of the glass equilibration tube were stirred for a period of 5 h, as initial studies had established that equilibrium was reached within about 2 h. The tube was then centrifuged, a sample (usually 100–200 μL) of the solution phase was withdrawn, and the absorption spectrum was measured after the sample was diluted with spectroscopic grade *n*-hexane. Absorbance measurements were carried out with a Shimdazu UV-2100 spectrophotometer. The solubility of C_{60} was calculated from the absorbance value at 328 nm. The validity of the Beer–Lambert law was checked by measuring the absorbance of standard solutions of C_{60} in hexane. The extinction coefficient at 328 nm was found to the 51238 $L \cdot mol^{-1} \cdot cm^{-1}$, in agreement with the reported value of 51290 $L \cdot mol \cdot cm^{-1}$.[7]

Chromatographic Separation Experiments. For the separation experiments, an alumina column of 60-mm diameter and 480-mm length was used. A benzene solution of the fullerene mixture was loaded onto alumina in a rotary evaporator. The loaded alumina was transferred to the column, and the fullerenes were eluted with cyclohexane. In some experiments, the fullerene mixture was dissolved in cyclohexane, before being loaded onto the column. The separation achieved in both methods was satisfactory.

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Synthesis of Amino-Containing Phosphines. The Use of Iminophosphorane as a Protecting Group for Primary Amines

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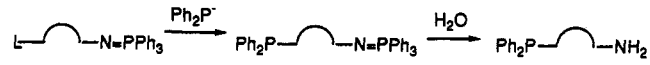
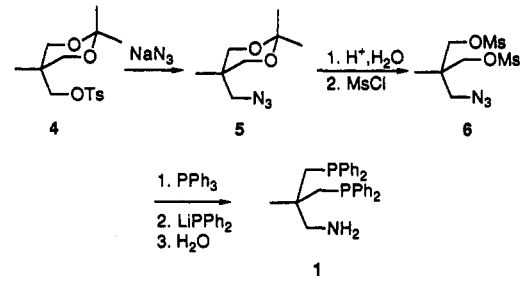
In the design of polydentate phosphines, the incorporation of "mixed" donor atoms for better control over the reactivities of the metal ions has received much attention recently. In this arena the copresence of primary amine and phosphine groups in the same ligand is of particular interest. However, the synthesis of these amino-containing phosphines has proven a challenge to chemists. In this report we describe the synthesis of ligands bearing both primary amine and tertiary phosphine donors.

Tertiary phosphines are readily prepared by the nucleophilic displacement of alkyl halides and sulfonates with R_2P^- anions; the amino group ultimately required, however, cannot be present in the substrate due to the possibility of N-alkylation. While there are many suitable protecting groups available,[1] the lengthy reaction sequence which this route would entail is not appealing. It would be ideal, however, if a simple derivative of the amine could be generated in the synthetic step. At the very least, one step could be deleted from the process. In order for this method to be effective, it is critical that the amino derivative be stable with respect to the phosphide anion and that it degrade readily to the free amine. It occurred to us that an excellent condidate for this role might be iminophosphorane, given that its hydrolytic cleavage behavior is well documented.[2-4] To explore this idea (Scheme I),

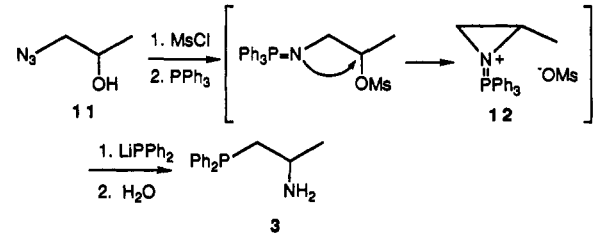
Scheme I



Scheme II



Scheme III



we investigated the synthesis of amino-containing phosphines **1–3**.

The synthesis of **1** is shown in Scheme II. Nucleophilic substitution of **4**[5] by sodium azide in DMF provided **5**. Hydrolysis of **5** in a mixture of THF and water under acidic conditions gave the corresponding diol, which was subsequently converted into mesylate **6** by treatment with mesyl chloride in the presence of triethylamine. Conversion of **6** to aminophosphine **1** was accomplished in a one-pot reaction by the following sequence: (i) formation of iminophosphorane **7** using triphenylphosphine in THF solution, (ii) substitution reaction by lithium diphenylphosphide, (iii) removal of the iminophosphorane protecting group. The desired tripodal phosphine **1** was isolated as a viscous oil (51% yield) by chromatography. The stability of iminophosphorane toward phosphide is evidenced by the formation of species **9**, which was characterized by its spectral data (see Experimental Section).

