Alkylidenephosphines and Diphosphetanes

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In studies of the reactivity and thermal stability of various alkylidenephosphines prepared from benzophenone and organylbis(trimethylsilyl)phosphines via a NaOH-catalyzed elimination of hexamethyldisiloxane (eq. 1a), detailed analy-

$$R_{R}^{1} C=E + \frac{(H_{3}C)_{3}Si}{x}P-R \xrightarrow{-(H_{3}C)_{3}Si-E-X} R_{R}^{1} C=P^{R}$$
 (eq. 1)

eq. 1a:
$$R^1 = H_5C_6$$
; E= O; X= $(H_3C)_3Si$
eq. 1b: $R^1 = (H_3C)_3C$; E= S; X= Li.2THF

ses of nmr-spectra and x-ray structure determinations prove the methyl derivative <u>1a</u> to dimerize to an 1,3-diphosphetane (<u>2a</u>), whereas from the iso-propyl compound <u>1b</u> the 1,2-diphosphetane <u>2b</u> is obtained [1]. This observation confirms our hypothesis that the formation of 1,2- or 1,3-diphosphetanes is determined by the steric requirements of the substituent at phosphorus.

Alkylidenephosphines with two bulky substituents at the carbon atom of the P=C moiety as e.g. two tert-butyl groups remain monomeric. These compounds are readily prepared from di(tert-butyl)thicketone and a lithium organyltrimethyl-silylphosphide (eq. 1b). With lithium bis(trimethylsilyl)phosphide a mixture of [di(tert-butyl)methylidene]trimethylsilylphosphine (3), tris(trimethylsilyl)-phosphine, and the structurally characterized 2,3-diphospha-1,3-butadiene 4 is obtained.

$$(H_{3}C)_{3}Si_{P=C} (CH_{3})_{3} (H_{3}C)_{3}C (H_{3}C)_{3}C (H_{3}C)_{3}C (H_{3}C)_{3}C (H_{3}C)_{3}C (H_{3}C)_{3}C (H_{3}C)_{3} (H_{3}C)_{3}C (H_{3}C$$

Treatment of compound $\underline{3}$ with methanol yields di(tert-butyl)methylidenephosphine $\underline{5}$ which dimerizes via a P-H addition of one molecule to the P=C group of a second one.

[1] G. Becker, B. Becker, W. Becker: Z. anorg. allg. Chem., in press.