

Supporting Information

**The First Crystal Structure of a Reactive Dirhodium Carbene Complex
and a Versatile Method for the Preparation of Gold Carbenes by
Rhodium-to-Gold Transmetalation**

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CRYSTALLOGRAPHIC SECTION

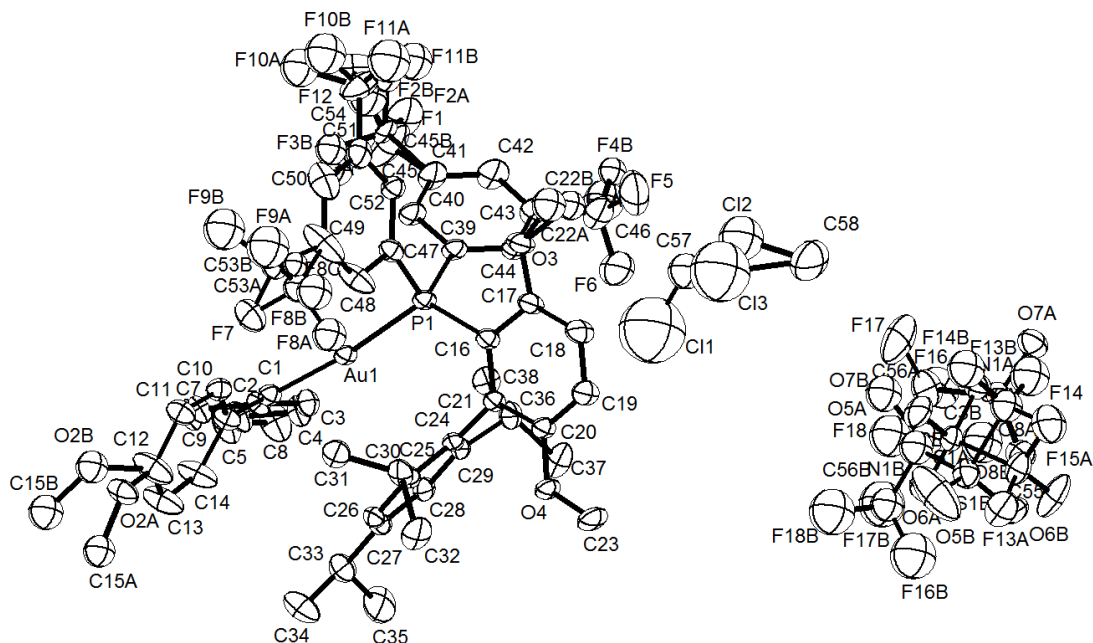
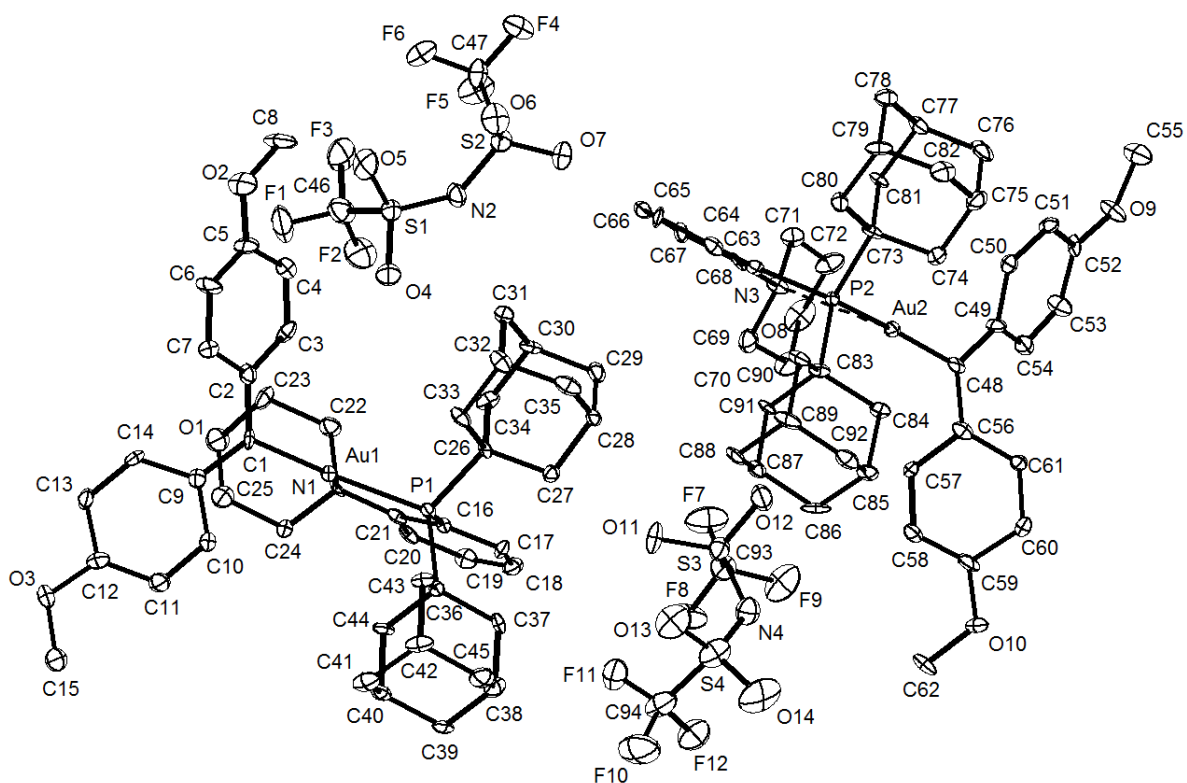


Figure S1. Molecular structure of the gold carbenoid 6b in the solid state.

