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Rearrangement of two 8-membered 1,5-diaza-3,7-diphosphacyclooctane rings into 16-membered P_4N_4 ligand on the gold(I) template

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General methods

All reactions and manipulations were carried out under dry argon with standard vacuum line techniques. The source pyridylphosphine and P_2N_2 ligand was synthesized according the described earlier methods [S1]. Gold(I) chloride was purchased from Sigma-Aldrich (Merck KGaA, Darmstadt, Germany) and was used as received. Solvents were purified, dried, deoxygenated and distilled before use. MALDI mass spectra were obtained on a Bruker ULTRAFLEX III mass spectrometer (laser Nd: YAG, λ 355 nm) in a linear mode without accumulation of mass spectra. ^{31}P NMR (162 MHz) spectra were recorded on a Bruker Avance-DRX 400 spectrometer. Chemical shifts are given in parts per million relative to 85% H_3PO_4 (^{31}P, external).

Reaction of the phosphine P_2N_2 with AuCl. To a suspension of a gold(I) chloride (100 mg, 0.43 mmol) in dichloromethane, a solution of **L** (138 mg, 0.287 mmol) was added. The reaction mixture was stirred for 1 h. The following evaporation of the solvent from the reaction mixture under low pressure left yellowish powder being a mixture of complexes **1-3**. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_P 2.2-14.7 (br.s), 14.7-28.7 (br.s)

