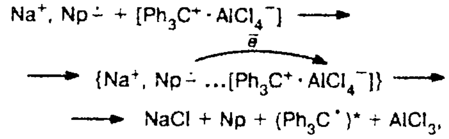
Based on the results obtained, we propose the following scheme of CL excitation:



$$\mathrm{Na^+, Np^{\dot{-}} + [Ph_3C^+\cdot AlCl_4^-] \longrightarrow \{Na^+, Np^{\dot{-}} \ldots [Ph_3C^+\cdot AlCl_4^-]\} \longrightarrow NaCl + Np + (Ph_3C^{\cdot})^* + AlCl_3,} \quad (1)$$

$$\mathrm{(Ph_3C^{\cdot})^* \longrightarrow Ph_3C^{\cdot}} + h\nu, \quad (2)$$

$$\mathrm{Ph_3C^{\cdot} \longrightarrow Unidentified\ products.} \quad (3)$$

The estimation of the heat effects calculated from the balance of the electrochemical redox potentials shows that the energy released at the primary stage of electron transfer (1) (ΔH = 3.26 eV) is quite enough for the formation of $(Ph_3C^{\cdot})^*$ (2.37 eV).

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A new method for the synthesis of α,β-acetylenic phosphines

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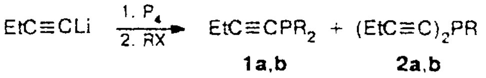
The reaction of alkali metal acetylenides with diorganylchlorophosphines is normally used to create the C_{sp}—P bond.[1] Using but-1-ynyllithium as an example, we have shown for the first time that alkynylphosphines can be obtained by the consecutive treatment of yellow phosphorus with lithium acetylenide and alkyl halide in THF. The reaction likely proceeds *via* the initial formation of but-1-ynylphosphide and di(but-1-ynyl)phosphide anions and results in a mixture of but-1-ynyldialkyl- (**1a,b**) and alkyldi(but-1-ynyl)phosphines (**2a,b**) (~1 : 1) in an overall yield of up to 20% (not optimized).



$$\mathrm{EtC{\equiv}CLi \xrightarrow[2.\ RX]{1.\ P_4} \underset{\mathbf{1a,b}}{EtC{\equiv}CPR_2} + \underset{\mathbf{2a,b}}{(EtC{\equiv}C)_2PR}}$$

R = Et (**a**); Pr (**b**); X = Br, Cl

But-1-ynyldiethylphosphine (1a) and di(but-1-ynyl)ethylphosphine (2a). But-1-yne (22 g, 0.41 mmol) was added to a 1.6 *M* solution (250 mL) of Bu^nLi in hexane. The but-1-ynyllithium that formed was added to a suspension of yellow phosphorus (3.1 g, 0.1 mol) in HMPTA (50 mL) and THF (150 mL). The reaction mixture was stirred for 1 h at 45—50 °C and cooled to –20 °C. Ethyl bromide (54.5 g, 0.5 mol) was added over 2 h. The mixture was stirred for 30 min, and a 10% aqueous solution of NH_4Cl (250 mL) was added. The organic layer was separated, and the aqueous solution was extracted with ether. Organic extracts were combined, washed with water, and dried with potassium carbonate. The ether was distilled off, and the residue was fractionated *in vacuo*. A product (1.0 g) with b.p. 40—45 °C (0.3 Torr) was obtained that contained, according to the GLC and GLC-MS data, 86% but-1-ynyldiethylphosphine (**1a**) and 11% di(but-1-ynyl)ethylphosphine (**2a**), as well as a product (2.5 g) with b.p. 50—70 °C (0.3 Torr) containing 10% phosphine **1a** and 72% phosphine **2a**. The yield of phosphine **1a** was 8% (1.1 g), and that of phosphine **2a** was 12% (1.9 g). GLC-MS, *m/z* (I_{rel} (%)): **1a**: 142 $[M]^+$ (100), 114 (44), 99 (20), 97 (14), 85 (84), 84 (13), 83 (53), 79 (14), 71 (29), 57 (43); **2a**: 166 $[M]^+$ (100), 137 (65), 109 (29), 97 (19), 95 (13), 91 (18), 83 (20), 77 (14), 57 (23). ^{1}H; ^{13}C; and ^{31}P NMR of the mixture of phosphines **1a** and **2a** ($CDCl_3$), δ: 2.32—2.24 (dq, $CH_2C{\equiv}C$, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,P}$ = 1.4 Hz); 1.72—1.51 (m, CH_2P); 1.25—0.98 (m, Me); 108.0 (RC≡); 73.3 (≡CP); 21.9, 19.3, 13.5; −39.0 (P) for phosphine **1a** and −61.4 (P) for phosphine **2a**. IR, ν/cm^{-1}: 2190 (νC≡C).