In analogy to **1**, this process has been successfully applied to the preparation of (3-aminopropyl)diphenylphosphine (**2**)[6] and (2-aminopropyl)diphenylphosphine (**3**) from the corresponding azides 1-azido-3-chloropropane (**10**) and 1-azido-2-propanol (**11**), respectively. The selective formation of **3** can be rationalized by the intervention of aziridine **12**[7] via nucleophilic attack of iminophosphorane at the adjacent carbon (Scheme III) and a subsequent ring

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opening by phosphide at the less substituted position. In fact, the cyclic intermediate 8 was also present when 7 was generated, as evidenced by the spectral data. Besides signals due to the aromatic protons and methyl protons of 8 in the ^{1}H NMR, two sets of doublet of doublet absorptions at δ 4.19 (dd, J = 7.5 Hz, J_{PNCH} = 3.6 Hz, 2 H) and δ 3.67 (dd, J = 7.5 Hz, J_{PNCH} = 2.6 Hz, 2 H), for H and H′, respectively, clearly indicate the formation of the four-membered ring. The downfield shift in the ^{31}P NMR (38.1 ppm) indicates that the phosphorus is being deshielded by the positive charge on the imino salt.

In summary, the use of iminophosphorane as a protecting group for a primary amine function results in a practical, efficient procedure for the preparation of amino-containing phosphines.

Experimental Section

All of the reactions, manipulations, and purification steps involving phosphines were performed under a nitrogen atmosphere. Compounds 4, 10, and 11 were prepared according to methods described previously.[5,8,9]

2-(Azidomethyl)-2-methyl-1,3-propanediol Isopropyl Acetal (5). A mixture of compound 4 (37.71 g, 120 mmol), NaN_3 (23.41 g, 360 mmol) and water (20 mL) in DMF (200 mL) was heated with an oil bath at 100 °C for 40 h. The reaction mixture was poured into water (400 mL) and extracted with ether (100 mL × 3). The organic extracts were combined, dried, and concentrated. The residue was chromatographed on silica (100 g) with elution of ethyl acetate/hexane (1:4). The eluate was collected and concentrated to give 5 as colorless liquid (17.05 g, 75%): ^{1}H NMR δ 3.52 (s, 4 H), 3.42 (s, 2 H), 1.36 (s, 3 H), 1.33 (s, 3 H), 0.76 (s, 3 H).

Anal. Calcd for $C_8H_{15}O_2N_3$: C, 51.88; H, 8.16; N, 22.69. Found: C, 51.84; H, 8.25; N, 23.12.

2,2-Bis[(methanesulfonyloxy)methyl]-1-azidopropane (6). A mixture of compound 5 (2.13 g, 11.4 mmol), water (2 mL), THF (10 mL), and a few drops of HCl was heated to reflux for 1 h. Concentration of the mixture provided a colorless liquid which solidified to yield a white solid (1.65 g). This material was dissolved in a solution of triethylamine (4.5 mL) in dichloromethane (50 mL) with stirring at ice-cooled temperature. Methanesulfonyl chloride (2.66 g, 23.2 mmol) was added dropwise to the above solution. The resulting mixture was allowed to warm to room temperature with stirring for another 2 h. A solution of 2% NaOH solution was added, and the organic layer was separated. The organic portion was washed with 10% HCl (30 mL) and saturated $NaHCO_3$ (30 mL). The solution was then dried in concentrated to give the desired product as a light-yellow viscous liquid (3.14 g, 92%): ^{1}H NMR δ 4.09 (s, 4 H), 3.42 (s, 2 H), 3.09 (s, 6 H), 1.10 (s, 3 H).

Anal. Calcd for $C_7H_{15}N_3O_6S_2$: C, 27.90; H, 5.02; N, 13.94. Found: C, 27.56; H, 5.28; N, 14.33.

2,2-Bis[(diphenylphosphino)methyl]-1-aminopropane (1). A solution of triphenylphosphine (3.49 g, 13.3 mmol) in THF (20 mL) was added to a solution of compound 6 (4.0 g, 13.3 mmol) in THF (50 mL), and the resulting solution was allowed to stir at room temperature for 24 h. Diphenylphosphide anion was prepared by treating diphenylphosphine (5.4 g, 29.0 mmol) in THF (100 mL) with a 1.6 M hexane solution of n-BuLi (20.5 mL, 32.8 mmol). The anion solution was added to the above iminophosphorane solution at 0 °C, and the resulting mixture was heated to reflux for 4 h. Degassed water (10 mL) was added, and the solution was refluxed for another 10 h. All solvents were removed by rotary evaporator, and the residue was chromatographed on silica (80 g) with elution of ethyl acetate. The eluate was collected and concentrated to give the desired produce as a clear colorless liquid which solidified to yield white solid (3.07 g, 51%): mp 57–59 °C; IR (neat) 3385, 3319 cm^{-1} (-NH_2); ^{1}H NMR δ 7.50–7.26 (m, 20 H), 2.65 (s, 2 H), 2.40–2.25 (m, 4 H), 1.00 (br, 2 H, -NH_2), 0.95 (s, 3 H); ^{13}C NMR δ 139.6 (d, J = 13 Hz), 132.8 (d, J = 21 Hz), 131.9 (d, J = 11 Hz), 128.3 (d, J = Hz), 51.7 (t, J = 9 Hz), 39.9 (m), 39.4 (m), 25.6 (t, J = 9 Hz); ^{31}P NMR δ -25.1.

