Supporting Information

Aurophilic Self-Assembly of a Mo₄Au₂ Phosphinidene Complex with an Unprecedented H-Shaped Planar Metal Core

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General Procedures and Starting Materials All manipulations and reactions were carried out under a nitrogen (99.9995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures,¹ and distilled prior to use. Petroleum ether refers to that fraction distilling in the range 65-70 °C. The compounds $[Mo_2Cp_2(\mu-\kappa^1:\kappa^1,\eta^6-PR^*)(CO)_2]$ (1), $[Mo_2Cp(\mu-\kappa^1:\kappa^1,\eta^5-PC_5H_4)(\eta^6-HR^*)(CO)_2]$ (2) (Cp= $\eta^5-C_5H_5$, R*= 2,4,6-C_6H_2'Bu_3),^2 and [AuCl(THT)] (THT= SC₄H₈),³ were prepared as described previously. All other reagents were obtained from the usual commercial suppliers and used as received. Filtrations were performed using diatomaceous earth unless otherwise stated. IR C–O stretching frequencies were measured in solution, are referred to as ν (CO) (solvent), and are given in cm⁻¹. Nuclear Magnetic Resonance (NMR) spectra were routinely recorded at 300.13 (¹H), 121.50 (³¹P{¹H}) or 75.47 MHz (¹³C{¹H}) at 290 K in CD₂Cl₂ solutions unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane or external 85% aqueous H₃PO₄ solutions (³¹P). Coupling constants (*J*) are given in Hz. The molar conductivity (Λ_M) of **6** was measured at room temperature, using 10⁻³ molL⁻¹ acetone solutions and is given in $\Omega^{-1}cm^2mol^{-1}$.

Preparative Procedures, Spectroscopic and Microanalytical Data for New Compounds.

Reaction of Compound 1 with [AuCl(THT)]. Solid [AuCl(THT)] (0.010 g, 0.031 mmol) was added to a CH₂Cl₂ solution (3 mL) of compound 1 (0.030 g, 0.020 mmol), and the mixture was stirred for 1 min to give a bright-red solution. Solvent was then removed under vacuum and the residue was extracted with CH₂Cl₂-petroleum ether (1:1, 10 mL), and the extract filtered. Removal of the solvents under vacuum gave a solid shown (by ³¹P and ¹H RMN) to be a mixture of the isomers $[AuMo_2ClCp_2(\mu-\kappa^1:\kappa^1,\eta^6-PR^*)(CO)_2]$ (3), and $[AuMo_2ClCp(\mu-\kappa^1:\kappa^1:\kappa^1,\eta^5-\mu^2)]$ PC_5H_4)(CO)₂(η^6 -HR*)] (4), in a ratio 3/4= 5. Full isomerization of 3 into 4 was accomplished by heating the above mixture in 1,2-dichloroethane solution (3 mL) at 313 K for 10 min. The violet resulting solution was then filtered and the solvent removed under vacuum from the filtrate to give compound 4 (0.020 g, 82 %) as a violet solid. Spectroscopic data for compound 3: ν (CO) (CH₂Cl₂): 1932 (vs), 1864 (s). ³¹P {¹H} NMR: δ 400.2 (s, br, μ_3 -PR*). ¹H NMR: δ 5.77 (s, br, 1H, C₆H₂), 5.72 (s, br, 1H, C₆H₂), 5.50 (s, 5H, Cp), 5.19 (d, J_{PH}= 2, 5H, Cp), 1.32, 1.26, 1.22 (3 x s, 3 x 9H, ^tBu). Data for compound 4: Anal. Calcd for C₃₀H₃₉ClAuMo₂O₂P: C, 40.63; H, 4.43. Found: C, 40.22; H, 4.60. ν(CO) (CH₂Cl₂): 1942 (vs), 1870 (s). ³¹P{¹H} NMR (C₆D₆): δ370.1 (s, br, μ_3 -PC₅H₄). ¹H NMR (C₆D₆): δ 5.05 (s, 5H, Cp), 4.97 (m, br, 4H, C₆H₃ and C₅H₄), 4.71 (m, 2H, C₅H₄), 4.00 (br, 1H, C₅H₄), 1.09 (s, 27H, ^{*t*}Bu) ppm.

Preparation of $[AuMo_2Cp_2(\mu_3 - \kappa^1 : \kappa^1, \eta^6 - PR^*)(CO)_2(THT)](PF_6)$ (5). A CH₂Cl₂ solution (5 mL) of $[Au(THT)_2][PF_6]$ (0.040 mmol) was prepared in situ by stirring [AuCl(THT)] (0.013 g,

