Supporting Information for:

Copper(I) Mediated Oligomerisation of a Phosphaalkyne

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S1. Removal of the CuI matrix from 2

S2. ^{31}P-NMR spectrum of the resulting mixture

S1. Removal of the CuI from 2

A solution of NaCN (800 mg, 16.3 mmol) in 20 ml H_2O was layered with 7 ml Et_2O and the mixture was thoroughly degassed by bubbling dinitrogen through it for 30 minutes. Solid **2**·x CH_3CN (100 mg, 0.1 mmol) was added and the mixture was vigorously stirred for 5 hours. After that time all the solid was dissolved and the Et_2O phase showed a pale yellow colour. Separation of the organic phase and removal of all volatiles yielded a yellow, oily residue (ca. 30 mg, 70 % based on $C_{20}H_{27}P_5$) from which $^{31}P\{^1H\}$-NMR data was recorded in C_6D_6 (see S2). On storage of the mixture at –30 °C for one month a few crystals of **6** were obtained, which were suitable for X-Ray crystallography (see S3). Yield: 30 mg (73%)

Supplementary Material (ESI) for Chemical Communications
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S2. ^{31}P-NMR spectrum of the resulting mixture

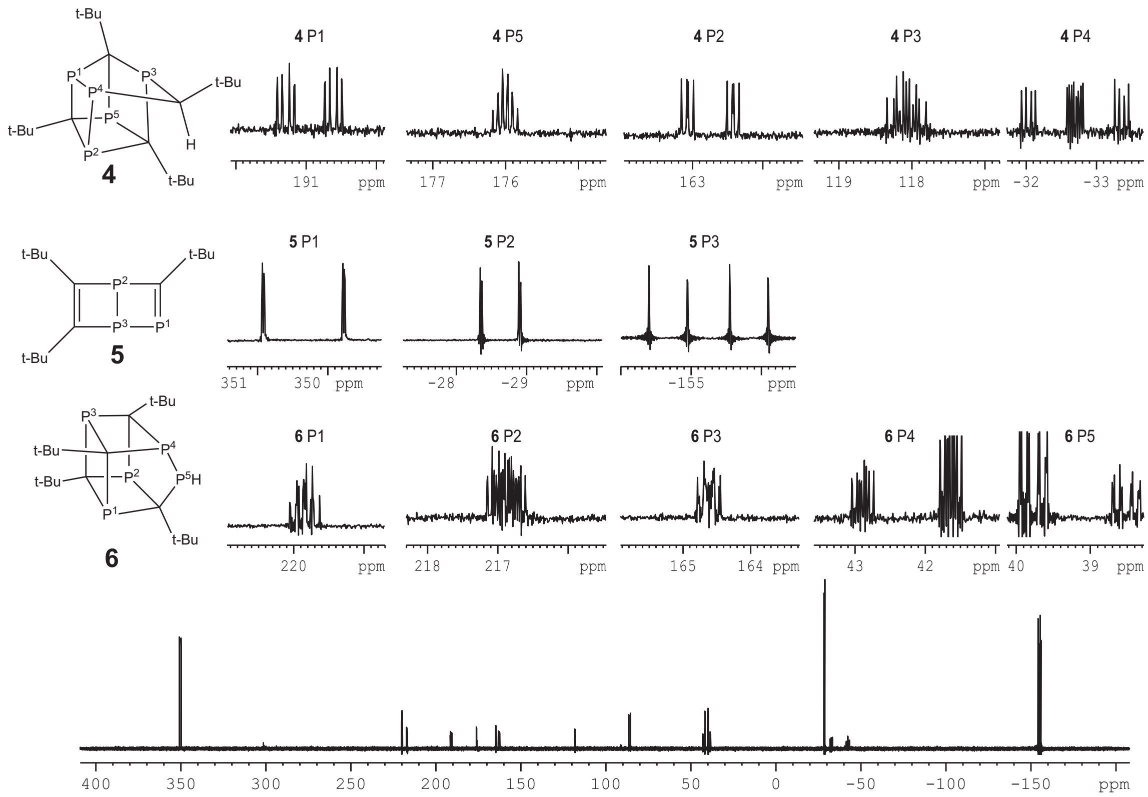
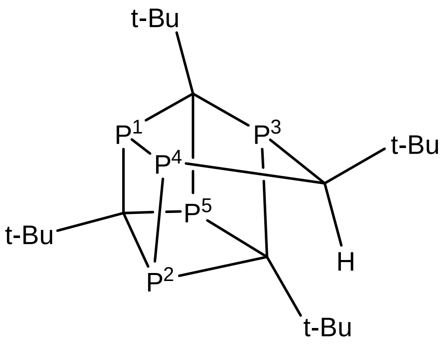
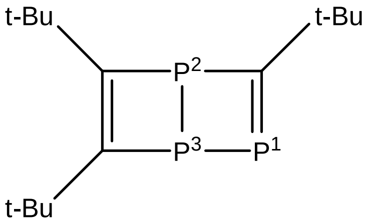


