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Controlled Self-Assembly of Gold Rings: The First Family of Organometallic Catenanes**

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Supporting Materials

Experimental Procedure *

*Synthesis of the digold (I) diacetylide complex **2***

$[AuCl(SMe_2)]$[1] (0.593 g, 2.01 mmol) was dissolved in the mixed solvents THF (180 mL)/MeOH (120 mL). To the solution was then added a solution of $Me_2C(4\text{-}C_6H_4OCH_2C{\equiv}CH)_2$[2] (0.306 g, 1.01 mmol) and NaO_2CMe (0.412 g, 5.02 mmol) in THF (20 mL)/MeOH (20 mL). The resulting mixture was stirred for 10 h to produce a bright yellow precipitate. The solid was then collected by filtration, washed with MeOH and Et_2O, and dried. Yield: 0.661 g, 94%. The solid is insoluble in common organic solvents. IR (Nujol): ν(C≡C) 2000 (w) cm^{-1}.

*Reaction of **2** with dppe*

A mixture of **2** (0.125 g, 0.180 mmol) and $Ph_2P(CH_2)_2PPh_2$ (0.079 g, 0.198 mmol) in CH_2Cl_2 (50 mL) was stirred for ca. 1 h to give a clear pale pink solution. Activated charcoal was then added to the solution, and the mixture was filtered. The filtrate was concentrated

(ca. 1-2 mL) and addition of Et_2O (100 mL) precipitated a white solid, complex **3a**. The powder was collected by filtration, washed with Et_2O and dried. Yield 0.137 g, 70%. IR (Nujol): ν(C≡C) 2130 (w) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 1.65 (s, 6H, 2Me), 2.51 (m, 4H, $2CH_2$), 4.75 (s, 4H, $2OCH_2$), 7.01 (m, 4H, $2C_6H_4$), 7.23 (m, 4H, $2C_6H_4$), 7.42-7.52 (m, 20H, 4Ph). ^{31}P NMR (CD_2Cl_2, 25 °C): δ = 40.26. ^{13}C NMR (CD_2Cl_2, 25 °C): δ = 24.1 (CH_2), 30.8 (Me), 41.6 ($\underline{C}Me_2$), 56.6 ($O\underline{C}H_2$), 114.9, 127.6 (both C_6H_4), 129.6, 129.7, 132.4, 133.6, 133.7 (all Ph), 143.5, 156.0 (both C_6H_4). Anal. Calcd for $C_{47}H_{42}Au_2P_2O_2$: C 51.57, H 3.87. Found: C 52.04, H 3.95. X-ray quality crystals were grown from slow diffusion of Et_2O into a CH_2Cl_2 solution of complex **3a**.

*Reaction of **2** with dppp*

A mixture of **2** (0.140 g, 0.201 mmol) and $Ph_2P(CH_2)_3PPh_2$ (0.091 g, 0.221 mmol) in CH_2Cl_2 (50 mL) was stirred for ca. 1 h to give a clear pale blue solution. Activated charcoal was then added to the solution, and the mixture was filtered. The filtrate was concentrated (ca. 1-2 mL) and addition of Et_2O (100 mL) precipitated a white solid containing a mixture of complexes **3b**, **4a** and a further unknown species. The powder was collected by filtration, washed with Et_2O and dried. Overall crude yield 0.180 g, 81 %. ^{31}P NMR (CD_2Cl_2, 25 °C): δ = 35.61, 34.56, 34.47, 31.67.

Recrystallisation of the mixture from CH_2Cl_2/Et_2O produced fine white crystals of complex **4a**. IR (Nujol): ν(C≡C) 2132 (w) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 1.42 (s, 6H, 2Me), 1.82 (m, 4H, $2CH_2$), 2.32 (m, 4H, CH_2), 4.55 (s, 4H, $2OCH_2$), 6.13 (m, 4H, $2C_6H_4$), 6.77 (m, 4H, $2C_6H_4$), 7.17-7.45 (m, 20H, 4Ph). ^{31}P NMR (CD_2Cl_2, 25 °C): δ = 31.67. ^{13}C NMR

(CD_2Cl_2, 25 °C): δ = 22.8 (CH_2), 28.3 (CH_2), 30.5 (Me), 40.8 ($\underline{C}Me_2$), 56.9 ($O\underline{C}H_2$), 115.1, 127.1 (both C_6H_4), 129.4, 129.5, 129.6, 131.0, 133.8 (all Ph), 143.0, 155.5 (both C_6H_4). Anal. Calcd for $C_{96}H_{88}Au_4P_4O_4$: C 52.00, H 4.00. Found: C 52.15, H 4.10. X-ray quality crystals were grown from slow diffusion of Et_2O/pentane into a nitrobenzene/MeOH/CH_2Cl_2/$C_2H_4Cl_2$ solution of pure complex **4a**.