Anal. Calcd for $C_{29}H_{32}NP_2$: C, 76.47; H, 6.86; N, 3.07. Found: C, 76.21; H, 6.52; N, 2.79.

Instead of the addition of water to the reaction mixture, THF solvent was removed and chloroform was added to the residue. The insoluble material was filtered off, and hexane was added to the filtrate to precipitate compound 9, which was very sensitive to water and identified by its spectral data: ^{1}H NMR δ 7.80–7.15 (m, 35 H), 3.12 (d, J_{PNCH} = 13.3 Hz, 2 H), 2.55 (dd, J_{HCH} = 14.2 Hz, J_{PCH} = 3.1 Hz, 2 H), 2.44 (dd, J_{HCH} = 14.2 Hz, J_{PCH} = 3.8 Hz, 2 H), 0.95 (s, 3 H); ^{13}C NMR (aliphatic) δ 55.8 (dt, J = 9, 5 Hz), 40.6 (m), 39.8 (m), 25.8 (t, J = 10 Hz); ^{31}P NMR δ -23.85 (-PPh$_2$), 7.5 (-N=PPh$_3$); FABMS (M + 1) 716.29.

(3-Aminopropyl)diphenylphosphine (2). A solution of triphenylphosphine (6.7 g, 25.6 mmol) in benzene (50 mL) was added to a solution of 3-chloropropyl azide (10) (3.0 g, 25.1 mmol) in benzene (50 mL) and stirred overnight. The benzene solvent was replaced with THF (100 mL). Diphenylphosphide anion was prepared by addition of a 1.60 M hexane solution of n-butyllithium to a solution of diphenylphosphine (5.2 g, 28.0 mmol) in THF and was added to the above solution. The resulting mixture was stirred at room temperature for 4 h. Water (10 mL) was then added, and the resulting mixture was heated to reflux overnight. All solvents were removed, and the residue was extracted with hexane (50 mL × 2). The extracts were dried, concentrated and distilled to give compound 2 as a colorless liquid (3.5 g, 58%): bp 136–138 °C (0.10 mmHg); ^{31}P NMR δ -15.6 (lit.[6] ^{31}P NMR δ -16.5).

(2-Aminopropyl)diphenylphosphine (3). Compound 3 was prepared from 11 in 56% yield by a method similar to that described for 1: by 140–142 °C (0.15 mmHg); IR 3362, 3287 cm^{-1}; ^{1}H NMR δ 7.50–7.25 (m, 10 H), 3.10–2.90 (m, 1 H), 2.30–2.05 (m, 2 H), 1.44 (br, 2 H), 1.19 (dd, J_{HCCH} = 6.4 Hz, J_{PCCCH} = 1 Hz, 3 H); ^{13}C NMR δ 139 (d, J = 13 Hz), 133.9 (d, J = 11 Hz), 132.5 (d, J = 19 Hz), 128.4 (d, J = 6 H), 44.9 (d, J = 15 Hz), 40.1 (d, J = 13 Hz), 25.5 (d, J = 8 Hz); ^{31}P NMR δ -21.4.

Anal. Calcd for $C_{15}H_{18}NP$ C, 74.05; H, 7.46; N, 5.76. Found: C, 74.39; H, 7.08; N, 5.41.

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A New Synthesis of Porphyrin Systems by Four Sequential [3 + 2] Cycloadditions of an Alkyne with Azaallenyl Radical Cations†

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Porphyrins are among the main synthetic targets of organic chemistry.[1] In addition, they are of current interest as physiological active compounds[2] and as complex ligands for catalytic reactions.[3] Their spectroscopic behavior has been investigated extensively.[4] Most synthetic approaches proceed by way of a quaternary pyrrole derivative,[5] and nowadays a biomimetic pathway is preferred.[6] In this paper, we report that a porphyrin system can be built up by four consecutive [3 + 2] cycloadditions between a cyclododecane functionalized with four azirine units and an acceptor-substituted ethyne derivative under conditions of photoinduced electron transfer (PET).

† Radical Ions and Photochemical Charge-Transfer Phenomena (Series A), Part 35, and Cycloadditions (Series B), Part 39. Series A, Part 34: Heidbreder, A.; Mattay, J. *Tetrahedron Lett.* **1992**, *33*, 1973. Series B, Part 38: Köbbing, St.; Mattay, J. *Tetrahedron Lett.* **1992**, *33*, 927.

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