ELECTRONIC SUPPORTING INFORMATION (ESI) FOR

Steric Control of the *in*/*out* Sense of Bridgehead Substituents in Macrobicyclic Compounds: Isolation of New "Crossed Chain" Variants of *in*/*out* Isomers

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General. Reactions were conducted under argon (dried with P_2O_5) using standard Schlenk techniques. Chemicals were utilized as follows: hexanes and CH_2Cl_2, dried and degassed using a Glass Contour solvent purification system; toluene and THF, distilled from Na/benzophenone or Na; $CDCl_3$, distilled from CaH_2; diethyl ether and methanol, used as received; PPh_3 (Mallinckrodt) and Me_2SAuCl (Aldrich) used as received; (*in,in*/*out,out*)-$P((CH_2)_{14})_3P$ ((*in,in*/*out,out*)-**1**),[s1] *out,out*-**1**·$(AuCl)_2$,[s2] *in,out*-**1**·$(AuCl)_2$,[s2] and $Li(2,6\text{-}C_6H_3(Trip)_2)\cdot OEt_2$ (Trip = 2,4,6-$C_6H_2(i\text{Pr})_3$),[s3] synthesized as reported earlier.

NMR spectra were recorded at ambient probe temperatures using a Varian NMRS 500 spectrometer or a Bruker Avance III 500 cryoprobe spectrometer, and referenced as follows: ^{1}H, residual internal $CHCl_3$ (δ = 7.24 ppm); ^{13}C, internal $CDCl_3$ (δ = 77.0 ppm); ^{31}P, external H_3PO_4 (δ = 0.00 ppm). Mass spectra were recorded using Applied Biosystems Voyager-DE STR (MALDI) and Applied Biosystems PE SCIEX QSTAR (ESI) instruments. Melting points were recorded with a Stanford Research Systems MPA 100 (OptiMelt) automated apparatus. Microanalyses were conducted by Atlantic Microlab, Inc.

Ph_3PAuCl (**2**). The following is a modification of a published synthesis.[s4] A Schlenk flask was charged with Me_2SAuCl (1.847 g, 6.27 mmol) and CH_2Cl_2 (100 mL) under subdued or red light. A solution of PPh_3 (1.645 g, 6.27 mmol) in CH_2Cl_2 (100 mL) was added with stirring. After 22 h, the suspension was filtered through neutral alumina (ca. Ø 5 cm × 5 cm). The filter cake was washed with CH_2Cl_2 (5 × 20 mL). The colorless filtrate/washings were combined and concentrated by rotary evaporation to ca. 20 mL. After ca. 18 h, the sample was cooled to –78 °C. Large crystals were isolated by filtration and washed with –78 °C diethyl ether (2 × 10 mL). The filtrate was treated with diethyl ether (25 mL). The resulting microcrystalline solid was isolated by filtration and washed with –78 °C diethyl ether (5 × 5 mL). The combined crops were dried by oil pump vacuum (22 h) to give **2** as a white crystalline solid (2.670 g, 5.397 mmol, 86%).

NMR ($CDCl_3$, δ (ppm)): ^{1}H (500 MHz) 7.53–7.43 (m, 15H, Ph); $^{13}C\{^1H\}$ (126 MHz) 134.1 (d, J_{CP} = 13.7 Hz, *o*-Ph), 132.0 (d, $^4J_{CP}$ = 2.6 Hz, *p*-Ph), 129.2 (d, J_{CP} = 11.9 Hz, *m*-Ph),[s5] 128.7 (d, $^1J_{CP}$ = 62.4 Hz, *i*-Ph); $^{31}P\{^1H\}$ (202 MHz) 33.8 (s).

$Ph_3PAu(2,6\text{-}C_6H_3(Trip)_2)$ (3). **Method A**. A Schlenk flask was charged with **2** (0.460 g, 0.930 mmol) and THF (20 mL). A solution of $Li(2,6\text{-}C_6H_3(Trip)_2)\cdot OEt_2$ and $1,3\text{-}C_6H_4(Trip)_2$ (1.00:0.23 mol ratio;[s6] 0.625 g, equivalent to 0.522 g/0.927 mmol of $Li(2,6\text{-}C_6H_3(Trip)_2)\cdot OEt_2$) in THF (15 mL) was added with stirring. After 21 h, the solvent was removed by oil pump vacuum. The colorless powder was dried by oil pump vacuum. After 18 h, hexanes (50 mL) were added, and the suspension was filtered through celite (ca. Ø 1.5 cm × 5 cm). The residue was extracted with hexanes (4 × 20 mL), and the extracts were similarly filtered. The combined colorless filtrates were concentrated by oil pump vacuum to ca. 30 mL. A precipitate formed. The sample was kept at –35 °C overnight and then cooled to –78 °C. The crude product was isolated by filtration, washed with hexanes (3 × 5 mL), and chromatographed on a silica column (Ø 4.5 × 30 cm) using hexanes/CH_2Cl_2 (gradient, 1:0 to 0:1 v/v). The solvents were removed from the product containing fractions by rotary evaporation and oil pump vacuum to give **3** as a white microcrystalline solid (0.296 g, 0.315 mmol, 34%).

Method B. A Schlenk flask was charged with **2** (0.650 g, 1.314 mmol) and THF (15 mL). A solution of $Li(2,6\text{-}C_6H_3(Trip)_2)$ (0.643 g, 1.316 mmol; generated in situ[s3]) in THF (15 mL) was added with stirring. After 16 h, the solvent was removed by oil pump vacuum. The residue was placed at the top of a silica gel column (Ø 4 cm × 20 cm), which was eluted with hexanes and then hexanes/CH_2Cl_2 (gradient, ending at 1:1 v/v). The solvents were removed from the product containing fractions by rotary evaporation and oil pump vacuum to give **3** as a white powder (0.922 g, 0.980 mmol, 75%), dec pt 156 °C (no melting; color turns yellow). Anal. Calcd for $C_{54}H_{64}AuP$ (941.03): C, 68.92; H 6.86; found: C, 69.39; H, 6.80.

