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. $Au_2(\mu\text{-dppm})Cl_2$ and $Au_2(\mu\text{-dppe})Cl_2$ were prepared according to standard literature procedures.[6c]

1: Silver trifluoroacetate (0.044 g, 0.2 mmol) was added to a suspension of $Au_2(dppm)Cl_2$ (0.085 g, 0.1mmol) in THF (10 mL). The mixture was stirred for 1h and then filtered through Celite to remove AgCl. An aqueous solution of the Na_2muco acid obtained by neutralizing H_2muco (0.014 g, 0.1 mmol) with 0.5 M NaOH in H_2O (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 $C_2H_4Cl_2$/MeOH (2:1). Yield: 38.1%. NMR in d_6-DMSO: $\delta(^1H)$ 7.35-7.78 (m, 40H, Ph), 4.61 (t, 4H), 6.07 (m, 4H), 7.02 (m, 4H); $\delta(^{31}P)$ 26.4 (s); IR(KBr)/cm^{-1}: ν(C=O) 1618, ν(P-C_{Ph}) 1102. Elemental analysis (%) calcd. for $C_{64}H_{60}Au_4O_{10}P_4$: 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 $Au_2(dppe)Cl_2$ was used instead of $Au_2(dppm)Cl_2$. The residue was recrystallized from CH_2Cl_2/MeOH (1:1). Yield: 56.5%. NMR in d_6-DMSO: $\delta(^1H)$ 7.53-7.89 (m, 40H, Ph), 2.90 (d, 8H), 6.07 (m, 4H), 7.00 (m, 4H); $\delta(^{31}P)$ 24.3 (s); IR(KBr)/cm^{-1}: ν(C=O) 1622, ν(P-C_{Ph}) 1104. Elemental analysis (%) calcd. for $C_{67}H_{64}Au_4Cl_4O_9P_4$: C: 41.2, H: 3.00; Found: C: 41.69, H: 3.05. 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 UV irradiation for 1h on each side of the glass slide respectively. For photodimerization in solution, 5 mg of compound **1** was dissolved in d$_6$-DMSO and the NMR tube was irradiated under UV irradiation for 1h. NMR in d$_6$-DMSO: δ(^{1}H) 7.38-7.73 (m, 40H, Ph), 4.59 (t, 4H), 3.78 (s, 4H), 5.75 (s, 4H); δ(^{31}P) 27.2 (s).

2: Compound **2** was irradiated similar to **1** to obtain the photodimerized product. NMR in d$_6$-DMSO: δ(^{1}H) 7.55-7.86 (m, 40H, Ph), 2.87 (d, 8H), 3.78 (s, 4H), 5.71 (s, 4H); δ(^{31}P) 27.4 (s).

Crystal Data: 1, $C_{64}H_{60}Au_4O_{10}P_4$ (for. wt. 1900.87). Monoclinic space group $P2_1/c$, a = 11.2747(10), b = 17.2947(14), c = 16.2187(14) Å, β = 103.224(2)°, V = 3078.7(5) Å^3, Z = 2, ρ_{calcd} = 2.051 g.cm^{-3}, μ = 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 $I > 2\sigma(I)$, Mo$_{k\alpha}$-Ray (λ = 71,073 pm) and R(int) = 0.0598. Each formula unit has two MeOH in the lattice. **CCDC:836596.**

2, $C_{67}H_{64}Au_4Cl_4O_9P_4$ (for. wt. 2066.73). Triclinic space group $P\bar{1}$, a = 13.1309(8), b = 14.7191(8), c = 18.2436(11)Å, α = 80.685(1), β = 81.181(1) γ = 87.496(1) °, V = 3437.8(3) Å^3, Z = 2, ρ_{calcd} = 1.997 g.cm^{-3}, μ = 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 $I > 2\sigma(I)$, Mo$_{k\alpha}$-Ray (λ = 71,073 pm) and R(int) = 0.0404. The molecule crystallized with two CH_2Cl_2 and one MeOH. Of these one of the $CH_2Cl_2$was disordered with two CH_2Cl 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.**

