).

$$2 \quad \overset{1}{R}\text{-}\overset{\ominus}{\underset{H}{C}}\text{-}\overset{\oplus}{PPh_3} \quad + \quad ClSnBu_3 \quad \longrightarrow \quad \overset{1}{R}\text{-}\overset{\ominus}{\underset{SnBu_3}{C}}\text{-}\overset{\oplus}{PPh_3} \quad + \quad (R\text{-}CH_2\text{-}PPh_3)^{\oplus}\,Cl^{\ominus}$$

$$\mathbf{33} \qquad\qquad\qquad \mathbf{34} \qquad\qquad\qquad\qquad \mathbf{35} \qquad\qquad\qquad \mathbf{36}$$

$$\underset{R^2}{\overset{H}{C}}{=}O$$

$$\mathbf{37} \qquad\qquad\qquad\qquad 2\,R^2\text{-}X \quad \mathbf{38}$$

$$\overset{Bu_3SnO}{\underset{H}{\overset{|}{R^2\text{-}\overset{2}{C}}}}\text{-}\overset{\ominus}{\underset{R^1}{\overset{\oplus}{C}}}\text{-}PPh_3 \quad \xrightarrow{\mathbf{37}} \quad \overset{OSnBu_3}{\underset{H}{\overset{|}{R^2\text{-}\overset{2}{C}}}}\text{-}\underset{R^1}{C}{=}CH\text{-}R^2 \quad \left[ \overset{R^1}{\underset{R^2}{\overset{2}{R\text{-}C}}}\text{-}\overset{\oplus}{PPh_3} \right]X^{\ominus} \quad + \quad XSnBu_3$$

$$\mathbf{39} \qquad\qquad\qquad\qquad \mathbf{40} \qquad\qquad\qquad\qquad \mathbf{41} \qquad\qquad\qquad \mathbf{34}$$
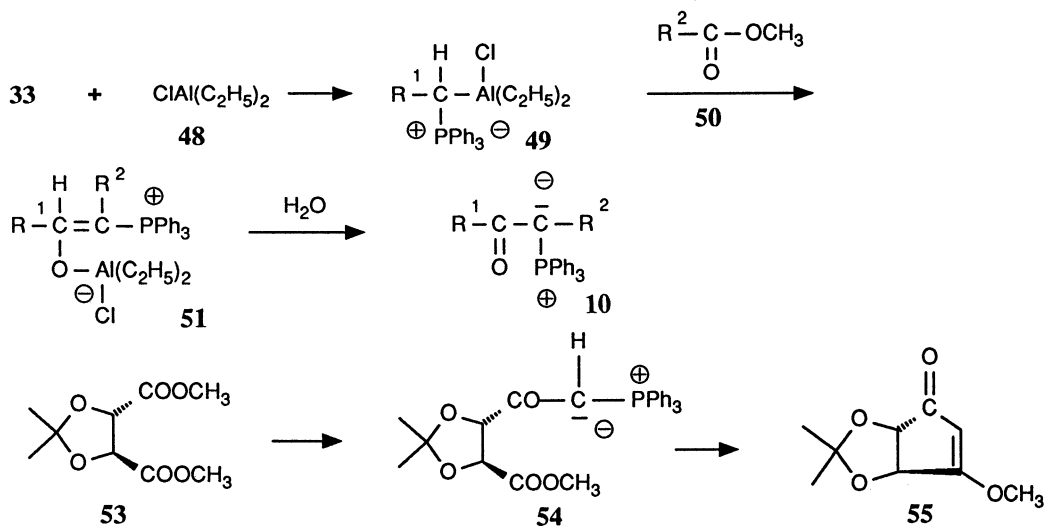
The alkyl chloroboranes **42** react with ylides **33** first under formation of an onium-ate complex **43**, which reacts further with a second mol **33** to yield phosphonium salt **36** and the di-alkylboryl substituted ylide **44**, which can be described by the mesomeric formulation **44a** ↔ **44b**. This is also proven by an X-ray structure analysis for $R^2$ = cyclopentyl, which gives a distance of 1.472 Å of the neighbouring atom to the ylidic C-atom (14,15).

$$33 \ + \ ClBR_2^2 \ \longrightarrow \ \underset{\textbf{43}}{\overset{\overset{\displaystyle H \ \ \ Cl}{|\ \ \ \ |}}{R^1-\underset{\overset{|}{\underset{\oplus}{P}Ph_3}}{\overset{|}{C}}-BR_2^2}} \ \overset{\textbf{33}}{\longrightarrow} \ \underset{\textbf{44a}}{R^1-\underset{\underset{\oplus}{P}Ph_3}{\overset{\ominus}{\underset{|}{C}}}-BR_2^2} \ \longleftrightarrow \ \underset{\textbf{44b}}{R^1-\underset{\underset{\oplus}{P}Ph_3}{\overset{\ominus}{C}}=BR_2^2} \ + \ 36$$

Ylides **33** react with the borane-dimethylsulfide complex **45** to the ate-onium complexes **46**, which rearrange on heating into complexes of monoalkyl boranes and triphenyl phosphanes, which can be applied in hydroboration reactions. With this technique, phoshonium ylides can be easily converted into storable monoalkyl borane complexes, giving a simple transition from "Wittig chemistry" to "Brown chemistry" (16).

$$33 \ + \ BH_3 \cdot S(CH_3)_2 \ \longrightarrow \ \underset{\textbf{46}}{R-\underset{\underset{\oplus}{P}Ph_3}{\overset{\overset{H}{|}}{\underset{|}{C}}}-\overset{\ominus}{B}H_3} \ \longrightarrow \ \underset{\textbf{47}}{R-CH_2 BH_2 \cdot PPh_3}$$