X-ray Crystal Structure Analysis of Complex 6b: $2(\text{C}_{54}\text{H}_{51}\text{AuF}_{12}\text{O}_4\text{P}) \cdot 2(\text{C}_2\text{F}_6\text{NO}_4\text{S}_2) \cdot 1.5(\text{CH}_2\text{Cl}_2)$, $M_r = 3127.45 \text{ g} \cdot \text{mol}^{-1}$, orange prism, crystal size $0.05 \times 0.11 \times 0.15 \text{ mm}^3$, triclinic, space group $P1$, $a = 12.4946(9) \text{ \AA}$, $b = 15.0801(10) \text{ \AA}$, $c = 18.5620(13) \text{ \AA}$, $\alpha = 66.395(6)$, $\beta = 74.422(7)$, $\gamma = 76.135(5)^\circ$, $V = 3052.3(4) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 1$, $D_{\text{calc}} = 1.701 \text{ g} \cdot \text{cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 2.679 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{\text{min}} = 0.72282$, $T_{\text{max}} = 0.88336$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $2.628 < \theta < 32.576^\circ$, 69224 measured reflections, 22150 independent reflections, 19212 reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.056$. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.053 [I > 2\sigma(I)]$, $wR_2 = 0.150$, 892 parameters. The CF_3 groups, the bis(trifluoromethylsulfonyl)imide anion, and the dichloromethane solute are disordered. The anion is disordered over two positions with unequal refined occupancy (0.76:0.24). Apart from two F atoms of the minor component of the disordered anion, all non-H atoms were located in a difference Fourier synthesis and refined. Disordered atoms were refined with isotropic atomic displacement parameters,

unless the partial atoms belonged to a major component. One trifluoromethyl group on the minor component was restrained to C_{3v} symmetry with an effective standard deviation of 0.02 on the interatomic distances (9 restraints), H atoms riding, $S = 1.064$, residual electron density 2.22 (0.06 Å from C11)/ -3.58 (0.67 Å from Au1) $e \text{ \AA}^{-3}$. **CCDC-1415140**.



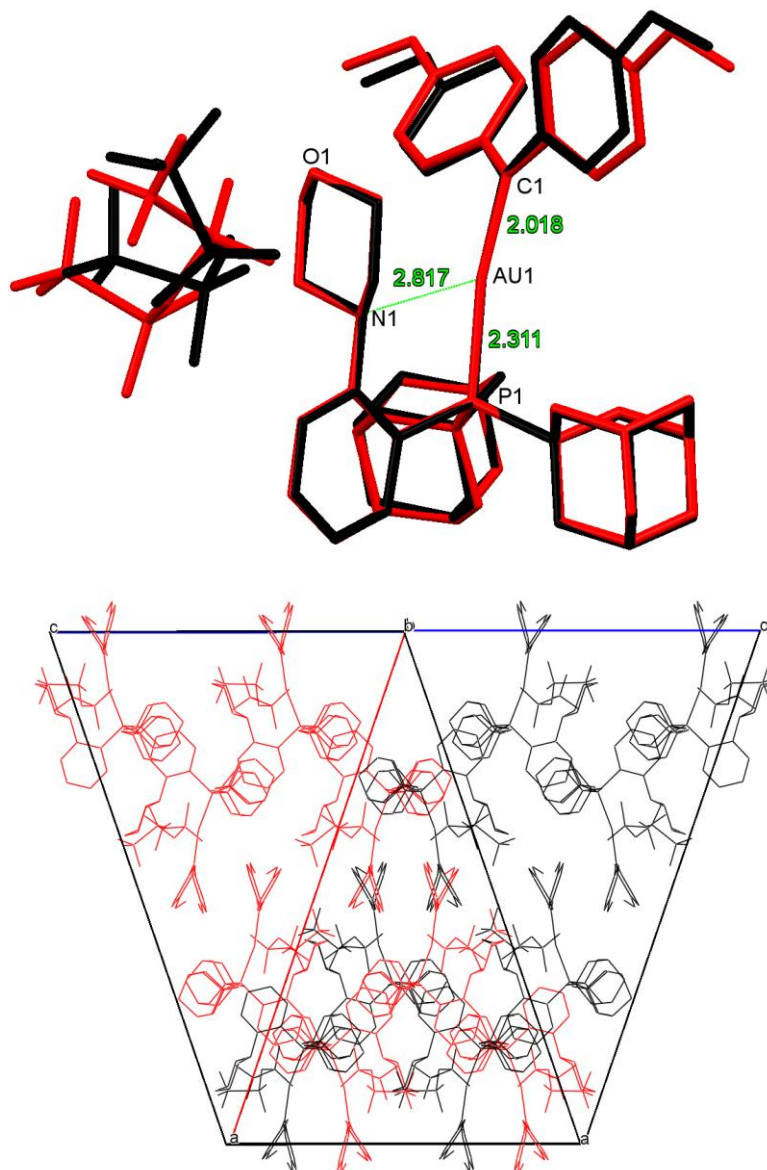


Figure S2. Molecular structure of the gold carbenoid 6c (top), superposition of the two independent ionic pairs in the asymmetric unit, and the nature of the crystal twinning (bottom).

X-ray Crystal Structure Analysis of Complex 6c: $(C_{45}H_{56}AuNO_3P) \cdot (C_2F_6NO_4S_2)$, $M_r = 1166.99 \text{ g} \cdot \text{mol}^{-1}$, red prism, crystal size $0.02 \times 0.05 \times 0.06 \text{ mm}^3$, monoclinic, space group $P2_1/c$, $a = 31.511(6) \text{ \AA}$, $b = 15.5189(11) \text{ \AA}$, $c = 20.487(3) \text{ \AA}$, $\beta = 108.88(3)^\circ$, $V = 9480(3) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 8$, $D_{calc} = 1.635 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 3.302 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{min} = 0.84536$, $T_{max} = 0.93714$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $2.625 < \theta < 33.219^\circ$, 65023 measured reflections, 33471 independent reflections, 18076 reflections with $I > 2\sigma(I)$, $R_{int} = 0.075$. Structure solved by direct

methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.068$ [$I > 2\sigma(I)$], $wR_2 = 0.126$, 1194 parameters. The crystal was pseudo-merohedrally twinned with a twin matrix of [1 0 1 0 -1 0 0 0 -1] and a refined batch scale factor of 0.4108(9). The atomic displacement parameters of several of the lighter atoms (C1 C48 C88 C91 N1 N3) were significantly prolate. The atomic displacement parameters of these atoms were restrained to be isotropic with an effective standard deviation of 0.01 (36 restraints) , H atoms riding, $S = 1.058$, residual electron density 2.28 (0.38 Å from Au2)/ -3.13 (0.72 Å from Au1) e Å⁻³.
CCDC-1415141.

