80 Hz) and a narrow triplet at −10.70 ppm (J_{H-P} = 19.2 Hz), which were assigned to the protons of B—H...Ir and Ru—H—Ir fragments, respectively. The signals of the H and C atoms of the coordinated diene ligand are exhibited in the ^1H NMR spectrum (in C_6D_6) and $^{13}C\{^1H\}$ NMR spectrum (in CD_2Cl_2) at δ 4.88 (br.s, 4 H, CH=CH), 2.06 (m, 4 H, CH_2), 1.54 (br.q, 4 H, CH_2) and at δ 67.3 (s, CH=CH), 32.0 (s, CH_2); the signals corresponding to the carborane ligand are observed as separate broadened singlets at δ 2.84 and 41.2, respectively. The signals of the phenyl groups of the phosphine ligands are observed in their normal regions: at δ 6.90—7.90 (m, 30 H) in the ^1H NMR spectra and at δ 127.6—137.3 (C_o, C_m, C_p, and C_{key}) in the ^{13}C NMR spectra. The IR spectrum of cluster **1** (pellets with KBr) exhibits a characteristic ν(B—H) band at 2580 cm^{-1} and ν(C—H) band at 3070 cm^{-1}; no absorption band corresponding to the bridged hydride was found in the spectrum. The magnetic equivalence of the carbon and hydrogen nuclei in the 1,5-cyclooctadiene and carborane ligands as well as the two equivalent phosphine ligands at the Ru atom [$^{31}P\{^1H\}$ NMR spectrum (C_6D_6), δ: 50.42 (s)] indicate the presence of symmetry in cluster **1** and suggests that the B(8) atom of the pentagonal open plane of the carborane cage participates in the B—H...Ir aghostic interaction. The typical low-field signal at +6.45 ppm ($J_{B-H} \approx 90$ Hz) in the ^{11}B NMR spectrum of the cluster in CH_2Cl_2 evidences the existence of this interaction; the signals of the other boron atoms of the carborane ligand are observed in a substantially higher field, namely, in the region from −8.0 to −25.0 ppm.

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1,3-Dipolar tris-cycloaddition of *tert*-butylphosphaacetylene to 2,4,6-triazido-3-chloro-5-cyanopyridine

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It has been shown recently that 1,3-cycloaddition even of such a reactive dipolarophile as norbornene to 2,4,6-triazido-3-chloro-5-cyanopyridine (**1**) occurs regioselectively to the azido group at position 4 of the pyridine cycle.[1,2] It has been established that considerable weakening of the properties of the α-azido groups in compound **1** as 1,3-dipoles is caused by their strong conjugation with the electron-acceptor pyridine system.[3] In this connection, study of the reaction of **1** with *tert*-butylphosphaacetylene (**2**) as the dipolarophile with

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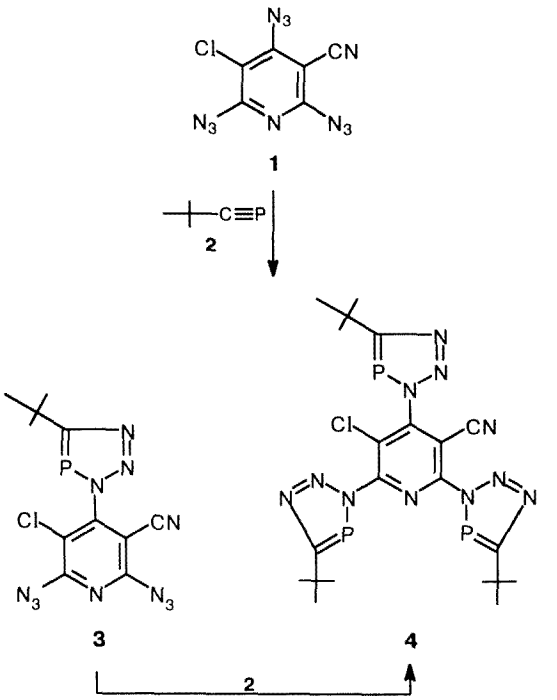
an exclusively high cycloaddition potential is of considerable interest.[4]

The addition of an equimolar amount of compound **2** to a solution of compound **1** in ether at 0 °C in an argon atmosphere results in the formation of monoadduct **3** and trisadduct **4** in a ratio of 3 : 1 (according to the ^{1}H NMR spectra). The same ratio of products **3** and **4** was observed in the reaction of compound **1** with 0.5 equiv. of phosphaalkyne **2**. However, trisadduct **4** as the sole reaction product was obtained upon the action of an excess of **2** on **1**.

