

Supporting Information for

A tetranuclear molecular rectangle from four gold(I) atoms linked by dicarbene and diphosphine ligands

Christian Radloff, Jan J. Weigand, and F. Ekkehardt Hahn

General remarks

All manipulations were performed under an argon atmosphere using standard Schlenk techniques or in a glove box. Solvents were distilled by standard procedures prior to use. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on Bruker AVANCE II 200 (QNP-probehead), Bruker AVANCE I 400 (BBO-Probehead) or Bruker AVANCE III 400 (BBFO-probehead) spectrometers. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent as an internal standard. Mass spectra were obtained with MicroTof (Bruker Daltonics, Bremen) or Varian MAT 212 spectrometers. The syntheses of the benzobisimidazolium salt has been described¹ and of $[\text{AuCl}(\text{THT})]^2$ have been described.

Synthesis

Complex [1]. Complex [1] was synthesized by transmetallation from the corresponding disilver complex. The disilver complex was prepared from 42 mg (0.077 mmol) of the benzo(bisimidazolium) salt and 18 mg (0.077 mmol) of Ag_2O . All reactants were suspended in dichloromethane (10 mL) and the reaction mixture was heated to 40 °C for 6 h. After cooling to ambient temperature 50 mg (0.154 mmol) of $[\text{AuCl}(\text{THT})]$ were added. The reaction mixture was stirred at ambient temperature for 12 h. Subsequently, insolubles were separated by filtration and the solvent was removed. The resulting powder was taken up in dichloromethane and the solution was filtered a second time. Removal of the solvent and drying in vacuum gave [1] as a colourless solid. Yield 62 mg (0.073 mmol, 95%). Single crystals of $[\text{1}]\cdot\text{CHCl}_3$ suitable for an X-ray diffraction study could be obtained by slow diffusion of diethyl ether into a saturated solution of [1] in chloroform. ^1H NMR (400 MHz, CDCl_3): δ 7.45 (s, 2H, Ar-H), 4.58 (t, $^3J = 7.2$ Hz, 8H, NCH_2), 1.97 (m, 8H, NCH_2CH_2), 1.46

(m, 8H CH₂CH₃), 0.99 (t, ³J = 7.2 Hz, 12H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 181.9 (C_{carbene}), 131.2 (Ar-C_{ipso}), 93.5 (Ar-C), 49.0 (NCH₂), 31.7 (NCH₂CH₂), 20.0 (CH₂CH₃) 13.7 (CH₃). MS (ESI HRMS): *m/z* = 869.169 [**1** + Na]⁺ (calcd for [**1** + Na]⁺ 869.170).

Compound [2](BF₄)₄. The compound was synthesized from 20 mg (0.024 mmol) of complex [**1**] and 9.4 mg (0.024 mmol) of dppe. Complex [**1**] and the dppe were dissolved in dichloromethane (5 mL) and the reaction mixture was stirred at ambient temperature room temperature for 30 min. Subsequently, 9.2 mg of silver tetrafluoroborate dissolved in dichloromethane (5 mL) were added. The reaction mixture was stirred for 12 h at ambient temperature under protection from light. Subsequently, insolubles were removed by filtration and the filtrate was brought to dryness. The obtained off-white solid was taken up in dichloromethane and the solution was filtered again. The filtrate was collected and layered with diethyl ether to yield [**2**](BF₄)₄ as colourless crystals. The crystals were collected, washed with pentane and dried in vacuum. Yield 21 mg (0.008 mmol, 68%). Single crystals suitable for a X-ray diffraction study could be obtained by slow diffusion of diethyl ether into a saturated solution of [**2**](BF₄)₄ in dichloromethane. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.83 (m, 16H, P-Ar-H_{ortho}), 7.82 (s, 4H, biscarbene-Ar-H), 7.65 (m, 8H, P-Ar-H_{para}), 7.64 (m, 16H, P-Ar-H_{meta}), 4.84 (m, 8H, NCH₂), 4.63 (m, 8H, NCH₂), 3.21 (d, ²J_{HP} = 10.3 Hz, 4H, PCH₂), 3.16 (d, ²J_{HP} = 10.3 Hz, 4H, PCH₂), 1.90 (m, 8H, NCH₂CH₂), 1.80 (m, 8H, NCH₂CH₂), 1.38 (m, 8H, CH₂CH₃), 1.28 (m, 8H, CH₂CH₃), 0.86 (t, ³J_{HH} = 7.2 Hz, 24H CH₃); ¹³C NMR (100 MHz, CD₂Cl₂): δ 197.6 (dd, ²J_{CP} = 124.5 Hz, ⁵J_{CP} = 1.6 Hz, C_{carbene}), 133.9 (m, P-Ar-C_{ortho}), 133.5 (P-Ar-C_{para}), 131.2 (biscarbene-Ar-C_{ipso}), 127.9 (dd, ¹J_{CP} = 60.4 Hz, ⁴J_{CP} = 2.6 Hz, P-Ar-C_{ipso}), 96.2 (biscarbene-Ar-CH), 50.0 (NCH₂), 33.2 (NCH₂CH₂), 20.7 (CH₂CH₃), 20.6 (m, PCH₂), 14.0 (CH₃); ³¹P NMR (161 MHz, CD₂Cl₂): δ 36.14. MS (MALDI, positive ions): *m/z* = 2610 [**2** + 3BF₄]⁺.