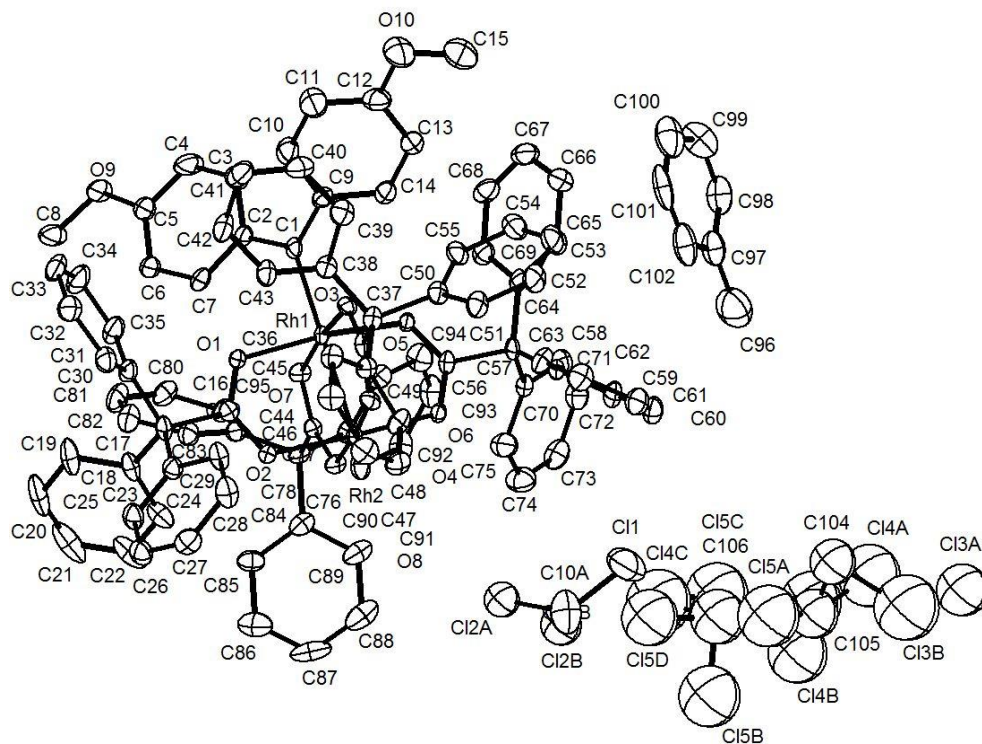


Figure S3. Crystal structure of the dirhodium carbene **4** ($[\text{C}_{95}\text{H}_{74}\text{O}_{10}\text{Rh}_2, \text{C}_7\text{H}_8, 2.5(\text{CH}_2\text{Cl}_2)]_n$, grown from fluorobenzene/ CH_2Cl_2 layered with cold toluene/pentane) in the solid state. Selected distances (Å) and angles (°): C1-Rh1 = 2.061(6), Rh1-Rh2 2.4233(6), Rh2-O9 2.488(5), C1-Rh1-Rh2 176.9(1), Rh1-Rh2-O9 170.6(1).

X-ray Crystal Structure Analysis of Complex 4 (grown from fluorobenzene/ CH_2Cl_2): $[\text{C}_{95}\text{H}_{74}\text{O}_{10}\text{Rh}_2, \text{C}_7\text{H}_8, 2.5(\text{CH}_2\text{Cl}_2)]_n$, $M_{r(n=1)} = 1885.81 \text{ g} \cdot \text{mol}^{-1}$, brown prism, crystal size 0.09 x 0.10 x 0.19 mm³, monoclinic, space group Pn , $a = 11.087(2) \text{ Å}$, $b = 20.565(3) \text{ Å}$, $c = 19.907(3) \text{ Å}$, $\beta = 101.362(3)^\circ$, $V = 4450.0(12) \text{ Å}^3$, $T = 100 \text{ K}$, $Z = 2$, $D_{\text{calc}} = 1.407 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ Å}$, $\mu(\text{Mo-K}\alpha) = 0.582 \text{ mm}^{-1}$, Gaussian integration (SADABS) absorption correction ($T_{\text{min}} = 0.93947$, $T_{\text{max}} = 0.96856$), Bruker AXS Mach3 $1\mu\text{S}$ Apex II diffractometer, $3.284 < \theta < 33.236^\circ$, 146147 measured reflections, 33710 independent reflections, 26755 reflections with $I > 2s(I)$, $R_{\text{int}} = 0.062$. Structure solved by direct methods (SHELXT) and refined by full-matrix least-squares (SHELXL) against F^2 to $R_1 = 0.059 [I > 2\sigma(I)]$, $wR_2 = 0.163$, 33710 parameters. The crystals contain solute dichloromethane and toluene, which were easily lost. The toluene molecule was located and refined using anisotropic atomic displacement parameters for the C atoms. The remaining region of the crystal was occupied by disordered dichloromethane. One solute dichloromethane molecule could be well resolved, with one Cl atom disordered over two positions, each with half occupancy. For the remaining

region a model of 1.5 disordered dichloromethane molecules was applied. Disordered atoms were refined with isotropic atomic displacement parameters. H atoms were calculated and refined using a riding model. Most likely bonding interactions were estimated for calculating the positions of the H atoms in the disordered region. The crystal investigated is an inversion twin with a refined batch scale factor for the minor component of 0.19(3). Several low-angle reflections ($> 6.3 \text{ \AA}$) were shadowed by the beamstop and removed from the dataset. $S = 0.981$, residual electron density $3.58 (0.77 \text{ \AA from Rh1}) / -1.92 (0.64 \text{ \AA from Rh1}) \text{ e \AA}^{-3}$. **CCDC-1428230**.