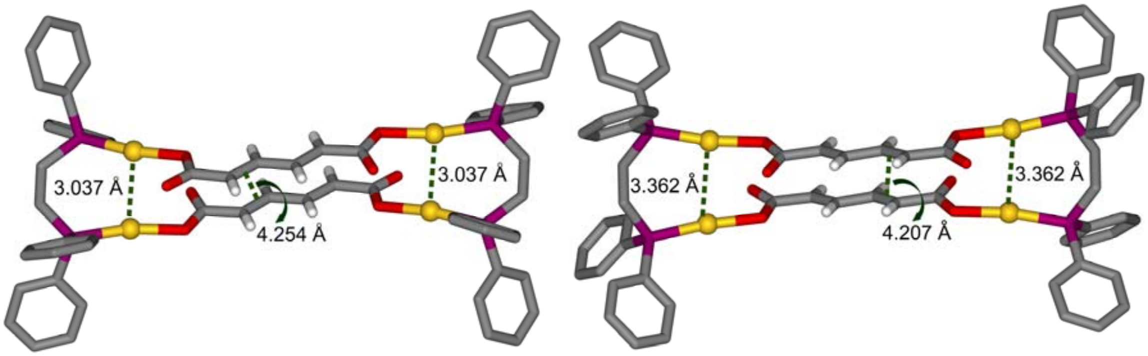

Fig S1. Molecular structures of the two independent units of **2** (left and right). The hydrogen atoms and solvents are omitted for clarity.

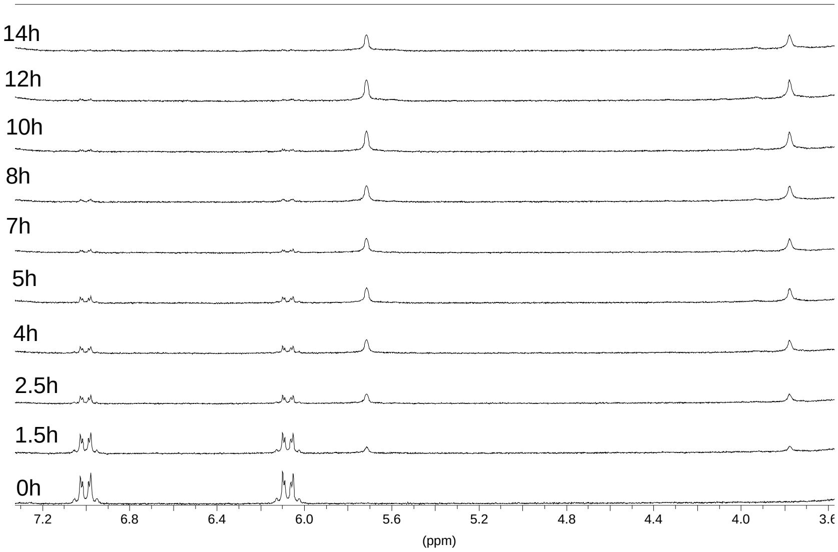

Fig S2. Stack plots of ^{1}H NMR during the progress of photodimerization reaction of complex **2** irradiated at room temperature. Only selected region 3.6-7.2 is shown for the clarity.

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.

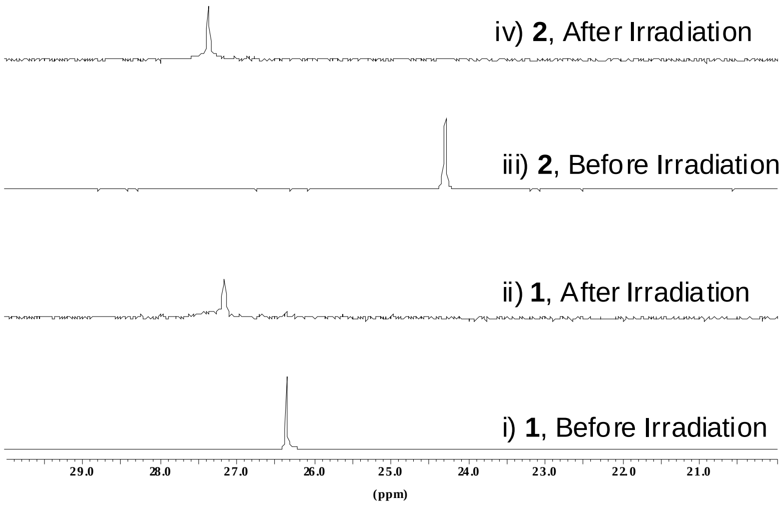

Fig S3. ^{31}P NMR spectra of complex **1** in d$_6$-DMSO i) before and ii) after irradiation and **2** in *d*$_6$-DMSO iii) before and iv) after irradiation under UV lamp.