NMR ($CDCl_3$, δ (ppm)): ^1H (500 MHz) 7.35–7.31 (m, 3 H, *p*-Ph), 7.25–7.21 (m, 6 H, *o*- or *m*-Ph), 7.16–7.10 (m, 3 H, C_6H_3), 6.98–6.93 (m, 10 H, *o*- or *m*-Ph, *m*-Trip), 2.98–2.85 (m, 6 H, $CH(CH_3)_2$), 1.19 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, *p*-$CH(CH_3)_2$), 1.08, 1.00 (2 d, $^3J_{HH}$ = 6.9 Hz, 12 H, *o*-$CH(CH_3)_2$); $^{13}C\{^1H\}$ (126 MHz)[s7] 176.9 (d, $^2J_{CP}$ = 112.9 Hz, *i*-C_6H_3), 148.2, 146.6, 145.8 (3 s, Trip, C_6H_3), 143.0 (d, J_{CP} = 2.0 Hz, *i*-Trip or *o*-C_6H_3), 134.1 (d, J_{CP} = 13.9 Hz, *o*-Ph), 131.3 (d, $^1J_{CP}$ = 48.1 Hz, *i*-Ph), 130.4 (d, $^4J_{CP}$ = 2.2 Hz, *p*-Ph), 128.4 (d, J_{CP} = 10.6 Hz, *m*-Ph),[s5] 126.0 (d, $^4J_{CP}$ = 6.4 Hz, *m*-C_6H_3), 123.8 (s, *p*-C_6H_3), 119.8 (s, *m*-Trip), 34.2 (s, *p*-$CH(CH_3)_2$), 30.1 (s, *o*-$CH(CH_3)_2$), 24.5, 24.1, 24.0 (3 × s, $CH(CH_3)_2$); $^{31}P\{^1H\}$ (202 MHz) 43.4 (s). MS (ESI+, *m/z* (rel. intensity)): 963.4 (100) $[M+Na]^+$, 941.4 (61) $[M+H]^+$.

***out,out*-1·(Au(2,6-C_6H_3(Trip)$_2$))$_2$. Method A**. A Schlenk tube was charged with *out*, *out*-**1**·$(AuCl)_2$ (0.050 g, 0.045 mmol) and THF (10 mL) and cooled to −78 °C. A solution of Li-(2,6-C_6H_3(Trip)$_2$) (0.044 g, 0.090 mmol; generated in situ[s3]) in THF (10 mL) was added dropwise with stirring over 20 min. The cold bath was allowed to warm to room temperature over 5 h. After an additional 18 h, the solvent was removed by oil pump vacuum to give a white solid. Preparative TLC (silica, coat thickness 1.5 mm, 20 × 20 cm, 2:1 v/v hexanes/CH_2Cl_2) afforded a product band that was extracted with CH_2Cl_2. The solvent was removed from the extract by oil pump vacuum to give *out,out*-**1**·(Au(2,6-C_6H_3(Trip)$_2$))$_2$ as a colorless oil that slowly solidified to a white powder (0.036 g, 0.018 mol, 40%), mp 132–139 °C. Anal. Calcd for $C_{114}H_{182}Au_2P_2$ (2008.55): C, 68.17; H 9.13; found: C, 69.49; H, 9.34.

Method B. A Schlenk flask was charged with a solution of **3** (0.047 g, 0.050 mmol) in THF (5 mL). A solution of (*in,in*/*out,out*)-**1** (0.017 g, 0.026 mmol) in THF (6 mL) was added with stirring. After 12 d, the solvent was removed by oil pump vacuum to give a colorless oil. Preparative TLC (silica, coat thickness 1.5 mm, 20 × 20 cm, 2:1 v/v hexanes/CH_2Cl_2) afforded a product band that was extracted with CH_2Cl_2 (a faster moving band contained PPh_3 and was discarded). The solvent was removed from the extract by oil pump vacuum to give *out,out*-**1**·(Au-(2,6-C_6H_3(Trip)$_2$))$_2$ as a colorless oil that slowly solidified to a white powder (0.025 g, 0.012 mmol, 46%).

NMR ($CDCl_3$, δ (ppm)): ^1H (500 MHz) 7.10–7.05 (m, 6 H, C_6H_3), 6.91 (s, 8 H, *m*-Trip), 2.93–2.81 (m, 12 H, $CH(CH_3)_2$), 1.25 (d, $^3J_{HH}$ = 6.9 Hz, 24 H, *p*-$CH(CH_3)_2$), 1.20–1.13, 1.00–0.90 (2 × m, 84 H, CH_2), 1.11 (d, $^3J_{HH}$ = 6.9 Hz, 24 H, *o*-$CH(CH_3)_2$), 1.08 (d, $^3J_{HH}$ = 6.9 Hz, 24 H, *o*-$CH(CH_3)_2$); $^{13}C\{^1H\}$ (126 MHz)[s7] 178.9 (d, $^2J_{CP}$ = 113.7 Hz, *i*-C_6H_3), 148.1, 146.6, 145.7 (3 s, Trip, C_6H_3), 142.9 (d, J_{CP} = 1.8 Hz, *i*-Trip or *o*-C_6H_3), 125.7 (d, $^4J_{CP}$ = 6.5 Hz, *m*-C_6H_3), 123.5 (s, *p*-C_6H_3), 119.5 (s, *m*-Trip), 34.1 (s, *p*-CH(CH_3)$_2$), 30.5 (d, J_{CP} = 13.1 Hz, CH_2), 30.0 (s, *o*-CH(CH_3)$_2$), 29.33, 29.31, 29.0, 28.4 (4 s, CH_2), 24.9 (d, J_{CP} = 27.0 Hz, CH_2), 24.4, 24.2, 24.1 (3 × s, CH(CH$_3$)$_2$), 23.4 (s, CH_2); $^{31}P\{^1H\}$ (202 MHz) 31.1 (s). MS (MALDI+, *m/z* (rel. intensity)): 2030.3 (10) $[M+Na]^+$, 2008.3 (5) $[M+H]^+$, 847.6 (99) [**1**·Au]$^+$.

***out,out*-1'·(Au(2,6-C_6H_3(Trip)$_2$))$_2$**. **Method A**. A Schlenk flask was charged with *out*, *out*- and *in,out*-**1**·(AuCl)$_2$ (54:46 ratio;[s2] 0.050 g, 0.045 or 0.024/0.021 mmol) and THF (10 mL) and cooled at −78 °C. A solution of Li(2,6-C_6H_3(Trip)$_2$) (0.044 g, 0.090 mmol; generated in situ[s3]) in THF (10 mL) was added dropwise with stirring over 20 min. The cold bath was allowed to warm to room temperature over 5 h. After 18 h, the solvent was removed by oil pump vacuum to give a white solid. Preparative TLC (silica, coat thickness 1.5 mm, 20 × 20 cm, 3:1 v/v hexanes/CH_2Cl_2) afforded two product bands, which were separately extracted with CH_2Cl_2 and taken to dryness by oil pump vacuum. The lower R_f band gave *out,out*-**1'**·(Au(2,6-C_6H_3-(Trip)$_2$))$_2$ as a colorless oil that slowly solidified to a white powder (0.010 g, 0.0050 mmol, 11% or 24% of theory). The higher R_f band gave *out,out*-**1**·(Au(2,6-C_6H_3(Trip)$_2$))$_2$ as a colorless oil that slowly solidified to a white powder (0.016 g, 0.0080 mmol, 18% or 33% of theory).