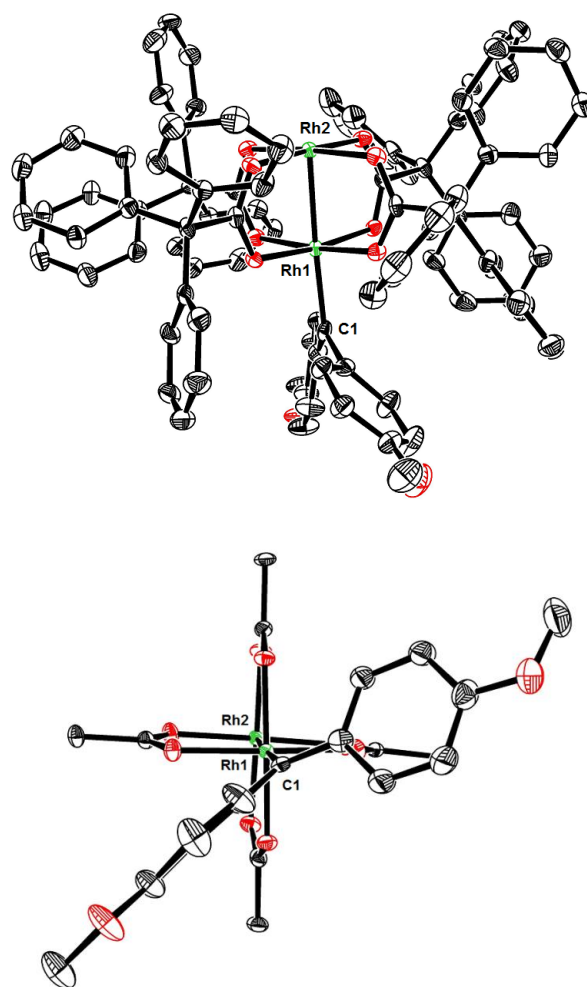


Figure S4. Crystal structure of the dirhodium carbene **4** (grown from fluorobenzene/ CH_2Cl_2 layered with cold toluene/pentane) in the solid state. Top: structure of the complex (without solutes); bottom: Newman-type projection along the C1-Rh1-Rh2 axis of the monomer, which shows the alignment of one of the *p*-MeOC₆H₄-rings with the carbene center and the eclipsed orientation of the entire carbene moiety relative to the dirhodium cage (its lateral phenyl rings are removed for clarity)

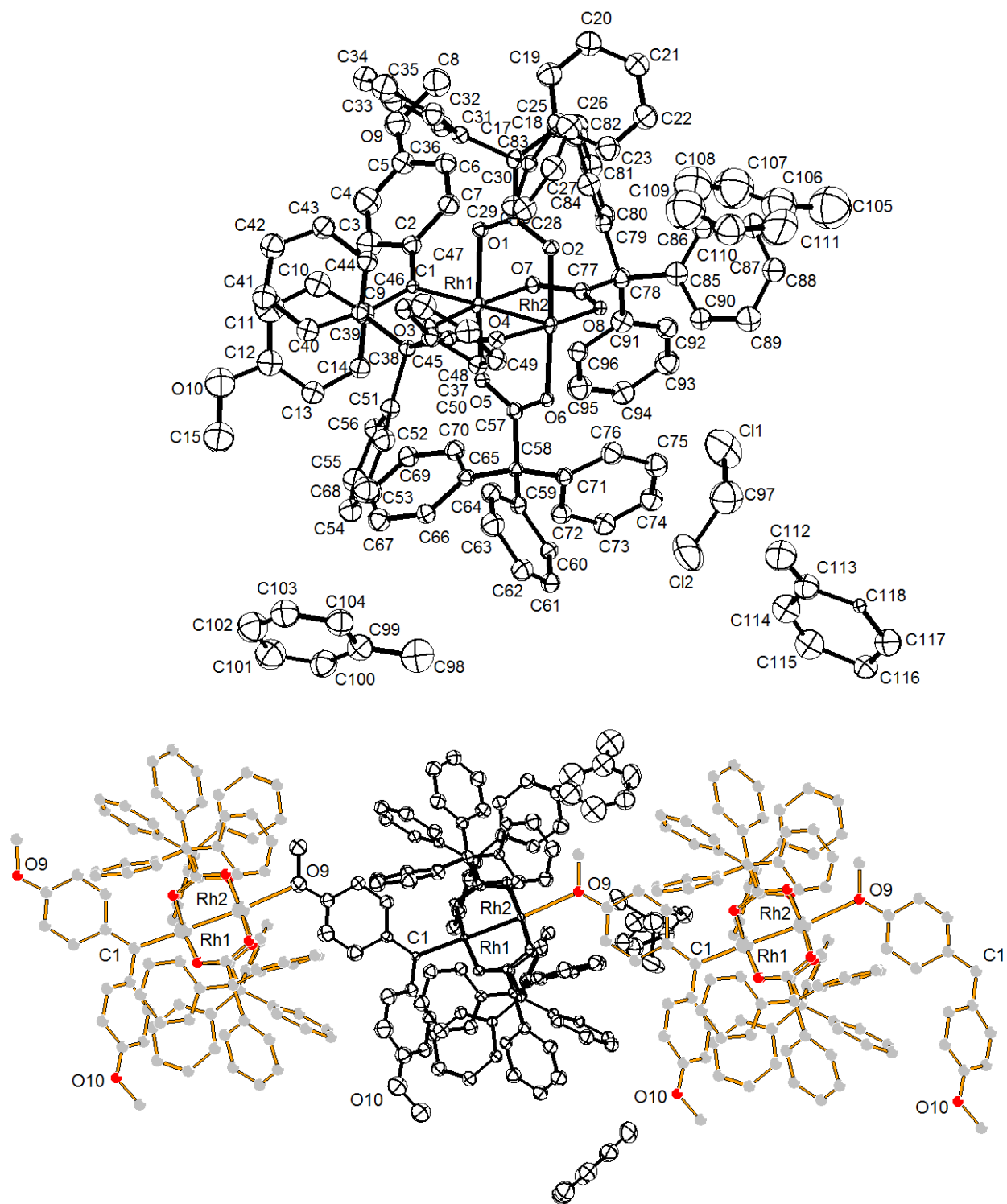


Figure S5. Crystal structure of the rhodium carbene 4 (grown from CH_2Cl_2 /toluene) in the solid state. Top: Monomer unit. Bottom: Part of the polymer chain; all atoms apart from Rh and Cl were restrained to be isotropic with an effective standard deviation of 0.001 (764 restraints)

