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). ^1H; ^{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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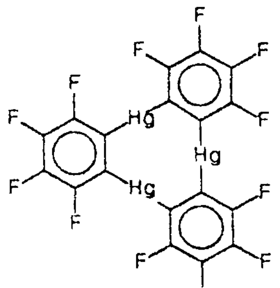
It is known that cyclic trimeric perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ (**1**) containing three mercury atoms in the planar nine-membered cycle[1] reacts readily with halide anions to form complexes. In the case of Br^- and I^-, the complexes isolated in the solid state have a 1 : 1 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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ion (2201 cm^{-1}) in the IR spectrum disappeared gradually, and new bands corresponding to the complexes $\{[(o\text{-}C_6F_4Hg)_3](BH_4)_2\}^{2-}$ (**2**) and $\{[(o\text{-}C_6F_4Hg)_3]_2(BH_4)\}^{-}$ (**3**) appeared. The composition of the complexes was established by the methods of molar ratios and isomolar series[5] from the IR spectra. The formation of a complex of **1** with $Bu_4N^+BH_4^-$ was also monitored by the NMR spectra.

Complex **2** contains two BH_4^- anions per molecule of the macrocycle (**1**) and is formed when an excess of BH_4^- with respect to **1** is used. The IR spectra of **2** in a THF solution are characterized by the bands of the stretching vibrations of the terminal and bridge BH bands (at 2300 and 2035 cm^{-1}) shifting relative to the band of the free BH_4^- ion to the high- and low-frequency regions, respectively. The ^{199}Hg NMR spectrum of a solution of **2** in THF at 200 K contains a signal at −13 ppm (from Ph_2Hg as external standard), which is strongly shifted relative to the signal of the initial compound **1** (−341 ppm). The $^{11}B\{^1H\}$ NMR spectrum of compound **2** at 200 K exhibits signals at −38 and −30 ppm assigned to the free and coordinated BH_4^- anions, respectively. The stability constant of **2** determined by the method of molar ratios is equal to 10^4 L^2 mol^{-2}, *i.e.*, the complex is quite stable.

Another complex **3** is formed at excess of **1** with respect to BH_4^- and, unlike **2**, contains only bridge BH bonds (νBH = 2129 and 2057 cm^{-1}). The ^{199}Hg NMR spectrum of compound **3** in THF at 200 K contains a signal at −154 ppm, while in its ^{1}H NMR spectrum a broad signal of the coordinated BH_4^- anion is observed at 4.5 ppm. No signal of the free BH_4^- ion (−0.1 ppm) is observed in the ^{1}H NMR spectrum of complex **3**. Complex **3** is even more stable than complex **2**: its stability constant is equal to 10^7 L^2 mol^{-2}.

The IR spectra of the solid films of complexes **2** and **3** on the CaF_2 and KBr supports contain the same νBH bands as the spectra of the solutions.

Binding of the BH_4^- anions with the mercury atoms in both complexes likely occurs due to the formation of the B—H—Hg bridges. A similar type of binding has been described previously[6] for the complex of the *o*-carboranylmercury macrocycle $(B_{10}Et_8H_2C_2Hg)_4$ with two *closo*-$[B_{10}H_{10}]^{2-}$ dianions. The observed reaction of **1** with $Bu_4N^+BH_4^-$ is the first example of the formation of complexes of borohydride anions with polymercury-containing macrocycles.

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