Method B. A Schlenk tube was charged with (*in,in*/*out,out*)- and *in,out*-**1** (54:46 ratio;[s1] 0.050 g, 0.077 or 0.042/0.035 mmol) in THF (10 mL). A solution of **3** (0.145 g, 0.154 mmol) in THF (10 mL) was added with stirring. After 21 d, the solvent was removed by oil pump vacuum to give a white solid. Preparative TLC (silica, coat thickness 1.5 mm, 20 × 20 cm, 5:1 v/v hexanes/CH_2Cl_2) afforded two product containing bands (a still faster moving band contained PPh_3 and was discarded), which were separately extracted with CH_2Cl_2 and taken to dryness by oil pump vacuum. The lower R_f band gave *out,out*-**1'**·(Au(2,6-C_6H_3(Trip)$_2$))$_2$ as a colorless oil that slowly solidified to a white powder (0.050 g, 0.025 mmol, 32% or 71% of theory). Calcd for $C_{114}H_{182}Au_2P_2$ (2008.55): C, 68.17; H 9.13; found: C, 69.24; H, 9.72. The higher R_f band gave *out,out*-**1**·(Au(2,6-C_6H_3(Trip)$_2$))$_2$ as a colorless oil that slowly solidified to a white powder (0.055 g, 0.027 mmol, 35% or 64% of theory).

NMR ($CDCl_3$, δ (ppm)): ^1H (500 MHz) 7.06-7.12 (m, 6H, C_6H_3), 6.92 (s, 8H, *m*-Trip), 2.95-2.82 (m, 12H, $CH(CH_3)_2$), 1.25 (d, $^3J_{HH}$ = 6.9 Hz, 24H, *p*-$CH(CH_3)_2$), 1.21-1.14, 1.05-0.90 (2 × m, 84H, CH_2), 1.12 (d, $^3J_{HH}$ = 6.9 Hz, 24H, *o*-$CH(CH_3)_2$), 1.09 (d, $^3J_{HH}$ = 6.9 Hz, 24 H, *o*-$CH(CH_3)_2$); $^{13}C\{^1H\}$ (126 MHz)[s7] 178.9 (d, $^2J_{CP}$ = 113.9 Hz, *i*-C_6H_3), 148.1, 146.6, 145.7 (3 s, Trip, C_6H_3), 143.0 (d, J_{CP} = 2.0 Hz, *i*-Trip or *o*-C_6H_3), 125.7 (d, $^4J_{CP}$ = 6.5 Hz, *m*-C_6H_3), 123.5 (s, *p*-C_6H_3), 119.5 (s, *m*-Trip), 34.2 (s, *p*-$CH(CH_3)_2$), 30.2 (d, J_{CP} = 11.7 Hz, CH_2), 30.0 (s, *o*-$CH(CH_3)_2$), 29.7, 29.4, 29.3, 29.0, 28.7, 28.4, 28.1, 27.6 (8 s, CH_2) 24.6 (d, J_{CP} = 27.0 Hz, CH_2, tentative, one line overlapping with upfield signal), 24.5 (s, *o*-$CH(CH_3)_2$), 24.3 (s, *p*-$CH(CH_3)_2$), 24.1 (s, *o*-$CH(CH_3)_2$), 23.8, 23.6, 23.4, 22.0 (4 s, CH_2); $^{31}P\{^1H\}$ (202 MHz) 31.8 (s).

Single Crystal X-ray Diffraction. Colorless rectangular plates of **3** were obtained by the slow evaporative concentration of a diethyl ether solution at room temperature. Colorless needles of the monosolvate *out,out*-**1**·$(Au(2,6\text{-}C_6H_3(Trip)_2))_2 \cdot OEt_2$ were grown by layering a diethyl ether solution of *out,out*-**1**·$(Au(2,6\text{-}C_6H_3(Trip)_2))_2$ with methanol at room temperature. Colorless plates of *out,out*-**1'**·$(Au(2,6\text{-}C_6H_3(Trip)_2))_2$ were obtained by vapor diffusion of ether into a methanol solution at room temperature. Data were collected as summarized in Tables s1 and s2.

Integrated intensities for each reflection were obtained by data reduction with the program APEX2.[s8] Cell parameters were obtained and refined with 94166, 248826, and 36197 reflections (independent reflections: 6802, 16224, and 8101, respectively).[s9] Data were corrected for absorption effects using SADABS.[s10] The structures were solved by direct methods and refined (weighted least squares refinement on F^2) using SHELXL-97 or 2013.[s11,s12] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in idealized positions and refined using a riding model.

The phenyl groups of **3** were disordered between two positions, and one of the methyl groups was disordered, which was modeled with restraints.[s13] The thermal ellipsoids of several carbon atoms in the methylene chains of *out,out*-**1**·$(Au(2,6\text{-}C_6H_3(Trip)_2))_2 \cdot OEt_2$ were elongated, suggesting disorder. However, efforts to model this disorder not only increased the number of parameters as well as restraints, but also did not afford improved reliability factors. SIMU and DELU restraints were used to keep the thermal parameters of the methylene carbon atoms meaningful. With *out*,*out*-**1'**·(Au(2,6-C_6H_3(Trip)$_2$))$_2$, an inversion center that contained the midpoint of the crossed chain was apparent. The elongated thermal ellipsoids of C46–C52 indicated disorder, which was modeled between two positions that refined to an occupancy ratio of 0.58:0.42. Restraints and/or constraints were used to keep the bond distances, angles, and thermal ellipsoids meaningful. Tables s1 and s2 give further data and refinement details. Key metrical parameters are provided in Tables s3-s5, and additional thermal ellipsoid plots in Figures s1-s3.

Powder X-ray Diffraction. Microcrystalline samples of *out*,*out*-**1**·(Au(2,6-C_6H_3(Trip)$_2$))$_2$·OEt_2 and *out*,*out*-**1'**·(Au(2,6-C_6H_3(Trip)$_2$))$_2$ were ground in mineral oil to fine particles of uniform size. The samples were mounted on nylon loop holders and reflections were collected from 3° to 45° at 110 K and later refined with Diffrac Plus EVA and the TOPAS Pawley method. Key data are provided in Table s6.