X-ray Crystal Structure Analysis of Complex 4 (grown from CH₂Cl₂/toluene): $[2(\text{C}_{95}\text{H}_{74}\text{O}_{10}\text{Rh}_2) \cdot 5(\text{C}_7\text{H}_8) \cdot 2(\text{CH}_2\text{Cl}_2)]_n$, $M_{r(n=1)} = 3793.23 \text{ g} \cdot \text{mol}^{-1}$, brown plate, crystal size 0.04 x 0.10 x 0.23 mm³, monoclinic, space group Pn , $a = 11.165(2) \text{ \AA}$, $b = 20.554(4) \text{ \AA}$, $c = 20.287(4) \text{ \AA}$, $\beta = 100.424(3)^\circ$, $V = 4578.9(16) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 1$, $D_{\text{calc}} = 1.376 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 0.482 \text{ mm}^{-1}$, multi-scan absorption correction ($T_{\text{min}} = 0.8751$, $T_{\text{max}} = 1.0$), Bruker AXS Mach3 $1\mu\text{S}$ Apex II diffractometer, $3.189 < \theta < 26.823^\circ$, 94762 measured reflections, 18745 independent reflections, 14236 reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.098$. Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.076 [I > 2\sigma(I)]$, $wR_2 = 0.224$, 1186 parameters. The crystals contain solvent dichloromethane and toluene, which were easily lost. One solute toluene molecule was refined with half occupancy. The crystal investigated is an inversion twin with a refined batch scale factor for the minor component of 0.18(5). All atoms apart from Rh and Cl were restrained to be isotropic with an effective standard deviation of 0.001 (764 restraints). The relatively small atomic displacement parameter of the carbene C atom compared with the larger atomic displacement of the unbound methoxy O atom indicate that chain termination groups may be present in the crystal. One solute toluene molecule was refined with half occupancy. The atomic displacement parameters of one C atom in one of the solute toluene molecules are smaller than those of their neighbours, indicating that this toluene molecule may be partially occupied by dichloromethane, H atoms riding, $S = 1.456$, residual electron density 2.49 (0.98 \AA from Rh2)/ -1.45 (0.83 \AA from Rh1) e \AA^{-3} . **CCDC-1415142.**

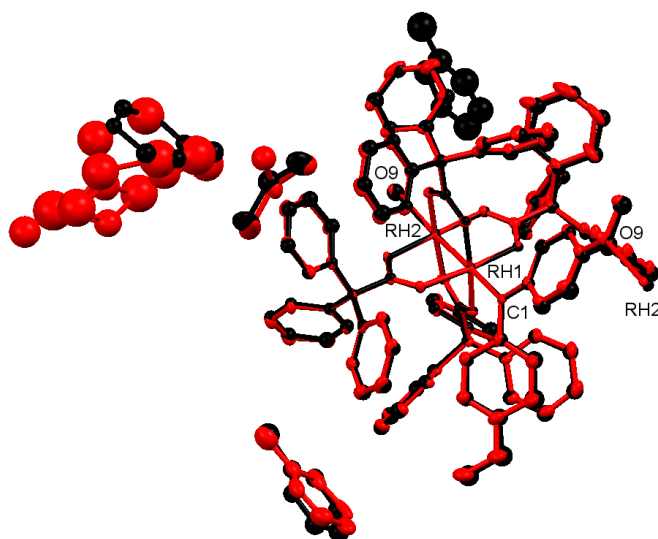
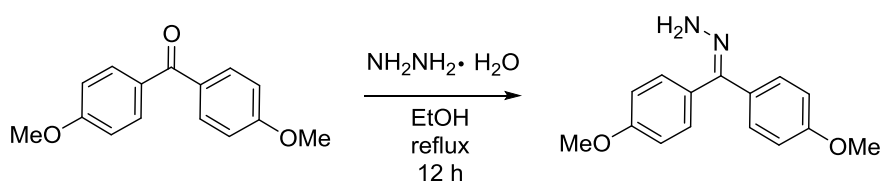


Figure S6. Superposition of a monomer unit of $[2(\text{C}_{95}\text{H}_{74}\text{O}_{10}\text{Rh}_2) \cdot 5(\text{C}_7\text{H}_8) \cdot 2(\text{CH}_2\text{Cl}_2)]_n$, (CCDC-1415142, black), with that of $[\text{C}_{95}\text{H}_{74}\text{O}_{10}\text{Rh}_2, \text{C}_7\text{H}_8, 2.5(\text{CH}_2\text{Cl}_2)]_n$, (CCDC-1428230, red), showing the similar conformation of the di-rhodium coordination polymer despite different crystal environments.

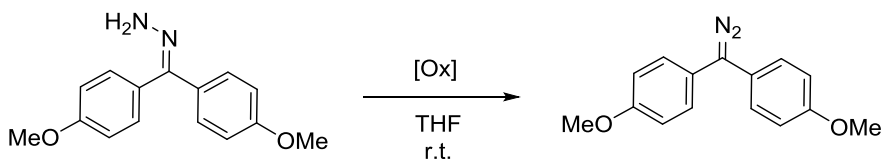
General. All reactions were carried out under argon in flame-dried glassware, ensuring rigorously inert conditions. The solvents were purified by distillation over the indicated drying agents: Et₂O (Mg/anthracene), CH₂Cl₂ (CaH₂), pentane (Na/K). NMR: Spectra were recorded on Bruker AV 400 or AV 500 spectrometers at the indicated temperatures with the chemical shifts (δ) given in ppm relative to TMS and the coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CD₂Cl₂: δ_c = 54 ppm; residual CHDCl₂ in CD₂Cl₂: δ_H = 5.32 ppm).

Bis(4-methoxyphenyl)methylene)hydrazine.



A mixture of 4,4'-dimethoxybenzophenone (7.0 g, 28.89 mmol) and hydrazine monohydrate (14 mL, 288.9 mmol) in EtOH (20 mL) was stirred at reflux temperature for 12 h. The solvent was distilled off under vacuum (10⁻³ mbar), the residue was taken up in ethyl acetate, and the resulting solution was washed with water (3 x 20 mL). The organic phase was dried over Na₂SO₄ and the solvent evaporated to give the title compound which was used without further purification (6.7 g, 90% yield), the analytical and spectroscopic data are consistent with those previously reported in the literature.¹

Bis(4-methoxyphenyl)diazomethane.



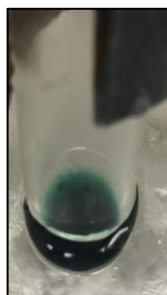
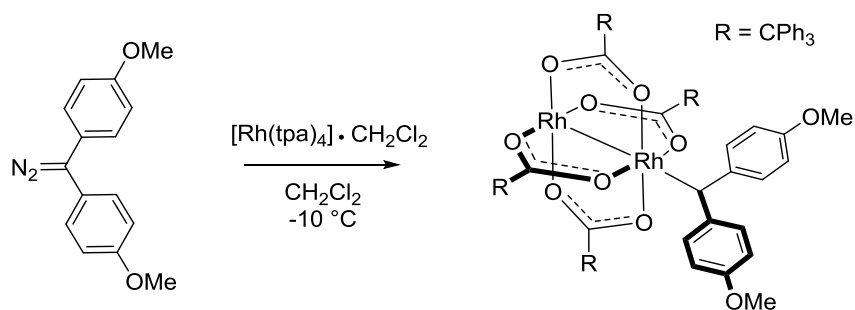
Method A: To a slurry of HgO (6.59 g, 30.43 mmol), Na₂SO₄ (5.4 g, 38.04 mmol) and bis(4-methoxyphenyl)methylene)hydrazine (6.5 g, 25.36 mmol) in THF (50 mL) were added 5-10 drops of a saturated solution of KOH in EtOH. The reaction mixture was wrapped in aluminum foil and stirred until TLC indicated full conversion. Filtration through a pad of Celite followed by removal of the solvent under

¹ P. J. Davis, L. Harris, A. Karim, A. L. Thompson, M. Gilpin, M. G. Moloney, M. J. Pound, C. Thompson, *Tetrahedron Lett.*, **2011**, 52, 1553-1556.

reduced pressure and washing of the residue with pentane (2 x 5 mL) gave the title compound as a purple solid (6.207 g, 96% yield).