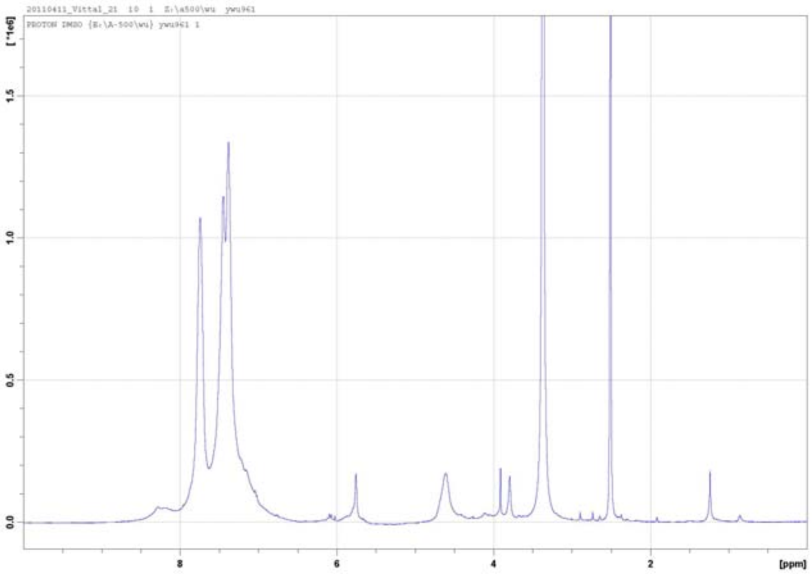

Fig S4. ^{1}H-NMR spectrum of freshly dissolved **1** in *d*$_6$-DMSO shows the presence of cyclooctadiene moiety favors [4+4] cycloaddition reaction.

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.

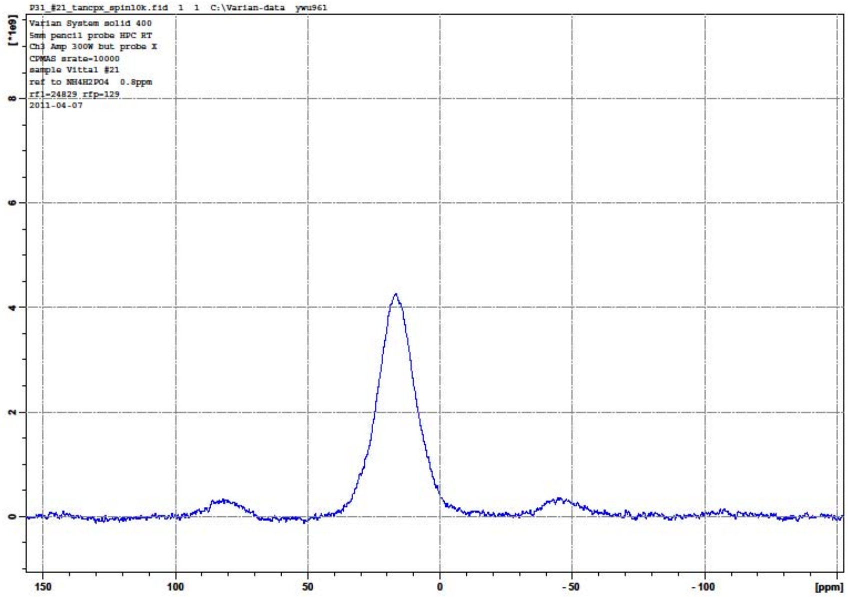

Fig. S5. Solid state ^{31}P-NMR spectrum of the sample **1** after irradiation. The presence of single peak confirms that it is [4+4] product.