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Preparation of Linear Phosphorus Compound Containing Two Hypervalent Centers. Acetylene-bis[triphenyl(phenylethynyl)phosphorane]

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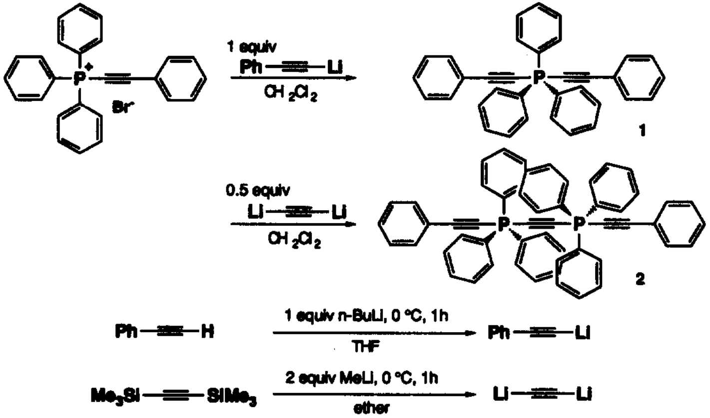
Abstract: A new linear acetylide-connected bis-phosphorane, acetylene-bis[triphenyl(phenylethynyl)phosphorane] (2) was synthesized in the reaction of triphenyl(phenylethynyl)phosphonium bromide with dilithioacetylide. Triphenylbis(phenylethynyl)phosphorane (1) was also prepared by a similar treatment of triphenyl(phenylethynyl)phosphonium bromide with lithium phenylacetylide.

Recently, much attention has been focused on preparation, structure, and reactivity of hypervalent organopnictogen compounds bound to aryl ligands.[2,3] However, there are a few reports on the preparation and reaction of hypervalent organopnictogen compounds containing ethynyl groups.[4,5] We report here the first preparation and characterization of acetylide-connected bis-phosphorane, acetylene-bis[phenylethynyl-(triphenyl)phosphorane] (2), together with triphenylbis(phenylethynyl)phosphorane (1).[6]

Phosphorane 2 was synthesized as follows (Scheme 1). To a stirred solution of triphenyl(phenylethynyl)-phosphonium bromide[7] (443 mg, 1.0 mmol) in anhydrous dichloromethane (2 mL) was added 0.18M dilithioacetylide (2.8 mL, 0.5 mmol) in anhydrous ether at -78 °C under an argon atmosphere. After stirring for 3h at -78 °C the mixture was treated with anhydrous ether (5 mL) at -78 °C. Insoluble precipitate was separated at -20 °C and a trace amount of solvent in the precipitate was removed under reduced pressure at 0 °C. Recrystallization from anhydrous ether under an argon atmosphere gave pure phosphorane 2 in 85% yield.[8]



Scheme 1

Phosphorane **1** was also prepared from the same phosphonium bromide with an equimolar amount of lithium phenylacetylide under a similar condition to that described above in 88% yield.[8] These two new phosphoranes are quite unstable to moisture and react readily with water to afford phenylacetylene, triphenylphosphine oxide, and complex mixtures of high molecular weight compounds. Thermolysis of these phosphoranes at 60 °C without solvent under an argon atmosphere gave diphenylbutadiyne (in the case of phosphorane **1**), triphenylphosphine, triphenyl-phosphine oxide, and complex mixtures of high molecular weight compounds, as well as antimony.[4] Further studies on stability, reactivity, and structure of these acetylide-connected phosphoranes are in progress

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8. Phosphorane **1**: milky crystals; mp 45-65 °C (decomp); ^1H NMR (500 MHz, CD_2Cl_2) δ 7.09-7.11 (m, 4H, 3,5-CPh), 7.16-7.22 (m, 6H, 2,4,6-CPh), 7.51-7.56 (m, 9H, 3,4,5-PPh), 8.19 (d, J_{PCCH}=17.8 Hz, 6H, 2,6-PPh); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 98.2 (d, J=16.6 Hz), 112.1 (d, J=41.5 Hz), 124.3, 127.4 (d, J=16.2 Hz), 127.7, 128.4, 130.2, 130.9, 131.4 (d, J=12.5 Hz), 142.0 (d, J=173.0 Hz); ^{31}P NMR (109 MHz, CD_2Cl_2) δ -120.4 (sept., J_{PCCH}=17.8 Hz); CI-MS *m/z* 465 (MH^+), 464 (M^+). Anal. calcd for $C_{34}H_{25}P$: C, 87.91; H, 5.42%. Found: C, 87.89, H, 5.45%. Phosphorane **2**: brown crystals; mp 43-58 °C (decomp); ^1H NMR (500 MHz, THF-d_8) δ 6.99-7.04 (m, 4H, 3,5-CPh), 7.09-7.13 (m, 6H, 2,4,6-CPh), 7.42-7.50 (m, 9H, 3,4,5-PPh), 8.22 (dd, J_{PCCH}=18.4 Hz, J=6.0 Hz, 12H, 2,6-PPh); ^{13}C NMR (125 MHz, THF-d_8) δ 98.6 (d, J=13.4 Hz), 103.3 (d, J=15.6 Hz), 112.5 (d, J=39.2 Hz), 127.9 128.5 (d, J=17.6 Hz), 128.7, 130.6, 131.4, 132.9 (d, J=13.3 Hz), 142.9 (d, J=172.9 Hz); ^{31}P NMR (109 MHz, THF) δ -120.3 (sept., J_{PCCH}=18.4 Hz); CI-MS *m/z* 650 (MH^+-101), 649 (M^+-101). Anal. calcd for $C_{54}H_{40}P_2$: C, 86.38; H, 5.37%. Found: C, 86.57, H, 5.53%. The structure of **2** was also supported by ^1H-^{13}C COSY spectrum.

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