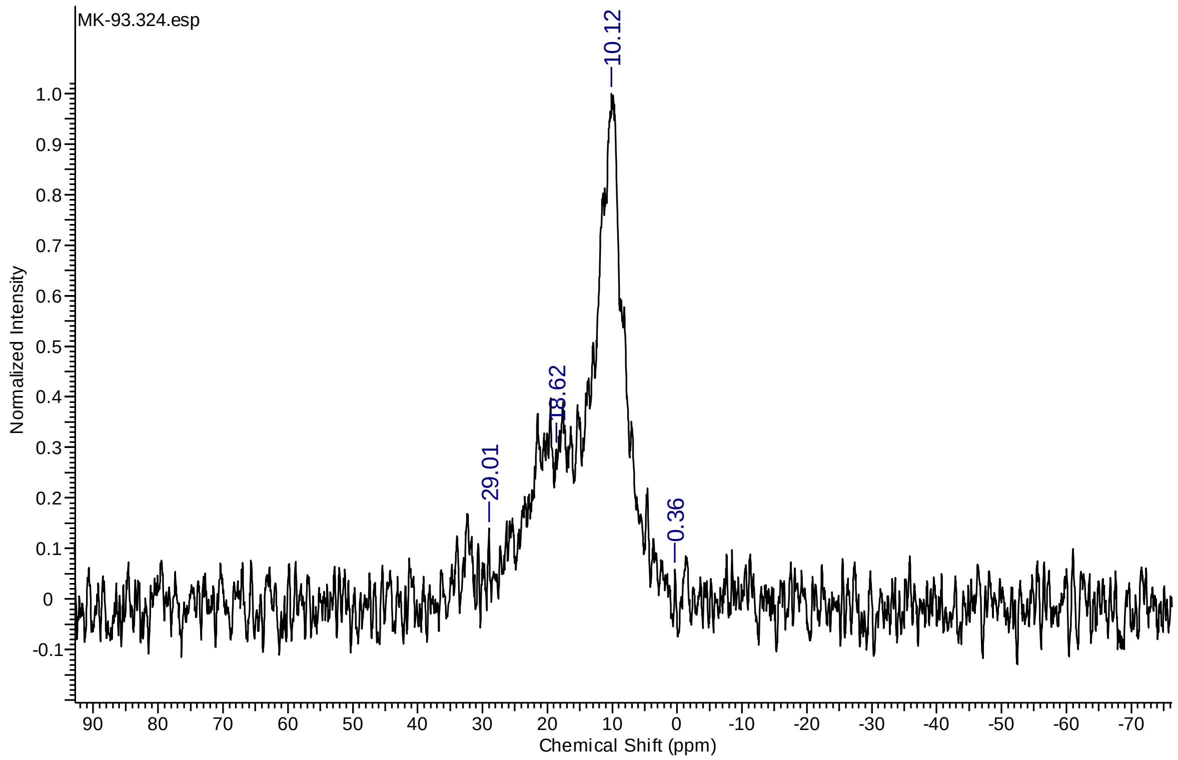


Figure S1. Fragment of ^{31}P-NMR-spectrum of reaction mixture

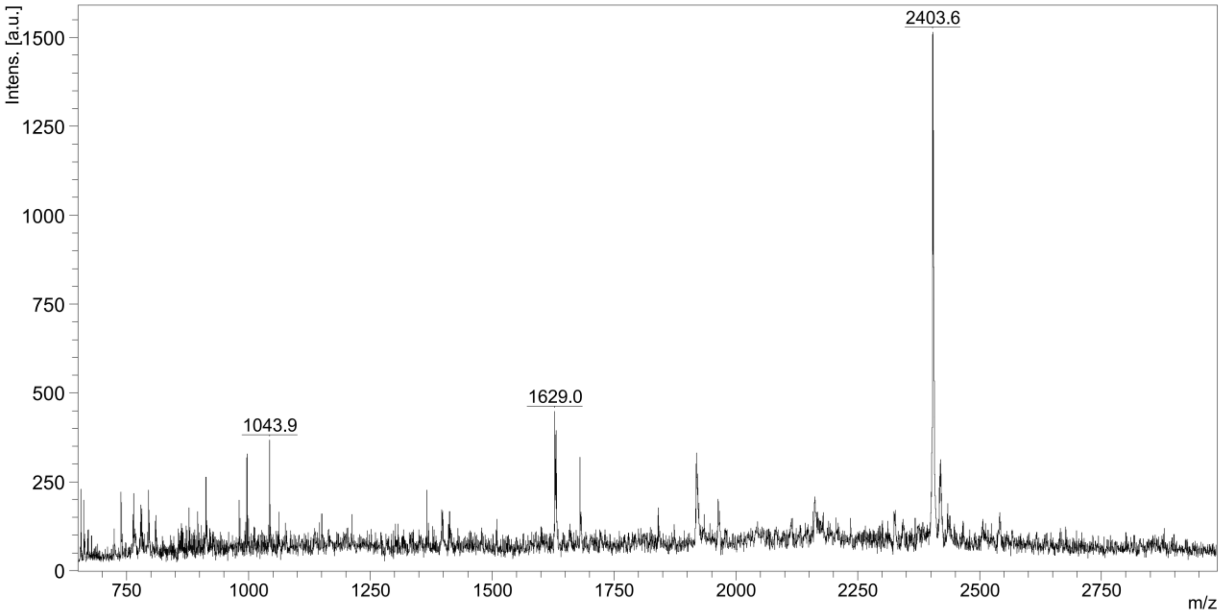
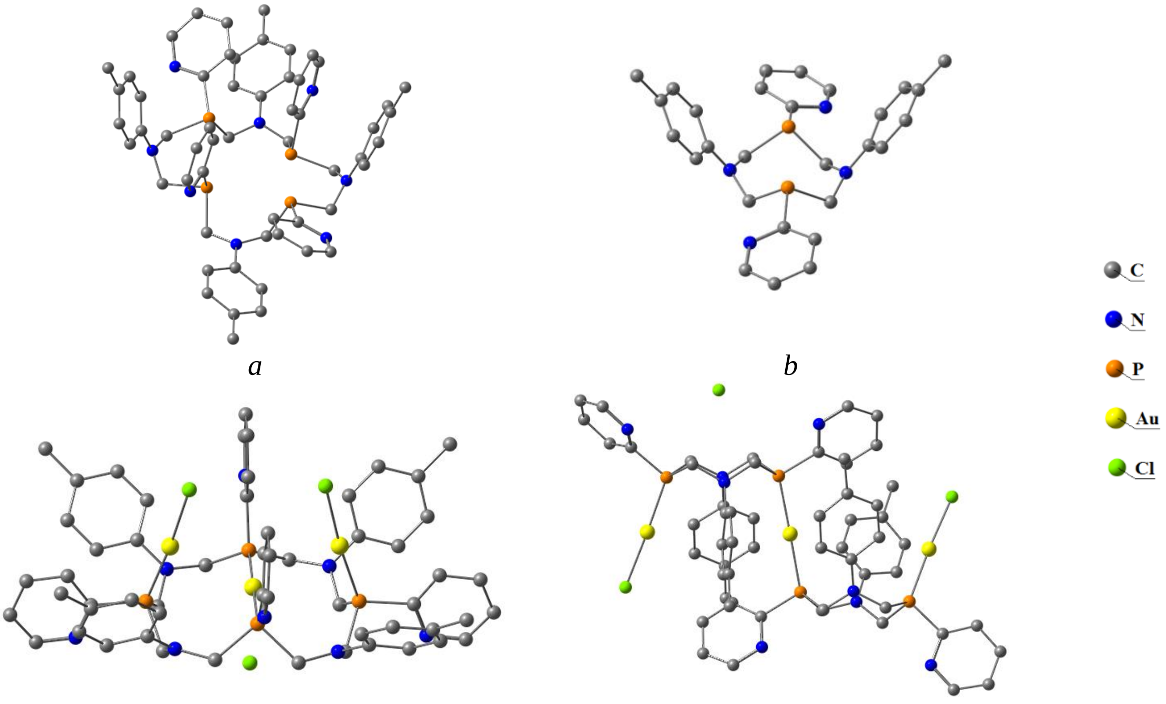