Fig. 1: ^{31}P{^{1}H}-NMR data (161 MHz; C_6D_6; H_3PO_4) and assignment for the identified products



4

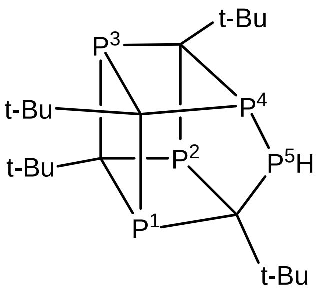
δ_P 190.9 (1P, ddd, ^1J(P^1, P^4) = 109.8 Hz, ^2J(P^1, P^3) = 27.7 Hz, ^2J(P^1, P^2) = 11.9 Hz, P^1), 176.0 (1 P, dd, ^2J(P^5, P^3) = 21.2 Hz, ^2J(P^5, P^4) = 10.8 Hz, P^5), 162.7 (1 P, ddd, ^1J(P^2, P^4) = 105.3 Hz, ^2J(P^2, P^3) = 15.2 Hz, ^2J(P^2, P^1) = 11.9 Hz, P^2) , 118.1 (1 P, dddd, ^2J(P^3, P^1) = 27.7 Hz, ^2J(P^3, P^4) = 22.2 Hz, ^2J(P^3, P^5) = 21.2 Hz, ^2J(P^3, P^2) = 15.3 Hz, P^3), –32.7 (1 P, dddd, ^1J(P^4, P^1) = 109.8 Hz, ^1J(P^4, P^2) = 105.3 Hz, ^2J(P^4, P^3) = 22.2 Hz, ^2J(P^4, P^5) = 10.8 Hz, P^4).



5

δ_P 350.8 (1P, dd, ^1J(P^1, P^3) = 186.2 Hz, J(P^1, P^2) = 3.4 Hz, P^1), –28.6 (1 P, dd, J(P^2, P^3) = 89.7 Hz, J(P^2, P^1) = 3.4 Hz, P^2), –155.3 (1 P, dd, ^1J(P^3, P^1) = 186.2 Hz, J(P^3, P^2) = 89.7 Hz, P^3).

See also: P. Binger, S. Leininger, K. Gather and U. Bergsträßer, *Chem. Ber.*, 1997, **130**, 1491.



6

δ_P 219.8 (1P, dddd, ^1J(P^1, P^2) = 20.8 Hz, ^2J(P^1, P^4) = 17.1 Hz, ^2J(P^1, P^5) = 16.3 Hz, ^2J(P^1, P^3) = 13.9 Hz, P^1), 216.9 (1 P, dddd, ^2J(P^2, P^5) = 41.4 Hz, ^2J(P^2, P^1) = 20.8 Hz, ^2J(P^2, P^3) = 15.5 Hz, ^2J(P^2, P^4) = 9.9 Hz, P^2), 164.6 (1 P, dddd, ^2J(P^3, P^4) = 22.4 Hz, ^2J(P^3, P^2) = 15.4 Hz, ^2J(P^3, P^1) = 13.9 Hz, ^2J(P^3, P^5) = 2.7 Hz, P^3) , 42.1 (1 P, dddd, ^1J(P^4, P^5) = 202.9 Hz, ^2J(P^4, P^3) = 22.4 Hz, ^2J(P^4, P^1) = 17.1 Hz, ^2J(P^4, P^2) = 9.9 Hz, P^4), 39.3 (1 P, dddd, ^1J(P^5, P^4) = 202.9 Hz, ^2J(P^5, P^2) = 41.4 Hz, ^2J(P^5, P^1) = 16.3 Hz, ^2J(P^5, P^3) = 2.7 Hz, P^5). The signal for P^5 splits into a doublet when measured without ^{1}H-decoupling (^1J(P^5, H) = 177.0 Hz)