Adducts **49** are formed from the ylides **33** and diethylaluminium chloride. They react with carboxylic esters **50** to the complexes **51**, for which X-ray structure analyses exist. The hydrolysis of **51** gives the acyl ylides **10**. According to this route, the acyl ylide **54** and also the corresponding bis-acyl ylide can easily be prepared from the acetonide of dimethyl tartrate (17). **54** undergoes an intramolecular Wittig reaction to **55** by epimerization. This represents a valuable synthon for the preparation of natural products, among others of carbocyclic nucleotides (18).

$$33 \ + \ ClAl(C_2H_5)_2 \ \longrightarrow \ \underset{\textbf{49}}{R-\underset{\underset{\oplus}{P}Ph_3}{\overset{\overset{H \ \ \ Cl}{|\ \ \ \ |}}{C}}-Al(C_2H_5)_2} \ \xrightarrow[\textbf{50}]{R^2-\overset{O}{\overset{||}{C}}-OCH_3}$$

**53** → **54** → **55**

As we have seen, acyl ylides **19** can easily be prepared from carboxylic acids or their derivatives. When these are reacted with triflate anhydride **46**, the triflate phosphonium salts **57** are formed, from which with triethyl amine **50** the acetylene phosphonium salts **59** are obtained in excellent yields. They are converted to the terminal acetylenes **60** by treating them with aqueous bases or with sodium amalgam or by electrolysis . This opens a relative simple preparative method to transform carboxylic acids **16** via **19** and **57** into acetylenes **60** (19).
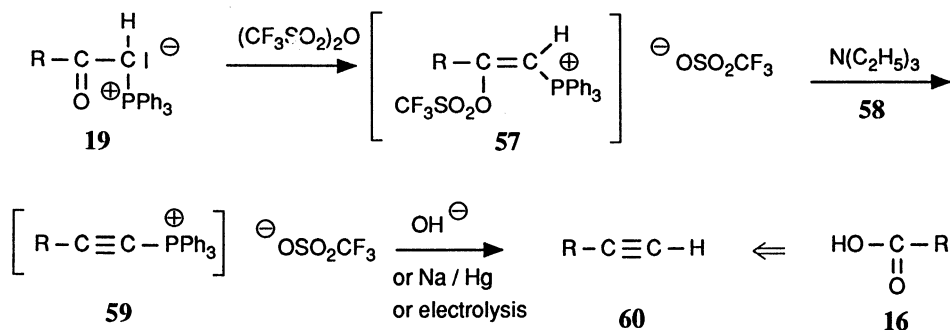
Hexaphenyl carbodiphosphorane **61** can be interpreted as a complex of two donor molecules (triphenyl phosphane) and an excited "naked" C-atom. Simple considerations lead one to expect that a $C_2$-molecule should be stabilized by a donor molecule at the one and an acceptor molecule at the other C-atom, as e. g. **62**. The $C_3$-molecule should be stabilized analogously by two donor groups at $C_1$ and $C_3$ (**63**), and $C_4$ again by a phosphane at $C_1$ and a borane at $C_4$ (**64**).
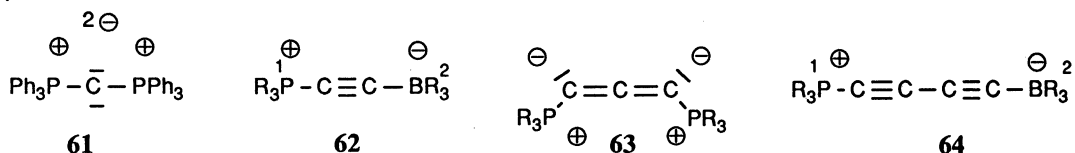


We were able to verify this concept as follows: the phosphane **65** was reacted with BuLi and subsequently with triphenyl borane to an ate-complex **66**, which afforded **67** with methyl iodide. An X-ray structure analysis of **67** could be performed (20). In an analogous way, we also obtained the stablized $C_4$ **69**, from which also an X-ray structure analysis is present (21).
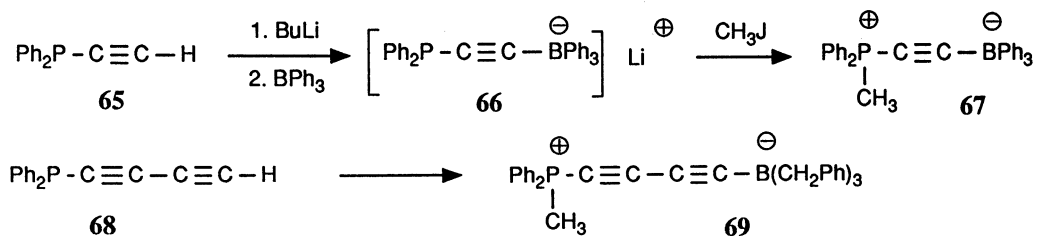


The preparation of the new cummulated bisylide **73** as a stabilized $C_3$-molecule succeeded in the following way: the bis-ylide **70** was transformed into the allenyl bis-phosphonium salt **71** with triflate anhydride. It was then deprotonated with sodium hexamethyl disilazane **3** giving **73** (22).
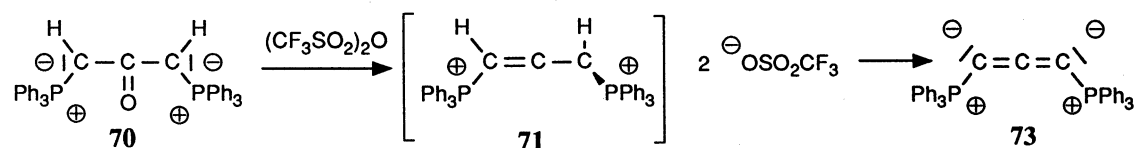
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