2-[Tris(dimethylamino)phosphonio]-1-phosphaethyne Tetraphenylborate, a Phosphonio-substituted Phosphaalkyne

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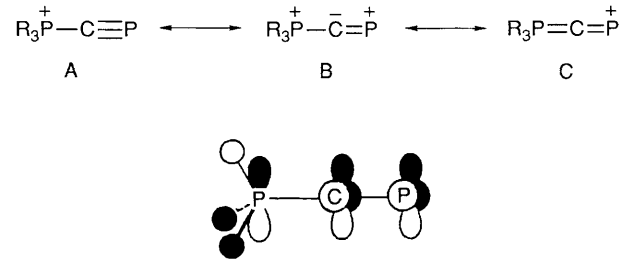
The reaction of [(dichlorophosphino)methyl]tris(dimethylamino)phosphonium tetraphenylborate **5** with an excess of 1,4-diazobicyclo[2.2.2]octane (DABCO) yields the new phosphonio-substituted phosphaalkyne, $[(Me_2N)_3P{-}C{\equiv}P)^+BPh_4^-$ **6**, which is trapped by secondary amines, phenols and mesityl azide.

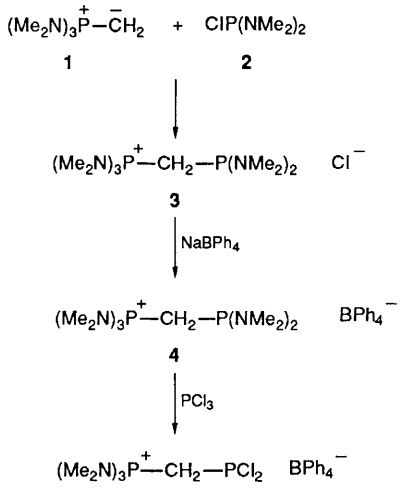
Recently we have reported on the synthesis and reactivity of 2-phosphonio-1-phosphaalkenes[1] (phosphavinylphosphonium salts) and a phosphonioiminophosphane.[2] In these compounds a phosphonium ion and a phosphenium ion formally compete for the electron density on the linking carbon atom. First results indicate an enhanced reactivity in [4+ 2] cycloadditions[1] and a crossing of the frontier orbitals[2,3] due to the strong electron withdrawing capability of the phosphonio group.[4] As a result of these studies we have become interested in the synthesis of a comparable functionalized phosphaalkyne.[5]

A qualitative picture of the bonding situation is outlined in Scheme 1. The π* orbital of the phosphonio group interacts with the p orbitals at the bridging carbon atom (negative hyperconjugation[4,6]) while these combine with the p orbitals at the low coordinated phosphorus atom in the usual manner to form (p–p)π bonds. Consequently, the bonding in a phosphonio-substituted phosphaalkyne may be expressed by the resonance forms *A*, *B* and *C* and their contribution to the electronic ground state of the molecule should be reflected in the reactivity.

The preparation of the phosphonium salt **5** is straightforward† and finds parallels in the literature[7] (Scheme 2). However, to our surprise the synthesis is restricted. It is impossible to change the amino group (*i.e.* NEt_2 or piperidine instead of NMe_2) or the counteranion (*i.e.* BF_4^- or PF_6^- instead of BPh_4^-). In every experiment an inseparable mixture of products has been obtained. Addition of an excess of DABCO or trimethylamine to **5** at −78 °C in methylene chloride, tetrahydrofuran or acetonitrile as solvent leads to a yellow suspension after warming up to room temperature. The ^{31}P NMR spectrum (in CD_2Cl_2) shows only two doublets centred at δ 57.4 and 190.3 with a coupling constant of 197.5 Hz (δ 60.1 and 196.8 in CD_3CN). Unfortunately, it is impossible to isolate the phosphaalkyne **6** (Scheme 3). The compound aggregates to yet unknown oligomers. The assumed structure of **6** on the basis of spectroscopic data‡ is supported by IGLO calculations[8] on $H_3P{-}C{\equiv}P^+$ **7**. Geometry optimization of **7** at the SCF level§ yields the following parameters: C≡P 1.511 Å; C–P 1.719 Å; P–H 1.394 Å; CPH 111.6°. The phosphorus carbon triple bond length in **7** is in good agreement with those calculated[10] or observed[11] before. For this structure the ^{31}P NMR chemical shifts are calculated to be δ 196 (C≡P) and δ −120 (PH_3) by means of the IGLO method;¶ the value of the ^{13}C NMR shift for the alkyne carbon is δ 105. Taking the solvent dependence of ^{31}P NMR shifts into