The single crystal structures of *out*,*out*-**1**·(Au(2,6-C_6H_3(Trip)$_2$))$_2$·OEt_2 and *out*,*out*-**1'**·(Au(2,6-C_6H_3(Trip)$_2$))$_2$ were compared to the powder diffraction data (Table s6). For each pair, the lattice parameters were very close, with deviations of less than 0.01 Å for *a*, *b*, and *c*. The superimposition of the diffraction intensities vs. angles afforded closely matched plots as portrayed in Figures s4 and s5. Therefore, both bulk samples of these complexes prove to be morphologically homogeneous and correspond to the single crystal structures.

References

(s1) Stollenz, M.; Barbasiewicz, M.; Nawara-Hultzsch, A. J.; Fiedler, T.; Laddusaw, R. M.; Bhuvanesh, N.; Gladysz, J. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 6647; *Angew. Chem.* **2011**, *123*, 6777.

(s2) Stollenz, M.; Bhuvanesh, N.; Reibenspies, J. H.; Gladysz, J. A. *Organometallics* **2011**, *30*, 6510.

(s3) Schiemenz, B.; Power, P. P. *Organometallics* **1996**, *15*, 958.

(s4) Mézailles, N.; Ricard, L.; Gagosz, F. *Org. Lett.* **2005**, *7*, 4133.

(s5) The phenyl ^{13}C NMR signal with the chemical shift closest to benzene is assigned to the meta carbon atom: Mann, B. E. *J. Chem. Soc., Perkin Trans. 2* **1972**, 30.

(s6) This ratio was assigned by ^1H NMR. The protonated material occurs in some batches of isolated Li(2,6-C_6H_3(Trip)$_2$)·OEt_2.

(s7) The number of hydrogen atoms bound to the carbon atom responsible for each signal was determined by ^{1}H,^{13}C-HSQC and ^{1}H,^{13}C-HMBC NMR experiments. Signals were assigned accordingly.

(s8) *APEX2*, *Program for Data Collection and Integration on Area Detectors*; BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.

(s9) *FRAMBO v. 4.1.05, Program for Data Collection on Area Detectors*; BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.

(s10) Sheldrick, G. M. SADABS, *Program for Absorption Correction for Data from Area Detector Frames*; University of Göttingen: Göttingen, Germany, 2008.

(s11) Sheldrick, G. M. *Acta Crystallogr*. **2008**, *A64*, 112.

(s12) SHELXS and SHELXL as implemented in APEX2

(s13) *SAINT (Version 7)*, *Program for Data Integration from Area Detector Frames*; BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.

Table s1. Single Crystal X-ray data for **3** and *out*,*out*-**1**·(Au(2,6-C_6H_3(Trip)$_2$))$_2$.

Compound	**3**	*out*,*out*-**1**·(Au(2,6-C_6H_3(Trip)$_2$))$_2$·OEt_2
Empirical formula	$C_{54}H_{64}PAu$	$C_{118}H_{192}OP_2Au_2$
Formula weight	940.99	2082.59
Temperature [K]	110(2)	110(2)
Diffractometer	Bruker D8 GADDS	Bruker D8 GADDS
Wavelength [Å]	1.54178	1.54178
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pna2_1$
Unit cell dimensions		
a [Å]	12.8975(10)	47.793(3)
b [Å]	12.5051(9)	13.1566(9)
c [Å]	28.706(3)	17.5594(12)
α [°]	90	90
β [°]	90.438(6)	90
γ [°]	90	90
Volume [Å^3]	4629.6(6)	11041.3(13)
Z	4	4
ρ_{calcd} [Mg m^{-3}]	1.350	1.253
μ [mm^{-1}]	6.538	5.528
F(000)	1928	4384
Crystal size [mm^3]	0.10 × 0.05 × 0.01	0.18 × 0.04 × 0.02
Range for data collection [°]	3.43 to 60.00	1.85 to 60.00
Index ranges	$-14 \le h \le 14$	$-53 \le h \le 53$
	$-14 \le k \le 14$	$-13 \le k \le 14$
	$-32 \le l \le 32$	$-19 \le l \le 19$
Reflections collected	94166	248826
Independent reflections	6802 [R(int) = 0.1607]	16224 [R(int) = 0.0744]
Max. and min. transmission	0.9375 and 0.5609	0.8975 and 0.4361
Data / restraints / parameters	6802 / 483 / 639	16224 / 349 / 1108
Goodness-of-fit on F^2	1.016	1.076
Final R indices [I>2σ(I)]	$R1 = 0.0470$, $wR2 = 0.1042$	$R1 = 0.0307$, $wR2 = 0.0658$
R indices (all data)	$R1 = 0.0742$, $wR2 = 0.1096$	$R1 = 0.0327$, $wR2 = 0.0664$
Largest diff. peak and hole [eÅ^{-3}]	1.523 and −1.226	0.899 and −1.018

Table s2. Single Crystal X-ray data for *out*,*out*-**1'**·(Au(2,6-C_6H_3(Trip)$_2$))$_2$.

Compound	*out*,*out*-**1'**·(Au(2,6-C_6H_3(Trip)$_2$))$_2$
Empirical formula	$C_{114}H_{182}P_2Au_2$
Formula weight	2008.46
Temperature [K]	110(2)
Diffractometer	Bruker D8 GADDS
Wavelength [Å]	1.54178
Crystal system	monoclinic
Space group	$P2_1$/c
Unit cell dimensions	
a [Å]	13.0821(9)
b [Å]	24.5540(17)
c [Å]	17.7022(13)
α [°]	90
β [°]	108.761(4)
γ [°]	90
Volume [Å^3]	5384.1(7)
Z	2
ρ_{calcd} [Mg m^{-3}]	1.239
μ [mm^{-1}]	5.644
F(000)	2108
Crystal size [mm^3]	0.13 × 0.08 × 0.01
Range for data collection [°]	3.192 to 60.886
Index ranges	$-14\leq h\leq 14$ $-27\leq k\leq 27$ $-19\leq l\leq 18$
Reflections collected	36197
Independent reflections	8101 [R(int) = 0.0622]
Max. and min. transmission	0.7519 and 0.5535
Data / restraints / parameters	8101 / 83 / 602
Goodness-of-fit on F^2	1.045
Final R indices [I>2σ(I)]	$R1 = 0.0435$, $wR2 = 0.1156$
R indices (all data)	$R1 = 0.0574$, $wR2 = 0.1228$
Largest diff. peak and hole [eÅ^{-3}]	2.385 and −1.509

Table s3. Key crystallographic distances (Å), bond angles, and torsion angles (deg) for **3**.

