Photoreactive Gold(I) Macrocycles with Diphosphine and trans, trans-Muconate Ligands

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Electronic Supplementary Information

Synthesis of Complexes: All reactions were performed under pure dry nitrogen or argon using standard Schlenk techniques and apparatus used were wrapped with aluminum foil as the gold compounds are light sensitive. Au₂(µ-dppm)Cl₂ and Au₂(µ-dppe)Cl₂ were prepared according to standard literature procedures.6c

1: Silver trifluoroacetate (0.044 g, 0.2 mmol) was added to a suspension of Au₂(dppm)Cl₂ (0.085 g, 0.1 mmol) in THF (10 mL). The mixture was stirred for 1 h and then filtered through Celite to remove AgCl. An aqueous solution of the Na₂muco acid obtained by neutralizing H₂muco (0.014 g, 0.1 mmol) with 0.5 M NaOH in H₂O (4 mL) was added to the resulting filtrate. After stirring for 2 h, the white solid product was collected by filtration, washed with THF and diethyl ether and dried under vacuum. The residue was then recrystallized from C₂H₄Cl₂/MeOH (2:1). Yield: 38.1%. NMR in d₆-DMSO: δ(¹H) 7.35-7.78 (m, 40H, Ph), 4.61 (t, 4H), 6.07 (m, 4H), 7.02 (m, 2H); δ(³¹P) 26.4 (s); IR(KBr)/cm⁻¹: ν(C=O) 1618, ν(P-C₆H₄) 1102. Elemental analysis (%) calcd. for C₆₄H₆₀Au₄O₁₀P₄: C: 40.5, H: 2.83; Found: C: 40.34, H: 2.77. FAB mass: m/z = 1837.3 (calcd 1836.8)

2: Compound 2 was obtained similar to 1, but Au₂(dppe)Cl₂ was used instead of Au₂(dppm)Cl₂. The residue was recrystallized from CH₂Cl₂/MeOH (1:1). Yield: 56.5%. NMR in d₆-DMSO: δ(¹H) 7.53-7.89 (m, 40H, Ph), 2.90 (d, 8H), 6.07 (m, 4H), 7.00 (m, 4H); δ(³¹P) 24.3 (s); IR(KBr)/cm⁻¹: ν(C=O) 1622, ν(P-C₆H₄) 1104. Elemental analysis (%) calcd. for C₆₇H₆₄Au₄Cl₄O₉P₄: C: 40.5, H: 2.83; Found: C: 40.34, H: 2.77. FAB mass: m/z = 1865.5 (calcd 1864.9)
**UV irradiation of complexes:** Photodimerization reactions were carried out using fibre optics of MAX-150 xenon light source (150 W) of 100% intensity and wave length range 280-350 nm.

1: 5-10 mg of compound 1 was packed between two Pyrex glass slides and was irradiated under 5 UV irradiation for 1h on each side of the glass slide respectively. For photodimerization in solution, 5 mg of compound 1 was dissolved in d6-DMSO and the NMR tube was irradiated under UV irradiation for 1h. NMR in d6-DMSO: $\delta$(1H) 7.38-7.73 (m, 40H, Ph), 4.59 (t, 4H), 3.78 (s, 4H), 5.75 (s, 4H); $\delta$(31P) 27.2 (s).

2: Compound 2 was irradiated similar to 1 to obtain the photodimerized product. NMR in d6-DMSO: $\delta$(1H) 7.55-7.86 (m, 40H, Ph), 2.87 (d, 8H), 3.78 (s, 4H), 5.71 (s, 4H); $\delta$(31P) 27.4 (s).

**Crystal Data:** 1, C₆₄H₆₀Au₄O₁₀P₄ (for. wt. 1900.87). Monoclinic space group P2₁/c, $a = 11.2747(10)$, $b = 17.2947(14)$, $c = 16.2187(14)$ Å, $\beta = 103.224(2)^\circ$, $V = 3078.7(5)$ Å³, $Z = 2$, $\rho_{\text{calc}} = 2.051$ g.cm⁻³, $\mu = 9.663$ mm⁻¹, $T = 223(2)$ K, $R1 = 0.0432$, $wR2 = 0.0885$, GOF = 0.987 for 7054 total reflections of which 5412 reflections have $I > 2\sigma(I)$, MoKα-Ray ($\lambda = 71,073$ pm) and R(int) = 0.0598. Each formula unit has two MeOH in the lattice. **CCDC:836596.**

2, C₆₇H₆₄Au₄Cl₄O₉P₄ (for. wt. 2066.73). Triclinic space group P$\overline{1}$, $a = 13.1309(8)$, $b = 20.14.7191(8)$, $c = 18.2436(11)$Å, $\alpha = 80.685(1)$, $\beta = 81.181(1)$ $\gamma = 87.496(1)$ $^\circ$, $V = 3437.8(3)$ Å³, $Z = 2$, $\rho_{\text{calc}} = 1.997$ g.cm⁻³, $\mu = 8.811$ mm⁻¹, $T = 223(2)$ K, $R1 = 0.0547$, $wR2 = 0.1412$, GOF = 0.978 for 15638 total reflections of which 12074 reflections have $I > 2\sigma(I)$, MoKα-Ray ($\lambda = 71,073$ pm) and R(int) = 0.0404. The molecule crystallized with two CH₂Cl₂ and one MeOH. Of these one of the CH₂Cl₂ was disordered with two CH₂Cl fragments pivoted on an un-disordered Cl4. The occupancy was refined to 0.48(3). Distance contraints were applied to this with the option ‘dfix’. **CCDC:836597.**
Fig S1. Molecular structures of the two independent units of 2 (left and right). The hydrogen atoms and solvents are omitted for clarity.

Fig S2. Stack plots of $^1$H NMR during the progress of photodimerization reaction of complex 2 irradiated at room temperature. Only selected region 3.6-7.2 is shown for the clarity.

The $^{31}$P NMR spectra were also recorded. The singlet peak at 26.4 ppm for 1 is shifted slightly to 27.2 ppm and 24.3 ppm for 2 is shifted to 27.4 ppm upon dimerization. This is consistent with the formation of the highly symmetrical cyclooctadiene complex which corroborates with the $^1$H NMR data.
We have recorded solid state $^1$H, $^{13}$C and $^{31}$P-NMR spectra of 1 to shed further lights on the mechanism of formation of [4+4] products. While $^1$H and $^{13}$C were too broad to give any useful information, $^{31}$P-NMR (given below) spectrum gave a single line indicating the formation of a symmetrical compound, i.e., [4+4] product. The spectrum is given below.
Fig. S5. Solid state $^{31}$P-NMR spectrum of the sample 1 after irradiation. The presence of single peak confirms that it is [4+4] product.