Scheme 1



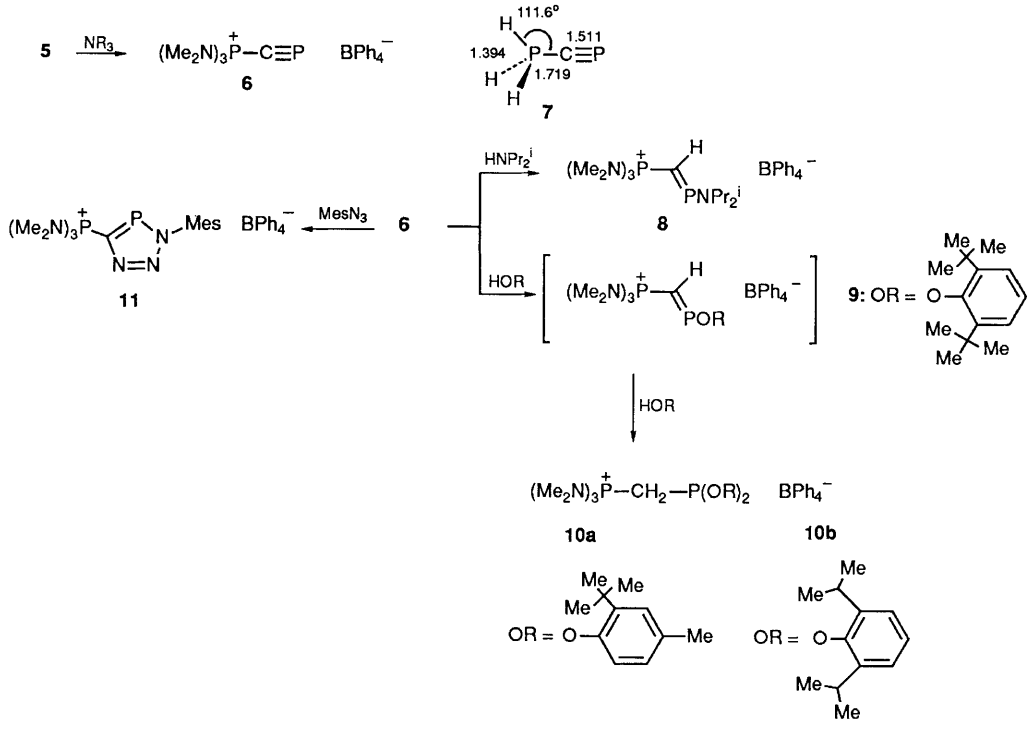
Scheme 2

† *Preparation of* **5**: A solution of tris(dimethylamino)phosphoranylidenemethane **1** in toluene (200 ml) was prepared according to the sodium amide procedure[14] from tris(dimethylamino)methylphosphonium bromide (12.9 g, 0.05 mol). This solution was slowly added to chlorobis(dimethylamino)phosphane (9.27 g, 0.06 mol) in toluene (50 ml) at −78 °C. After warming to room temp. the reaction mixture was dried in vacuum at 60 °C and the resulting [bis(dimethylamino)phosphanylmethyl]tris(dimethylamino)phosphonium bromide **3** was used without further purification. It was dissolved in methylene chloride (200 ml) and sodium tetraphenylborate (17.1 g, 0.05 mol) was added. The suspension was stirred for about 0.5 h at room temp. and then filtered. To the slightly yellow solution PCl_3 (17.17 g, 0.125 mol) was added and the reaction mixture refluxed for 1 h. After several minutes **5** started to precipitate. After cooling to room temp. the white solid was collected by filtration and dried in vacuum (21.52 g, 0.036 mol), 72% yield, m.p. 166 °C; ^1H NMR ($CDCl_3$): δ 2.73 (d, $^3J_{PH}$ 10.5 Hz, 18 H, Me), 3.84 (dd, $J_{P^{III}H}$ 11.2 Hz, $J_{P^{V}H}$ 15.7 Hz, 2 H, CH_2), 6.83–7.37 (m, 20 H, Ar H); ^{31}P NMR (referenced to H_3PO_4) ($CDCl_3$): δ 52.2 (d, $^2J_{PP}$ 51.3 Hz, $PNMe_2$), 174.3 (d, $^2J_{PP}$ 51.3 Hz, PCl_2).

‡ **6**: ^1H NMR (CD_2Cl_2): δ 2.55 (d, $^3J_{PH}$ 10.0 Hz, 18 H, Me), 6.78–7.35 (m, 20 H, Ar H); ^{13}C NMR (CD_2Cl_2): δ 36.6 (s, CH_3), 121.6, 125.4, 135.0 (s, *o*-C, *m*-C, *p*-C, Ar C, BPh_4^-), 163.3 (q, $^1J_{BC}$ 49.2 Hz, *ipso*-C, BPh_4^-), 163.3 (q, $^1J_{BC}$ 49.2 Hz, *ipso*-C, BPh_4^-). ^{11}B NMR (referenced to $BF_3{\cdot}OEt_2$) (CD_2Cl_2): δ −6.4 (s, BPh_4^-).