Au(1)···Au(1)[a]	9.9322(8)	C(2)-C(7)-C(8)	120.5(6)
Au(1)-C(1)	2.088(7)	C(2)-C(7)-C(12)	119.5(7)
Au(1)-P(1)	2.2910(19)	C(1_1)-P(1)-C(1_3)	102.5(4)
C(1)-C(2)	1.378(10)	C(1_1)-P(1)-C(1_5)	107.0(4)
C(1)-C(6)	1.377(10)	C(1_3)-P(1)-C(1_5)	104.5(3)
C(2)-C(7)	1.515(10)	C(1_1)-P(1)-Au(1)	114.6(3)
C(6)-C(22)	1.515(11)	C(1_3)-P(1)-Au(1)	110.3(3)
P(1)-C(1_1)	1.792(7)	C(1_5)-P(1)-Au(1)	116.6(2)
P(1)-C(1_3)	1.837(7)	Au(1)-C(1)-C(2)-C(7)	4.9(10)
P(1)-C(1_5)	1.815(6)	Au(1)-C(1)-C(6)-C(22)	–3.2(11)
C(1)-Au(1)-P(1)	176.6(2)	C(1)-C(2)-C(7)-C(8)	–89.7(9)
C(2)-C(1)-Au(1)	118.2(5)	C(1)-C(2)-C(7)-C(12)	85.9(9)
C(6)-C(1)-Au(1)	120.7(6)	C(1)-C(6)-C(22)-C(23)	86.5(10)
C(1)-C(2)-C(7)	120.6(7)	C(1)-C(6)-C(22)-C(27)	–90.0(10)
C(1)-C(6)-C(22)	120.3(7)		

[a] Shortest intermolecular distance.

Table s4. Key crystallographic distances (Å) and angles (deg) for *out*,*out*-**1**·(Au(2,6-C_6H_3-(Trip)$_2$))$_2$·OEt_2.

	Chain 1	Chain 2	Chain 3
P(1)···P(2)		10.769(2)	
Au(1)···Au(2)[a]		15.0266(9)	
Au(1)···Au(1)[b]		13.157(1)	
Au(2)···Au(2)[b]		11.2621(6)	
Au(1)···Au(2)[b]		10.4888(6)	
Au(1)-C(43)		2.058(5)	
Au(2)-C(79)		2.059(5)	
Au(1)-P(1)		2.2805(14)	
Au(2)-P(2)		2.2770(13)	
P(1)-C(1/15/29)	1.828(7)	1.823(6)	1.820(7)
P(2)-C(14/28/42)	1.833(5)	1.825(5)	1.827(5)
C(1/15/29)-C(2/16/30)	1.534(7)	1.530(7)	1.544(8)
C(2/16/30)-C(3/17/31)	1.553(8)	1.515(7)	1.500(8)
C(3/17/31)-C(4/18/32)	1.552(8)	1.540(8)	1.536(8)
C(4/18/32)-C(5/19/33)	1.507(8)	1.511(7)	1.508(8)
C(5/19/33)-C(6/20/34)	1.563(8)	1.510(8)	1.457(8)
C(6/20/34)-C(7/21/35)	1.462(8)	1.536(8)	1.567(8)
C(7/21/35)-C(8/22/36)	1.502(8)	1.499(9)	1.537(8)

C(8/22/36)-C(9/23/37)	1.511(7)	1.584(8)	1.526(7)
C(9/23/37)-C(10/24/38)	1.533(7)	1.431(9)	1.525(6)
C(10/24/38)-C(11/25/39)	1.523(7)	1.540(8)	1.519(6)
C(11/25/39)-C(12/26/40)	1.527(6)	1.477(8)	1.524(6)
C(12/26/40)-C(13/27/41)	1.531(6)	1.534(7)	1.528(6)
C(13/27/41)-C(14/28/42)	1.518(6)	1.523(7)	1.531(6)
C(43)-Au(1)-P(1)		178.97(15)	
C(79)-Au(2)-P(2)		178.81(15)	
Au(1)-P(1)-C(1/15/29)	112.6(2)	115.3(2)	117.9(2)
Au(2)-P(2)-C(14/28/42)	114.42(18)	110.79(19)	114.55(17)
C(1/15/29)-P(1)-C(15/29/1)	101.8(3)	104.9(3)	102.4(4)
C(14/28/42)-P(2)-C(28/42/14)	105.6(3)	105.4(3)	105.3(3)
P(1)-C(1/15/29)-C(2/16/30)	114.2(4)	112.0(4)	120.3(5)
P(2)-C(14/28/42)-C(13/27/41)	113.3(4)	112.1(4)	117.4(4)
C(1/15/29)-C(2/16/30)-C(3/17/31)	110.7(6)	111.7(5)	115.9(7)
C(2/16/30)-C(3/17/31)-C(4/18/32)	116.8(7)	112.2(6)	113.7(7)
C(3/17/31)-C(4/18/32)-C(5/19/33)	117.8(7)	112.3(6)	123.8(10)
C(4/18/32)-C(5/19/33)-C(6/20/34)	116.6(8)	113.1(6)	110.8(8)
C(5/19/33)-C(6/20/34)-C(7/21/35)	114.7(7)	115.6(7)	119.0(8)
C(6/20/34)-C(7/21/35)-C(8/22/36)	112.4(7)	114.2(8)	105.9(7)
C(7/21/35)-C(8/22/36)-C(9/23/37)	114.6(7)	97.4(8)	115.1(6)
C(8/22/36)-C(9/23/37)-C(10/24/38)	112.7(5)	102.7(9)	112.7(5)
C(9/23/37)-C(10/24/38)-C(11/25/39)	111.3(5)	116.6(10)	114.8(5)
C(10/24/38)-C(11/25/39)-C(12/26/40)	114.4(5)	113.4(9)	113.0(5)
C(11/25/39)-C(12/26/40)-C(13/27/41)	114.2(5)	109.4(7)	113.7(4)
C(12/26/40)-C(13/27/41)-C(14/28/42)	112.8(4)	117.7(6)	112.6(4)
Au(1)-P(1)-P(2)		172.5	
Au(2)-P(2)-P(1)		147.4	

[a]Intramolecular. [b]Shortest intermolecular distance.