Method B: A solution of $\text{Pb}(\text{OAc})_4$ (11.88 g, 26.8 mmol) in CH_2Cl_2 (40 mL) was added over 60 min to a solution of the hydrazone (5.299 g, 20.7 mmol) in CH_2Cl_2 (30 mL) at -20°C , causing an immediate appearance of a deep purple/violet color. Once the addition was complete, the mixture was allowed to reach ambient temperature and stirring was continued for 60 min. The reaction was quenched with water (50 mL), the organic phase was dried over Na_2SO_4 and evaporated to give the product as a violet solid (5.162 g, 98%). The material can be recrystallized from CH_2Cl_2 /pentane (1:6). Its analytical and spectroscopic data are consistent with those previously reported in the literature.¹

Complex 4.

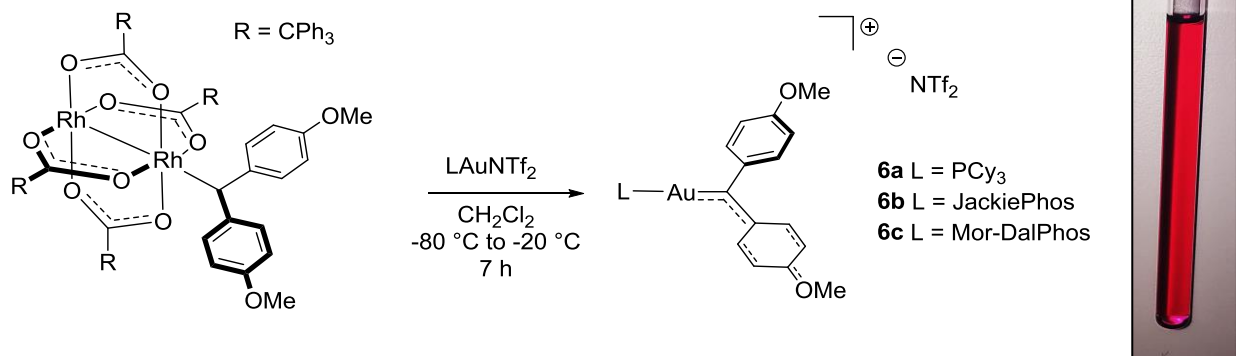


Solutions of $[\text{Rh}(\text{tpa})_4] \cdot \text{CH}_2\text{Cl}_2$ (30 mg) and **3** (5.3 mg) in dry CH_2Cl_2 (1 mL each) were prepared under rigorously inert conditions and chilled to -10°C . The solution containing **3** was quickly added to the $[\text{Rh}(\text{tpa})_4] \cdot \text{CH}_2\text{Cl}_2$ solution without stirring, leading to a vigorous effervescence and a concomitant color change to dark turquoise. Crystals suitable for X-ray diffraction could be obtained by layering the solution with cold pentane/toluene (1:1) at -20°C .

^1H NMR (500 MHz, CD_2Cl_2 , 253 K): $\delta = 7.50$ (d, $J = 8.9$, 4H, H_3), 7.04 (t, $J = 7.3$, 12H, H_{12}), 6.79 (t, $J = 7.7$, 24H, H_{11}), 6.47 (d, $J = 9.0$, 4H, H_4), 6.43 (d, $J = 7.3$, 24H, H_{10}), 3.82 (s, 6H, H_6); ^{13}C NMR (126 MHz, CD_2Cl_2 , 253 K):² $\delta = 268.9$ (C_1), 190.7 (C_7), 164.8 (C_5), 148.1 (C_2), 143.3 (C_9), 135.8 (C_3), 130.8 (C_{10}), 127.4 (C_{11}), 126.7 (C_{12}), 113.9 (C_4), 69.0 (C_8), 56.2 (C_6); IR (film, cm^{-1}): 3057, 2926, 1588, 1491, 1445, 1364, 1251, 1169, 1036, 809, 746, 699; HRMS (ESI⁺): calcd. for $[\text{C}_{95}\text{H}_{74}\text{O}_{10}\text{Rh}_2]^+$: 1580.33725; found 1580.33844.

² The ^{13}C -signals were determined by ^1H - ^{13}C HSQC/ ^1H - ^{13}C HMBC.

General procedure for the preparation of the gold carbenoids 6a-c

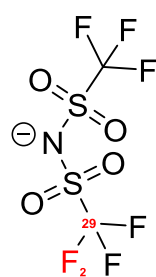
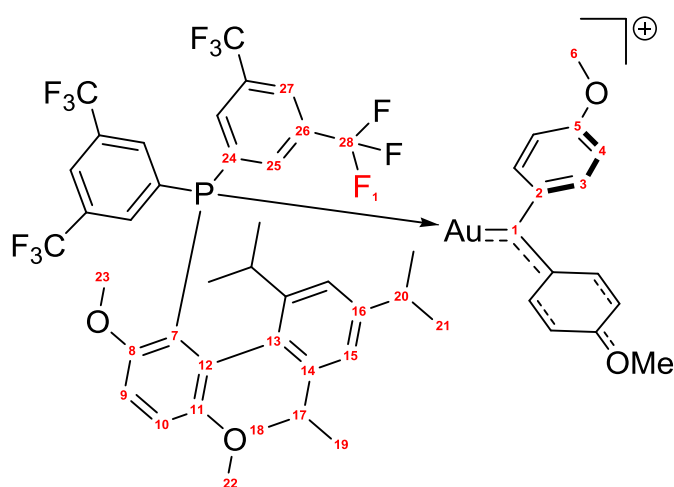