0.040 mmol) and TIPF₆ (0.015g, 0.043mmol) in the presence of THT (0.1 mL, excess) for 5 min. The solution was filtered using a canula and then added to a solution of compound **1** (0.025 g, 0.038 mmol) in CH₂Cl₂ (1 mL), to give a red solution instantaneously. Solvent was then removed under vacuum, the residue was extracted with toluene (5 mL), and the extract was filtered with a canula. Removal of the solvent under vacuum gave compound **5** as a red microcrystalline solid (0.032 g, 77%). The crystals used in the X-ray study of **5** were grown by slow diffusion at 253 K of a layer of diethyl ether into a concentrated solution of the complex in CH₂Cl₂. Anal. Calcd for C₃₄H₄₇F₆AuMo₂O₂P₂S: C, 37.65; H, 4.37. Found: C, 37.62; H, 4.40. ν (CO) (CH₂Cl₂): 1937 (vs), 1869 (s). ³¹P{¹H} NMR: δ 420.0 (s, μ_3 -PR*). ¹H NMR: δ 5.88 (s, br, 2H, C₆H₂), 5.55, 5.24 (2 x s, 2 x 5H, Cp), 3.43, 2.16 (2 x m, br, 2 x 4H, CH₂), 1.46, 1.36 (2 x s, br, 2 x 9H, *o-'*Bu), 1.26 (s, 9H, *p-'*Bu).

Preparation of $[{AuMo_2Cp(\mu_3 - \kappa^1 : \kappa^1, \eta^5 - PC_5H_4)(CO)_2(\eta^6 - HR^*)}_2](PF_6)_2$ (6). <u>Method A:</u> Solid TIPF₆ (0.009 g, 0.026 mmol) was added to a CH₂Cl₂ solution (4 mL) of compound 4 (0.020 g, 0.023 mmol), and the mixture was stirred for 5 min to give a green suspension. Solvent was then removed under vacuum, the residue was extracted with MeCN (10 mL) and the extract was filtered. Removal of the solvent from the filtrate and washing of the residue with petroleum ether (3 mL) gave compound **6** as a green microcrystalline solid (0.020 g, 89 %). The crystals used in the X-ray study of 6 were grown by slow diffusion at 253 K of a layer of diethyl ether and CH₂Cl₂ into a concentrated solution of the complex in acetone. Anal. Calcd for C₆₀H₇₈F₁₂Au₂Mo₄O₄P₃: C, 36.16; H, 3.95. Found: C, 36.06; H, 3.91. Λ_{M} : 176. ν (CO) (MeCN): 1942 (vs), 1880 (s). ³¹P{¹H} NMR (acetone- d_6) δ 347.9 (s, μ_3 -PC₅H₄). ¹H NMR (acetone- d_6) δ 6.86 (s, 1H, C₆H₃), 6.74 (s, br, 2H, C₆H₃ and C₅H₄), 6.35, 5.96 (2 x m, 2 x 1H, C₅H₄), 5.87 (s, 5H, Cp), 5.45 (s, 1H, C₆H₃), 5.23 (m, 1H, C₅H₄), 1.28 (s, br, 27H, ^tBu). <u>Method B</u>: Using a canula, a CH₂Cl₂ solution (3 mL) of compound 2 (0.023g, 0.035 mmol) was slowly added (5 min) to a filtered CH₂Cl₂ solution (5 mL) of [Au(THT)₂][PF₆] (0.034 mmol), the latter being prepared in situ by stirring [AuCl(THT)] (0.011 g, 0.034 mmol) and TlPF₆ (0.013 g, 0.037 mmol) in the presence of THT (0.1 mL, excess)for 5 min. A green suspension was formed immediately, and the mixture was further stirred for 15 min. The solvent was then removed and the residue washed with CH₂Cl₂-petroleum ether (1:1, 5 mL). Workup of the washed residue as described above yielded compound 6 as a green microcrystalline solid (0.018 g, 80 %).

X-ray Structure Determination for Compound 5. Data collection for $5 \cdot CH_2Cl_2$ was performed at 100(2) K on a Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu-K α radiation ($\lambda = 1.5418$ Å). Images were collected at a 65 mm fixed crystal-detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image (7-

35 s). Data collection strategy was calculated with the program CrysAlis Pro CCD.⁴ Data reduction and cell refinement was performed with the program CrysAlis Pro RED.⁴ An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED.⁴ Using the program suite WinGX,⁵ the structure was solved by Patterson interpretation and phase expansion, and refined with full-matrix least squares on F^2 using SHELXL97.⁶ During the solution process, the compound was found to crystallize with a molecule of dichloromethane. During the final stages of the refinement, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined anisotropically, except for atom C(21), which was refined isotropically to prevent its temperature factors from becoming non-positive definite. All hydrogen atoms were geometrically placed and refined using a riding model.

X-ray Structure Determination for Compound 6. Data collection, reduction and absorption correction for 6.2CH₂Cl₂ was performed as described for **5** (exposure time per image 10-40 s). Using the program suite WinGX,⁵ the structure was solved by direct methods using SIR92,⁷ and refined with full-matrix least squares on F^2 using SHELXL97.⁶ During the solution process, the cation was found to be placed on an inversion center of the unit cell, and to crystallize with two molecules of dichloromethane. During the final stages of the refinement all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined anisotropically, except for atom C(4), which was refined isotropically to prevent its temperature factors from becoming non-positive definite. All hydrogen atoms were geometrically placed and refined using a riding model.

References

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Figure S-1. ORTEP drawing (30 % probability) of the structure of the cation in compound **5**, with H atoms omitted for clarity.



Figure S-2. ORTEP drawing (30 % probability) of the structure of the cation in compound **6**, with H atoms omitted for clarity.