Table s5. Key crystallographic distances (Å) and angles (deg) for *out*,*out*-**1'**·(Au(2,6-C$_6$H$_3$-(Trip)$_2$))$_2$.

	Chain 1	Chain 2	Chain 3
P(1)···P(2)		11.3104(6)	
Au(1)···Au(1')[a]		15.4884(8)	
Au(1)···Au(1)[b]		9.4408(5)	
Au(1)-C(1)		2.070(5)	
Au(1)-P(1)		2.2746(15)	
P(1)-C(44/57'/37)	1.816(6)	1.846(7)	1.817(7)
C(44/57'/37)-C(45/56'/38)	1.531(10)	1.545(9)	1.528(9)

C(45/56'/38)-C(46/55'/39)	1.544(8)	1.515(10)	1.511(10)
C(46/55'/39)-C(47/54'/40)	1.555(15)	1.502(10)	1.530(10)
C(47/54'/40)-C(48/53'/41)	1.498(14)	1.548(10)	1.522(11)
C(48/53'/41)-C(49/52'/42)	1.514(14)	1.541(9)	1.544(12)
C(49/52'/42)-C(50/51'/43)	1.508(14)	1.561(15)	1.519(12)
C(50/51'/43)-C(51/50'/43')	1.559(16)		1.536(15)
C(1)-Au(1)-P(1)		176.81(15)	
Au(1)-P(1)-C(44/57'/37)	111.9(2)	110.1(2)	114.6(2)
C(44/57'/37)-P(1)-C(57'/37/44)	104.3(3)	110.4(3)	104.9(3)
P(1)-C(57'/37/44)-C(56'/38/45)	112.6(5)	119.1(5)	113.5(4)
C(44/57'/37)-C(45/56'/38)-C(46/55'/39)	117.0(8)	112.8(6)	113.9(6)
C(45/56'/38)-C(46/55'/39)-C(47/54'/40)	110.7(9)	114.8(6)	114.7(6)
C(46/55'/39)-C(47/54'/40)-C(48/53'/41)	114.0(10)	114.3(6)	113.6(7)
C(47/54'/40)-C(48/53'/41)-C(49/52'/42)	112.4(9)	108.8(8)	114.8(7)
C(48/53'/41)-C(49/52'/42)-C(50/51'/43)	113.4(9)	117.9(12)	114.6(7)
C(49/52'/42)-C(50/51'/43)-C(51/50'/43')	113.6(10)	116.6(11)	112.1(8)
Au(1)-P(1)-P(1')		152.5	

[a]Intramolecular. [b]Shortest intermolecular distance.

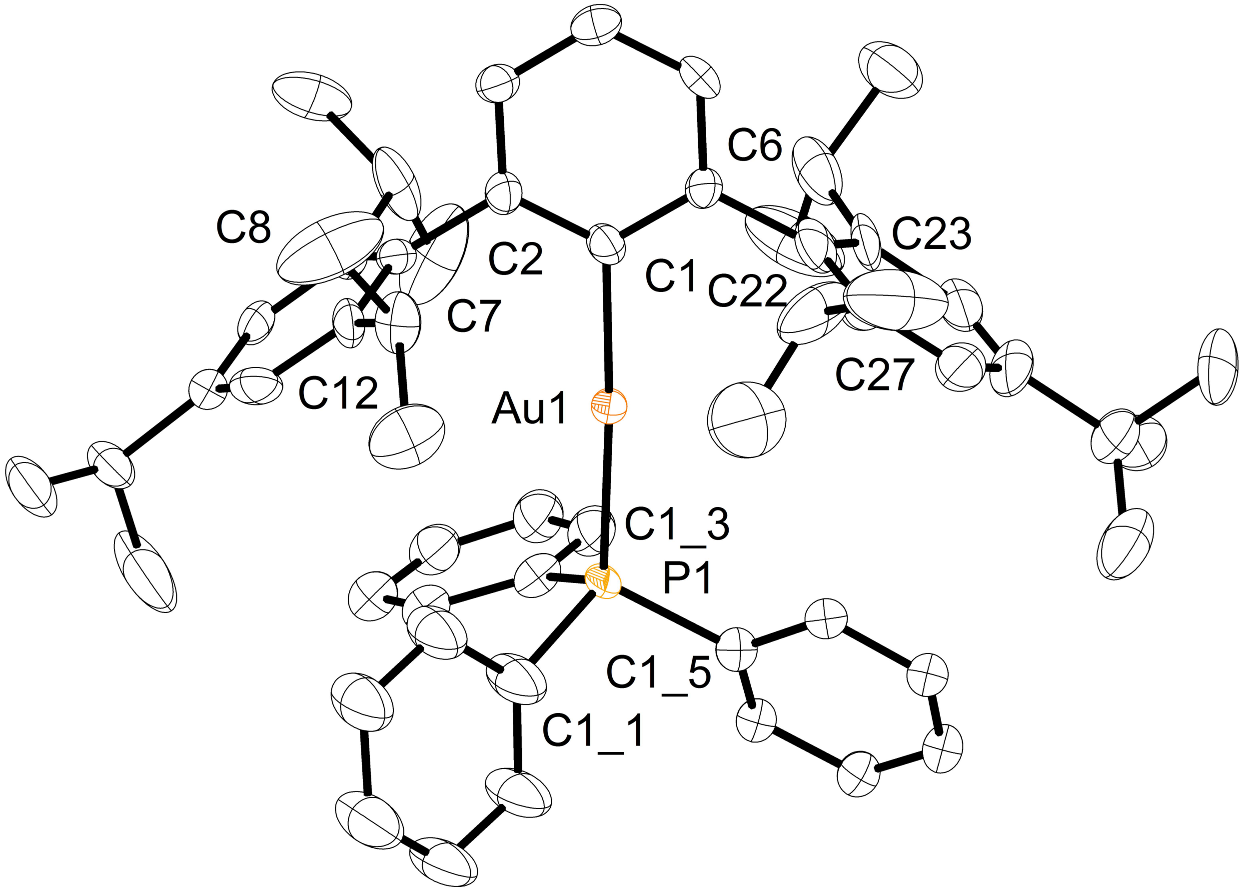

Figure s1. Thermal ellipsoid plot of the molecular structure of **3** (50% probability level). The dominant confirmation is depicted (see experimental paragraph for further details).