*Reaction of **2** with dppb*

A mixture of **2** (0.115 g, 0.165 mmol) and $Ph_2P(CH_2)_4PPh_2$ (0.078 g, 0.183 mmol) in CH_2Cl_2 (50 mL) was stirred for ca. 1 h to give a clear pale blue solution. Activated charcoal was then added to the solution, and the mixture was filtered. The filtrate was concentrated (ca. 1-2 mL) and addition of Et_2O (100 mL) precipitated a white solid, complex **4b**. The powder was collected by filtration, washed with Et_2O and dried. Yield 0.125 g, 68 %. IR (Nujol): ν(C≡C) 2132 (w) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 1.64 (s, 6H, 2Me), 1.74 (m, 4H, $2CH_2$), 2.35 (m, 4H, $2CH_2$), 4.76 (s, 4H, $2OCH_2$), 7.00 (m, 4H, $2C_6H_4$), 7.20 (m, 4H, $2C_6H_4$), 7.42-7.64 (m, 20H, 4Ph). ^{31}P NMR (CD_2Cl_2, 25 °C): δ = 38.73. ^{13}C NMR (CD_2Cl_2, 25 °C): δ = 27.9 (CH_2), 28.4 (CH_2), 31.0 (Me), 41.7 ($\underline{C}Me_2$), 56.8 ($O\underline{C}H_2$), 114.8, 127.7 (both C_6H_4), 129.4, 129.6, 131.9, 133.5, 133.7 (all Ph), 143.5, 156.2 (both C_6H_4). Anal. Calcd for $C_{98}H_{92}Au_4P_4O_4$: C 52.42, H 4.15. Found: C 52.46, H 4.20. X-ray quality crystals were grown from slow diffusion of Et_2O into a $CDCl_3$ solution of complex **4b**.

*Reaction of **2** with dpppe*

A mixture of **2** (0.127 g, 0.182 mmol) and $Ph_2P(CH_2)_5PPh_2$ (0.089 g, 0.202 mmol) in CH_2Cl_2 (50 mL) was stirred for ca. 1 h to give a clear pale pink solution. Activated charcoal was then added to the solution, and the mixture was filtered. The filtrate was concentrated (ca. 1-2 mL) and addition of Et_2O (100 mL) precipitated a white solid, complex **4c**. The powder was collected by filtration, washed with Et_2O and dried. Yield 0.145 g, 70 %. IR (Nujol): ν(C≡C) 2130 (w) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 1.57 (m, 6H, $3CH_2$), 1.64 (s, 6H, 2Me), 2.35 (m, 4H, $2CH_2$), 4.74 (s, 4H, $2OCH_2$), 6.95 (m, 4H, $2C_6H_4$), 7.17 (m, 4H, $2C_6H_4$), 7.43-7.67 (m, 20H, 4Ph). ^{31}P NMR (CD_2Cl_2, 25 °C): δ = 37.36. ^{13}C NMR (CD_2Cl_2, 25 °C): δ = 25.5 (CH_2), 28.0 (CH_2), 31.1 (Me), 32.8 (CH_2), 41.9 ($\underline{C}Me_2$), 56.9 ($O\underline{C}H_2$), 114.7, 127.9 (both C_6H_4), 129.4, 129.6, 131.8, 133.5, 133.7 (all Ph), 143.6, 156.2 (both C_6H_4).

* Gold complexes are protected from light by using darkened flasks throughout.

All NMR spectra were recorded using a 300 MHz Varian Gemini spectrometer.

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[2] A. M. Sladkov, V. V. Korshak, A. G. Makhsumov, *Izv. Akad. Nauk SSSR Ser. Khim.* **1963**, 1343-1345; *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.),* **1963**, 1220-1222.

2 = $[(AuC{\equiv}CCH_2OC_6H_4C(Me)_2C_6H_4OCH_2C{\equiv}CAu)_x]$

3a = $[Au(\mu\text{-}Ph_2P(CH_2)_2PPh_2)Au(\mu\text{-}C{\equiv}CCH_2OC_6H_4C(Me)_2C_6H_4OCH_2C{\equiv}C)]$

3b = $[Au(\mu\text{-}Ph_2P(CH_2)_3PPh_2)Au(\mu\text{-}C{\equiv}CCH_2OC_6H_4C(Me)_2C_6H_4OCH_2C{\equiv}C)]$

4a = $[Au(\mu\text{-}Ph_2P(CH_2)_3PPh_2)Au(\mu\text{-}C{\equiv}CCH_2OC_6H_4C(Me)_2C_6H_4OCH_2C{\equiv}C)]_2$

4b = $[Au(\mu\text{-}Ph_2P(CH_2)_4PPh_2)Au(\mu\text{-}C{\equiv}CCH_2OC_6H_4C(Me)_2C_6H_4OCH_2C{\equiv}C)]_2$

4c = $[Au(\mu\text{-}Ph_2P(CH_2)_5PPh_2)Au(\mu\text{-}C{\equiv}CCH_2OC_6H_4C(Me)_2C_6H_4OCH_2C{\equiv}C)]_2$