§ Basis set: double zeta augmented with one set of d functions on phosphorus and carbon and one set of p functions on hydrogen. The program package described in ref. 9 was used.

¶ Basis set: triple zeta augmented with two sets of d functions on phosphorus, one set of d functions on carbon and one set of p functions on hydrogen; this basis set is often referred to as basis II in IGLO calculations.



Scheme 3

account, the IGLO calculation is in excellent agreement with the experiment. All attempts to observe the alkyne carbon in a ^{13}C NMR experiment failed. The ^{31}P NMR shift of **6** exceeds that of $Me_3Si–C{\equiv}P$,[12] which had the most low-field shifted ^{31}P resonance of the known phosphaalkynes (by δ 100) and might be explained by the contribution of resonance forms *B* and *C* to the electronic ground state.

Chemical proof for the assigned structure of **6** is obtained by simple trapping reactions (Scheme 3). Addition of diisopropylamine to **6** yields quantitatively, based on NMR data, the phosphavinyl phosphonium salt **8** {^{31}P NMR: δ 55.1 [d, $^2J_{PP}$ 139.3 Hz, $P(NMe_2)_3$], 298.2 (d, $^2J_{PP}$ 139.3 Hz, $PNPr^i_2$)}. Note that phosphaalkynes do not usually react with amines and the observation of 1,2-addition indicates the activation of the phosphorus–carbon triple bond by the tris(dimethylamino)-phosphonium group. When 2,6-di-(*tert*-butyl)phenol is added, the mono adduct **9** can be observed by NMR spectroscopy {^{31}P NMR: δ 43.9 [d, $^2J_{PP}$ 102.6 Hz, $P(NMe_2)_3$], 361.2 (d, $^2J_{PP}$ 102.64 Hz, POR)}. However, it is unstable and decomposes to a mixture of unidentified products. The sterically less demanding phenols 2-*tert*-butyl-4-methylphenol and 2,6-diisopropylphenol add twice and the phosphonium salts **10a** {^{31}P NMR (CD_2Cl_2): δ 54.17 [d, $^2J_{PP}$ 55.0 Hz, $P(NMe_2)_3$], 157.4 [d, $^2J_{PP}$ 55.0 Hz, $P(OR)_2$]} and **10b** {^{31}P NMR (CD_2Cl_2): δ 53.7 [d, $^2J_{PP}$ 24.4 Hz, $P(NMe_2)_3$], 179.4 [d, $^2J_{PP}$ 24.4 Hz, $P(OR)_2$]} are isolated. Finally, regioselective [2 + 3] cycloaddition with mesityl azide yields the phosphonio-substituted 1,2,3,4-triazaphosphole **11**, which is characterized by NMR spectroscopy.‖ In general cycloadditions with azides serve as experimental proof for phosphaalkynes.[13]

‖ **11**: ^1H NMR ($CDCl_3$): δ 1.85 (s, 6 H, *o*-Me-mesityl), 2.26 (s, 3 H, *p*-Me-mesityl), 2.45 (d, $^3J_{PH}$ 10.5 Hz, NCH_3), 6.71–7.44 (m, 22 H, Ar H); ^{31}P NMR ($CDCl_3$): δ 42.1 (d, $^2J_{PP}$ 66 Hz, $PNMe_2$), 218.8 (d, $^2J_{PP}$ 66 Hz, P_{ring}); ^{13}C NMR ($CDCl_3$): δ 17.2 (d, $^4J_{PC}$ 1.15 Hz, *o*-Me-mesityl), 20.6 (s, *p*-Me-mesityl), 36.4 (dd, $^3J_{PC}$ 4.2 Hz, $^4J_{PC}$ 2.5 Hz, NCH_3), 121.3 (s, CH-BPh_4^-), 125.0 (s, CH-BPh_4^-), 129.1 (s, *m*-CH-mesityl), 133.4 (d, $^2J_{PC}$ 7.06 Hz, *ipso*-C-mesityl), 133.8 (d, $^3J_{PC}$ 2.3 Hz, *o*-C-mesityl), 140.2 (s, *p*-C-mesityl), 163.3 (q, $^1J_{BC}$ 49.2 Hz, *ipso*-C, BPh_4^-), 164.6 (dd, $^1J_{P^{V}C}$ 99.2 Hz, $^1J_{P^{III}C}$ 50.4 Hz, $C_{phosphole}$).

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