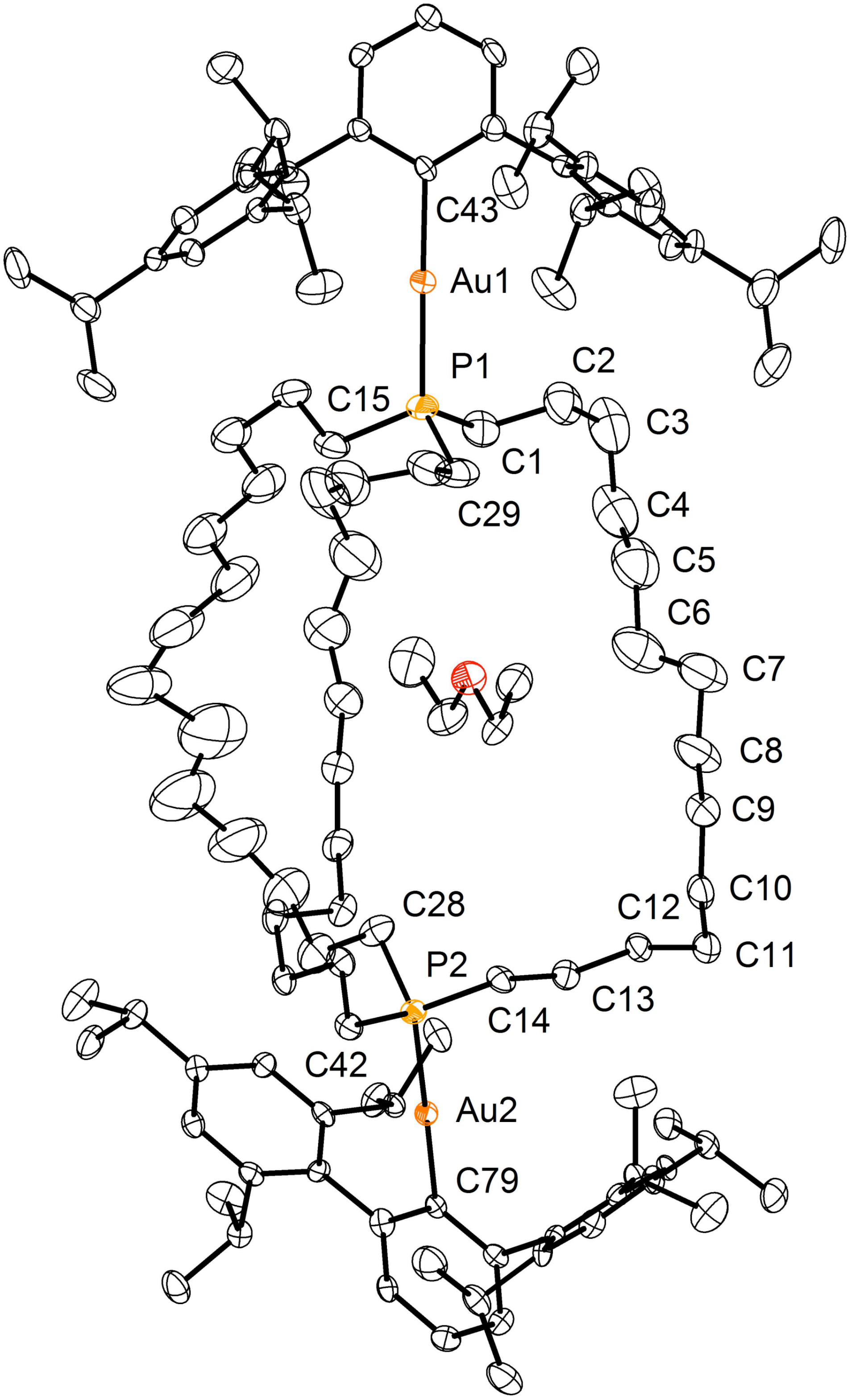

Figure s2. Thermal ellipsoid plot of the molecular structure of *out*,*out*-**1**·(Au(2,6-C_6H_3(Trip)$_2$))$_2$ ·OEt_2 (50% probability level).