Figure S2 MS MALDI mass-spectrum of the mixture of complexes **1-3**

Computational Methods. Quantum chemical calculations were performed with the Gaussian-16 [S2] suite of programs. The hybrid PBE0 functional [S3] and the Ahlrichs' triple-ζ def-TZVP AO basis set [S4] were used for optimization of all structures. The D3 approach [S5] to describe the London dispersion interactions together with the Becke–Johnson (BJ) damping function [S6–S8] were employed as implemented in the Gaussian-16 program.



a *b*

c *d*

Figure S3 Optimized structures of ligands **P₄N₄** (*a*), **P₂N₂** (*b*) and complexes **2** (*c*) and **2a** (*d*).

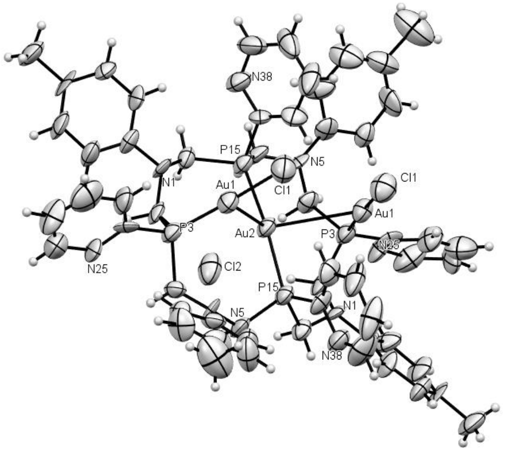


Figure S4 Ortep view of the molecular structure of the complex **2**. Thermal ellipsoids were shown with the probability 50%.

Table S1 Selected bond lengths and distances for the optimized structures **P_4N_4** and **P_2N_2**. For both complexes Au1 – peripheral gold ions bonded to one phosphorus, Au2 – central gold ions coordinated to two P atoms.

Distances and angles	calculated				X-Ray
	P_2N_2	**2a**	**P_4N_4**	**2**	**2**
C-P, Å	**1.90**	**1.85 – 1.88**	**1.87 – 1.89**	**1.87 – 1.89**	**1.78 – 1.84**
C-N, Å	**1.43 – 1.44**	**1.42 – 1.44**	**1.44**	**1.42 – 1.43**	**1.43 – 1.45**
P-C_{Py} , Å	**1.85**	**1.83 – 1.84**	**1.85**	**1.83 – 1.84**	**1.79**
N-$C_{p\text{-}Tol}$, Å	**1.39**	**1.38 – 1.42**	**1.39 – 1.40**	**1.39 – 1.40**	**1.40**
Au1-Au2, Å	**-**	**5.53, 5.62**	**-**	**3.25**	**3.18**
P3-Au1, Å	**-**	**2.27**	**-**	**2.28**	**2.22**
P15-Au2, Å	**-**	**2.33**	**-**	**2.34**	**2.33**
Au1-Cl1, Å	**-**	**2.32 – 2.34**	**-**	**2.33**	**2.28**
Au2-Cl2, Å	**-**	**-**	**-**	**2.96**	**3.18**
C-N-C, °	**116**	**117 – 118**	**115 – 117°**	**117 – 118**	**118 - 121**
C-P-C, °	**100**	**103 – 107**	**97 – 98**	**96, 102**	**95 - 103**

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