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But-1-ynyldipropylphosphine (1b) and di(but-1-ynyl)-propylphosphine (2b) were obtained in yields of 10% and 8%, respectively, by the procedure presented above using propyl chloride (instead of ethyl bromide). GLC-MS, *m/z* (I_{rel} (%)): **1b**: 170 $[M]^+$ (57), 155 (58), 128 (98), 127 (58), 100 (100), 99 (54), 86 (52), 85 (79), 83 (55), 57 (54); **2b**: 180 $[M]^+$ (100), 165 (89), 137 (77), 123 (54), 109 (65), 97 (54), 91 (53), 85 (59), 83 (77), 57 (79). ^{1}H; ^{13}C; and ^{31}P NMR of the mixture of phosphines **1b** and **2b**, δ: 2.31—2.23 (dq, $CH_2C{\equiv}C$); 1.65—1.44 (m, CH_2CH_2P); 1.71—1.10 (m, Me of $EtC{\equiv}C$ fragment); 1.04—0.97 (t, Me in Pr radical); 107.3 ($RC{\equiv}$); 73.1 (${\equiv}CP$); 29.7, 19.3, 15.7, 13.8; −48.5 (P) for phosphine **1b** and −66.7 (P) for phosphine **2b**. IR, ν/cm^{-1} 2190 ($\nu C{\equiv}C$).

GLC-mass spectra were recorded on an LKB-2091/152 GLC-mass spectrometer. NMR spectra were recorded in $CDCl_3$ on a Bruker AC 300 spectrometer. IR spectra were obtained on a Specord IR-75 spectrometer. The ratio of phosphines **1** and **2** in the mixture was determined by GLC on a Varian 3400 chromatograph.

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Crown compounds for anions. Binding of borohydride anions by cyclic trimeric perfluoro-*o*-phenylenemercury

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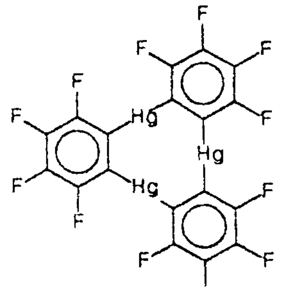
It is known that cyclic trimeric perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ (**1**) containing three mercury atoms in the planar nine-membered cycle[1] reacts readily with halide anions to form complexes. In the case of Br^- and I^-, the complexes isolated in the solid state have a 1 : 1 composition and, according to the X-ray diffraction analysis data, are polymeric multideck sandwiches $\{[(o\text{-}C_6F_4Hg)_3]X_n\}^{n-}$ (X = Br, I) in which each halide anion is symmetrically coordinated with six mercury atoms of two adjacent molecules of the macrocycle.[2,3] Complex **1** with the thiocyanate anion (1 : 1), described previously,[4] has a similar polymeric structure. In this complex, the SCN^- ions are coordinated with the mercury atoms through the sulfur atom. In this work, we report on the ability of macrocycle **1** to bind efficiently borohydride anions to form complexes, whose composition depends on the ratio of the reagents.



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Experiments were carried out at −20 °C in an atmosphere of Ar by gradual addition of **1** to a solution of $Bu_4N^+BH_4^-$ in THF. The course of the reaction was monitored by IR spectroscopy. As compound **1** was added, the band of the νBH vibrations of the free BH_4^-

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