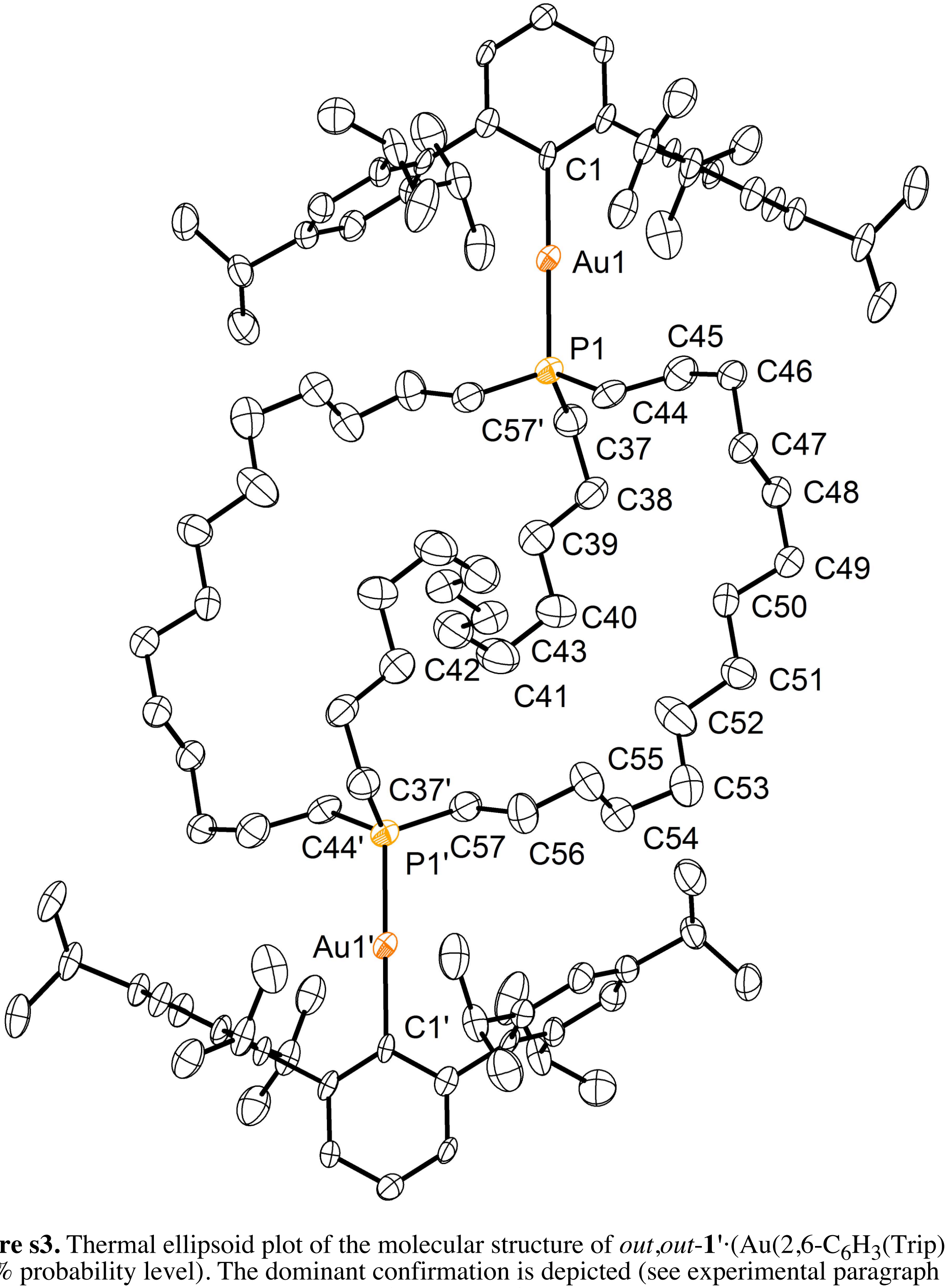

Figure s3. Thermal ellipsoid plot of the molecular structure of *out*,*out*-**1'**·(Au(2,6-C_6H_3(Trip)$_2$))$_2$ (50% probability level). The dominant confirmation is depicted (see experimental paragraph for further details).

Table s6. Powder X-ray Data.

Compound	*out,out*-**1**·(Au(2,6-$C_6H_3(Trip)_2$))$_2$·OEt_2	*out,out*-**1'**·(Au(2,6-$C_6H_3(Trip)_2$))$_2$
Empirical formula	$C_{118}H_{192}OP_2Au_2$	$C_{114}H_{182}P_2Au_2$
Temperature [K]	110(2)	110(2)
Diffractometer	Bruker D8 GADDS	Bruker D8 GADDS
Wavelength [Å]	1.54056	1.54056
Space group	*P*na2$_1$	*P*2$_1$/c
Unit cell dimensions		
a [Å]	47.8414253	13.1043679
b [Å]	13.2258989	24.4930209
c [Å]	17.5958420	17.7644314
α [°]	90	90
β [°]	90	108.7101
γ [°]	90	90
Volume [Å^3]	11133.69605	5400.45206
R indices	Rexp' = 5.67	Rexp' = 8.24
	Rwp' = 2.88	Rwp' = 4.64

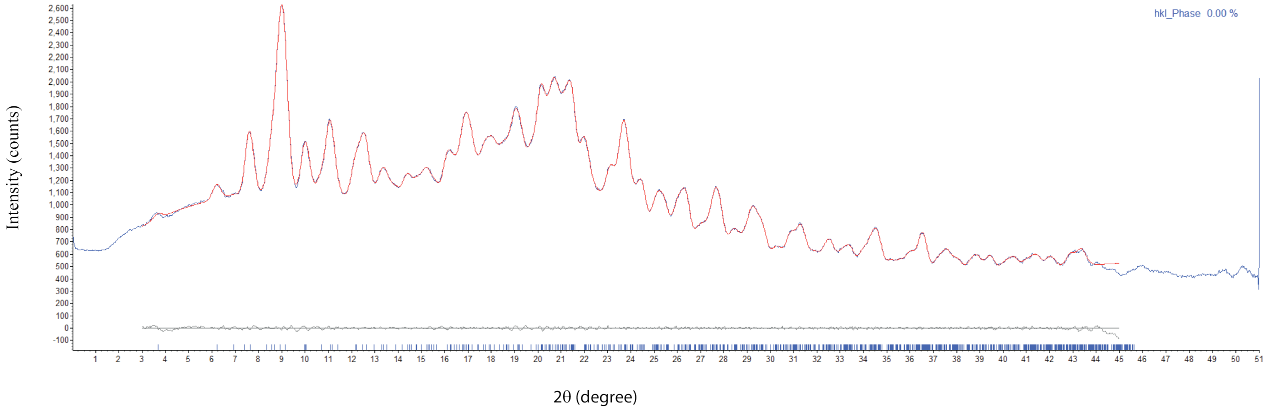

Figure s4. X-ray powder (red) diffraction pattern of *out,out*-**1**·(Au(2,6-$C_6H_3(Trip)_2$))$_2$·OEt_2. superimposed onto the single crystal (blue) X-ray diffraction data (further details: see above).

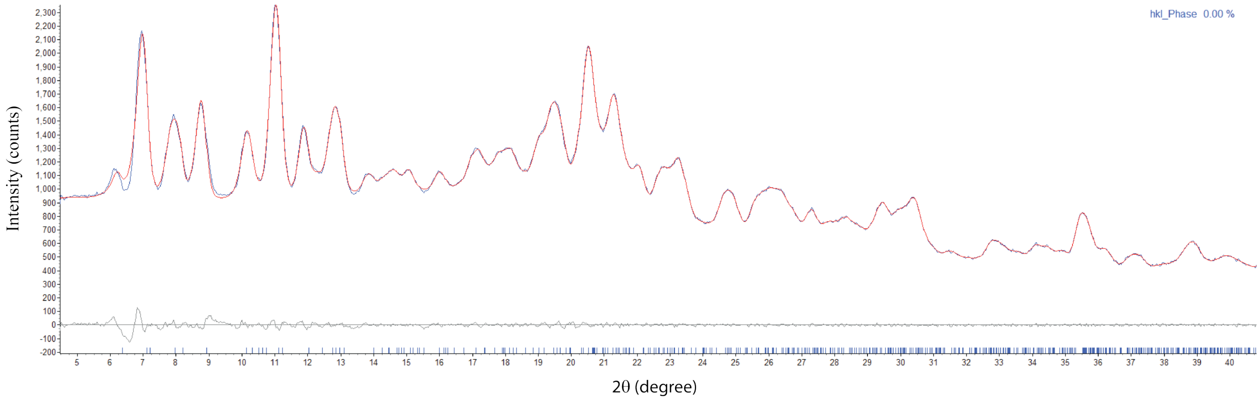

Figure s5. X-ray powder (red) diffraction pattern of *out,out*-**1'**·(Au(2,6-$C_6H_3(Trip)_2$))$_2$ imposed over the single crystal (blue) X-ray diffraction data (further details: see above).