It can be seen from the data presented above that the reaction of substituted pyridine **1** with *tert*-butylphosphaacetylene occurs regioselectively with the initial addition of **2** to the γ-azido group of **1**, as in the case of norbornene. In turn, the monoadduct **3** formed readily reacts with extremely reactive phosphaalkyne **2** to give trisadduct **4**. The higher reactivity of the α-azido groups of compound **3** compared to that of the α-azido groups of the original compound **1** is likely caused by the influence of the electron-donor triazaphosphole cycle in the molecule of **3**, which favors an increase in the negative charge on the α-N atoms of its azido groups. Thus, no intermediate bisadducts could be detected in noticeable concentrations, when the reaction of compound **1** with **2** was monitored using ^{31}P NMR spectroscopy, which testifies to the very high reactivity of α-azido groups in pyridines with two electron-donor triazaphosphole substituents. An interesting feature of the ^{31}P NMR spectrum of trisadduct **4** is the equivalence of the P atoms of the two α-triazaphosphole cycles, which is manifested as the signal at 181.2 ppm, whose intensity is fourfold higher than that of the signal of the P atom of the γ-triazaphosphole cycle (at 177.9 ppm).



2,6-Diazido-4-(3*H*-1,2,3,4-triazaphospholo)-3-chloro-5-cyanopyridine (3). M.p. 181—182 °C. IR (KBr), ν/cm^{-1}: 2230 (C≡N); 2150 (N_3). ^{1}H NMR ($CDCl_3$), δ: 1.47 (d, 9 H, 3 Me, $^4J_{P,H}$ = 1.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 199.6 (d, C=P, $^1J_{P,C}$ = 59.2 Hz); 155.0 (s, C(2)); 154.7 (s, C(6)); 149.8 (d, C(4), $^2J_{P,C}$ = 7.9 Hz); 112.6 (s, C(3)); 110.3 (s, C≡N); 94.1 (s, C(5)); 35.5 (d, CMe_3, $^2J_{P,C}$ = 15.0 Hz); 31.2 (d, 3 Me, $^3J_{P,C}$ = 8.2 Hz). ^{31}P NMR ($CDCl_3$), δ: 180.3.

2,4,6-Tris(3*H*-1,2,3,4-triazaphospholo)-3-chloro-5-cyanopyridine (4). M.p. 117—118 °C. IR (KBr), ν/cm^{-1}: 2225 (C≡N). ^{1}H NMR ($CDCl_3$), δ: 1.47 (d, 9 H, 3 Me, $^4J_{P,H}$ = 0.7 Hz); 1.45 (d, 9 H, 3 Me, $^4J_{P,H}$ = 1.4 Hz); 1.43 (d, 9 H, 3 Me, $^4J_{P,H}$ = 1.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 200.6 (d, C=P, $^1J_{P,C}$ = 57.6 Hz); 200.1 (d, C=P, $^1J_{P,C}$ = 59.3 Hz); 199.6 (d, C=P, $^1J_{P,C}$ = 57.7 Hz); 153.7 (d, C(2), $^2J_{P,C}$ = 7.6 Hz); 150.9 (d, C(6), $^2J_{P,C}$ = 9.3 Hz); 149.9 (d, C(4), $^2J_{P,C}$ = 9.3 Hz); 122.4 (s, C(3)); 110.5 (s, C≡N); 101.5 (s, C(5)); 35.71 (d, CMe_3, $^2J_{P,C}$ = 15.3 Hz); 35.65 (d, CMe_3, $^2J_{P,C}$ = 14.4 Hz); 35.56 (d, CMe_3, $^2J_{P,C}$ = 11.7 Hz); 31.3 (d, 3 Me, $^3J_{P,C}$ = 7.6 Hz); 31.2 (d, 3 Me, $^3J_{P,C}$ = 8.5 Hz); 31.1 (d, 3 Me, $^3J_{P,C}$ = 9.3 Hz).

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