Crystal structure determinations. X-ray diffraction data were collected with a Bruker AXS APEX diffractometer equipped with a rotation anode at 153(1) K using graphite monochromated Mo-Kα radiation, λ = 0.71073 Å. Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART³ program package. Structure solutions were found with the SHELXS-97 package⁴ using the heavy-atom method and were refined with SHELXL-97⁵ against *F*² using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions.

Crystal data for [1]·CHCl₃. Formula C₂₅H₃₉N₄AuCl₅, $M = 966.79$, colourless crystal, $0.13 \times 0.10 \times 0.09$ mm, monoclinic, space group $P2_1/n$, $a = 13.8358(12)$, $b = 14.9350(13)$, $c = 16.0256(14)$, $\beta = 104.0690(10)$, $V = 3212.2(5) \text{ \AA}^3$, $\lambda = 0.71073$, $\rho_{\text{calc}} = 1.999 \text{ g cm}^{-3}$, $\mu = 9.561 \text{ mm}^{-1}$, ω - and ϕ -scans, 36327 measured intensities ($3.5^\circ \leq 2\theta \leq 59.1^\circ$), semi-empirical absorption correction ($0.3695 \leq T \leq 0.4799$), 9013 independent ($R_{\text{int}} = 0.0387$) and 6660 observed ($I \geq 2\sigma(I)$) intensities, $Z = 4$, $R = 0.0385$, $wR = 0.0996$ for 6660 observed intensities ($I \geq 2\sigma(I)$) and refinement of 329 parameters against all $|F^2|$ with hydrogen atoms on calculated positions ($wR2 = 0.1080$ for all data).

Crystal data for [2](BF₄)₄. Formula C₁₀₀H₁₂₄N₈Au₄B₄F₁₆P₄, $M = 2697.06$, colourless crystal, $0.25 \times 0.08 \times 0.01$ mm, triclinic, space group $P-1$, $a = 11.9916(6)$, $b = 12.7206(6)$, $c = 19.6897(9)$, $\alpha = 96.2600(7)$, $\beta = 94.4715(8)$, $\gamma = 117.7115(7)$, $V = 2614.7(2) \text{ \AA}^3$, $\lambda = 0.71073$, $\rho_{\text{calc}} = 1.713 \text{ g cm}^{-3}$, $\mu = 5.732 \text{ mm}^{-1}$, ω - and ϕ -scans, 29898 measured intensities ($2.1^\circ \leq 2\theta \leq 59.1^\circ$), semi-empirical absorption correction ($0.3283 \leq T \leq 0.9449$), 14572 independent ($R_{\text{int}} = 0.0298$) and 11690 observed ($I \geq 2\sigma(I)$) intensities, $Z = 1$, $R = 0.0305$, $wR = 0.0709$ for 11690 observed intensities ($I \geq 2\sigma(I)$) and refinement of 673 parameters against all $|F^2|$ with hydrogen atoms on calculated positions ($wR2 = 0.0754$ for all data). The cation of [2]⁴⁺ resides on a crystallographic inversion centre. The asymmetric unit contains 1/2 formula units of [2](BF₄)₄.

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