A solution of [LAuNTf₂] in CH₂Cl₂ (1 mL) was added dropwise at –78 °C to a freshly prepared solution of complex **4** (*vide supra*) in CH₂Cl₂ (2 mL) and the resulting mixture was stirred at this temperature for 5 h. The temperature was then allowed to slowly rise to –10 °C (cryostat) and stirring was continued at this temperature for 4 h. The solvent was carefully distilled off in high vacuum (10^{–4} mbar) at –10 °C. The residue was dissolved in cold Et₂O (1 mL, –20 °C) and the resulting solution was slowly cooled to –80 °C to give a mixture of dark red, bright-red or green microcrystalline materials. The supernatant was syphoned off via cannula and the solid material dissolved in cold CH₂Cl₂ (1 mL, –20 °C). The solution was carefully layered with cold Et₂O (2 mL, –20 °C) and the mixture was again cooled to –80 °C. The mother liquor was removed via cannula and the bright red crystalline residue dissolved in cold CH₂Cl₂ (1 mL, –20 °C). The solution was then carefully layered with cold pentane (1 mL, –20 °C) and cold toluene (1 mL, –20 °C), and was slowly cooled to –80 °C to give bright red/pink crystals of the gold carbenoid suitable for X-ray diffraction.

Complex 6a. Prepared from [Rh(tpa)₄]•CH₂Cl₂ (190 mg, 0.13 mmol), **3** (34 mg, 0.13 mmol) and [(Cy)₃PAuNTf₂] (100 mg, 0.13 mmol) as a pink crystalline material (83 mg, 64% yield). The spectroscopic data are consistent with those previously reported in the literature;³ IR (film, cm^{–1}): 2931, 2855, 1350, 1191, 1135, 1059, 612.

³ G. Seidel, A. Fürstner, *Angew. Chem. Int. Ed.* **2014**, *53*, 4807-4811; *Angew. Chem.* **2014**, *126*, 4907-4911.

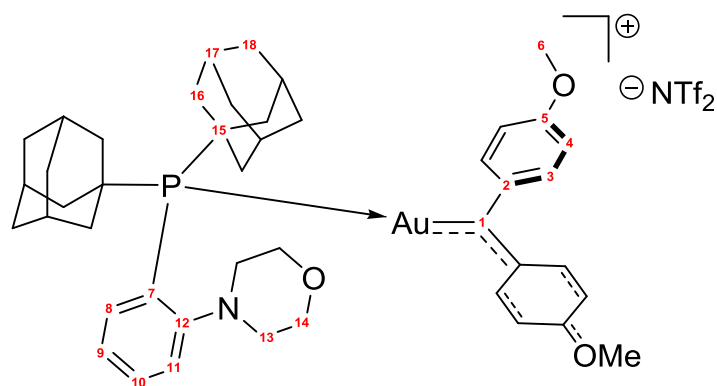
Complex 6b. Prepared from $[\text{Rh}(\text{tpa})_4]\bullet\text{CH}_2\text{Cl}_2$ (113 mg, 0.08 mmol), **3** (20 mg, 0.08 mmol) and



$[(\text{JackiePhos})\text{AuNTf}_2]$ (100 mg, 0.08 mmol) as a pink/red crystalline material (34 mg, 29% yield). ^1H NMR (500 MHz, CD_2Cl_2 , 273 K) δ = 8.10 (s, 2H, H_{27}), 7.92 (d, J = 12.1, 4H, H_{25}), 7.46 (d, J = 9.0, 4H, H_3), 7.40 (d, J = 9.2, 1H, H_{10}), 7.15 (dd, J = 9.3, 4.1, 1H, H_9), 7.10 (d, J = 9.0, 4H, H_4), 6.95 (s, 2H, H_{15}), 4.05

(s, 6H, H_6), 3.70 (s, 3H, H_{22}), 3.46 (s, 3H, H_{23}), 2.46 (hept, J = 6.2, 2H, H_{17}), 2.30 (hept, J = 6.9, 1H, H_{20}), 1.04 (d, J = 6.9, 6H, H_{19}), 0.96 (d, J = 6.7, 6H, H_{18}), 0.79 (d, J = 6.9, 6H, H_{21}); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2 , 273 K): δ = 274.7 (d, J = 103.7, C_1), 170.6 (C_5), 155.8 (d, J = 1.6, C_8), 153.6 (d, J = 14.3, C_{11}), 149.6 (C_{16}), 147.5 (C_{14}), 143.2 (d, J = 2.1, C_3), 142.5 (C_2), 137.2 (d, J = 22.2, C_{12}), 133.4 (d, J = 13.1, C_{25}), 133.0 (d, J = 54.6, C_{24}), 132.6 (qd, J = 34.2, 11.2, C_{26}), 131.4 (d, J = 9.2, C_{13}), 125.6 (C_{27}), 123.1 (q, J = 274.0, 273.5, C_{28}), 122.8 (C_{15}), 120.2 (q, J = 322.0, C_{29}), 118.8 (d, J = 1.8, C_{10}), 116.2 (C_4), 112.8 (d, J = 5.1, C_9), 112.0 (d, J = 57.1, C_7), 57.5 (C_6), 56.0 (C_{22}), 55.6 (C_{23}), 33.7 (C_{20}), 31.7 (C_{17}), 24.9 (C_{18}), 23.7 (C_{19}), 23.4 (C_{21}); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 273 K): δ = 30.2; $^{19}\text{F}\{^1\text{H}\}$ NMR (470 MHz, CD_2Cl_2 , 273 K): δ = -63.3 (F_1), -79.7 (F_2); IR (film, cm^{-1}): 2966, 1355, 1279, 1187, 1129, 1057; HRMS (ESI+): calcd. for $[\text{C}_{54}\text{H}_{51}\text{O}_4\text{AuF}_{12}\text{P}]^+$: 1219.29934; found 1219.30019.

Complex 6c. Prepared from $[\text{Rh}(\text{tpa})_4]\bullet\text{CH}_2\text{Cl}_2$ (153 mg, 0.11 mmol), **3** (27 mg, 0.11 mmol) and $[(\text{Mor-DalPhos})\text{AuNTf}_2]$ (100 mg, 0.11 mmol) as a

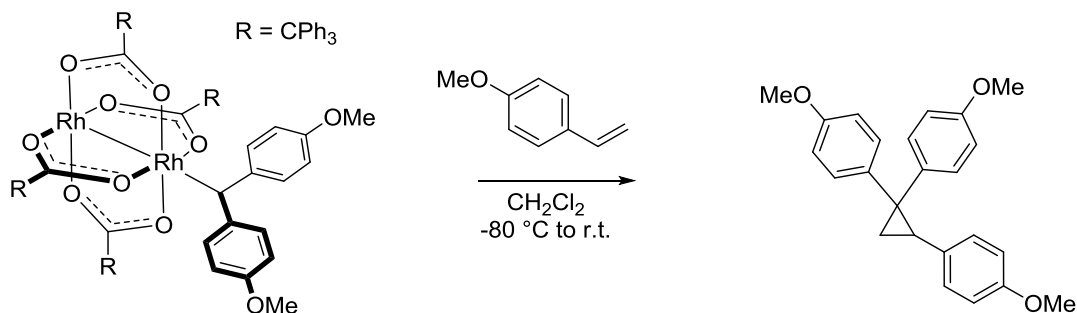


pink/red crystalline material (58 mg, 47% yield). ^1H NMR (500 MHz, CD_2Cl_2 , 273 K): δ = 7.94 (d, J = 8.6, 4H, H_3), 7.84 (t, J = 7.1, 1H, H_8), 7.69 – 7.59 (m, 2H, H_{10} , H_{11}), 7.46 (t, J = 7.4, 1H, H_9), 7.22 (d, J = 8.6, 4H, H_4), 4.05 (s, 6H, H_6), 3.69 (t, J = 11.1, 2H, H_{14a}), 3.60 (d, J = 9.8, 2H, H_{14b}), 3.04 (t, J = 9.9,

2H, H_{13a}), 2.62 (d, J = 11.7, 2H, H_{13b}), 2.32 – 2.10 (m, 12H, H_{16}), 2.04 (br. s, 6H, H_{17}), 1.81 – 1.63 (m, 12H, H_{18}); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2 , 273 K): δ = 289.8 (d, J = 90.1, C_1), 169.8 (C_5), 158.7 (d, J = 8.7, C_{12}),

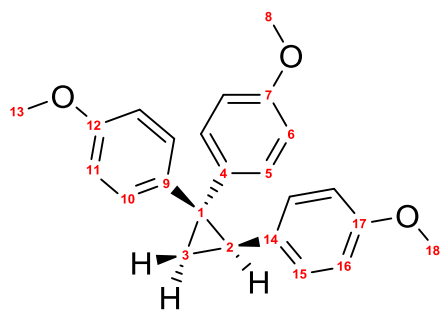
144.0 (C₂), 141.4 (d, *J* = 1.6, C₃), 136.8 (C₈), 133.5 (C₁₀), 127.6 (d, *J* = 4.6, C₁₁), 127.1 (d, *J* = 5.7, C₉), 125.4 (d, *J* = 41.1, C₇), 116.3 (C₄), 67.6 (C₁₄), 57.3 (C₆), 55.1 (C₁₃), 42.7 (d, *J* = 2.8, C₁₆), 42.1 (d, *J* = 19.4, C₁₅), 36.7 (C₁₈), 29.0 (d, *J* = 9.6, C₁₇); ³¹P{¹H} NMR (202 MHz, CD₂Cl₂, 273 K): δ = 55.7; ¹⁵N NMR (51 MHz, CD₂Cl₂, 273 K):⁴ δ = -314.0; IR (film, cm⁻¹): 2958, 2922, 2851, 1355, 1279, 1188, 1139, 1058; HRMS (ESI⁺): calcd. for [C₄₅H₅₆NO₃AuP]⁺: 886.3657; found 886.36536.

Cyclopropanation of 4-Methoxystyrene.



With preformed **4:** When an excess of 4-methoxystyrene (13.9 μL, 0.104 mmol) was added to a dark turquoise solution of complex **4** (33 mg, 0.021 mmol) in CH₂Cl₂ (2 mL) at -78 °C followed by slow warming (cryostat), the dark turquoise color started to fade away leading to a slightly green colored solution when -10 °C was reached. The solution was warmed to ambient temperature and the reaction monitored by GC/MS, which showed that the only low molecular weight product was the desired cyclopropane, which was identified by comparison with authentic material (see below).

Reference Material: A solution of bis-4-(methoxyphenyl)diazomethane (100 mg, 0.39 mmol) in pentane (5.0 mL) was added dropwise over 1 h at room temperature to a solution of [Rh(tpa)₄]•CH₂Cl₂ (2.8 mg, 0.002 mmol) and 4-methoxystyrene (0.26 mL, 1.97 mmol) in pentane (3 mL). After complete addition the mixture was stirred for 1 h before the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (10% ethyl acetate/hexane) to give the title compound as a white solid (94 mg, 66% yield). ¹H NMR (400 MHz, CD₂Cl₂, 300 K): δ = 7.22 (d, *J* = 8.9, 2H, H₅), 7.01 (d, *J* = 8.8, 2H, H₁₀), 6.83 (d, *J* = 8.7, 2H, H₁₅), 6.79 (d, *J* = 8.9, 2H, H₆), 6.65 (d, *J* = 8.7, 2H, H₁₁), 6.65 (d, *J* = 8.8, 2H, H₁₆), 3.75 (s,



⁴ Recorded by ¹H/¹⁵N HMBC.

3H, H₈), 3.70 (s, 3H, H₁₈), 3.69 (s, 3H, H₁₃), 2.72 (dd, *J* = 9.0, 6.6, 1H, H₂), 1.82 (dd, *J* = 6.4, 5.3, 1H, H_{3a}), 1.64 (dd, *J* = 9.0, 5.2, 1H, H_{3b}); ¹³C{¹H} NMR (101 MHz, CD₂Cl₂, 300 K): δ = 158.4 (C₇), 158.4 (C₁₂), 158.2 (C₁₇), 140.5 (C₄), 133.8 (C₁₄), 132.3 (C₁₀), 131.6 (C₉), 129.5 (C₁₅), 129.2 (C₅), 114.2 (C₆), 113.8 (C₁₆), 113.6 (C₁₁), 55.8 (C₈), 55.6 (C₁₃), 55.6 (C₁₈), 38.2 (C₁), 31.6 (C₂), 20.6 (C₃); HRMS (ESI⁺): calcd. for [C₂₄H₂₄O₃Na]⁺: 383.16176; found 383.16184.

