

A Step Forward in Gold-Silver Metallophilicity. An AuAg₄ Moiety with a Square Pyramidal Arrangement.

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Electronic Supplementary Information

Experimental section.

NBu₄[Au(3,5-C₆F₃Cl₂)₂] (1): To a freshly prepared diethyl ether solution of Li(3,5-C₆F₃Cl₂) (15 mmol) at -78°C and under an argon atmosphere was added [AuCl(tht)] (1.60 g, 5 mmol). After 30 min. of stirring NBu₄Br (1.77 g, 5.5 mmol) was also added and the mixture was stirred overnight, allowing the temperature to increase slowly. A white precipitate was filtered off and washed with water, diethyl ether and *n*-hexane (3x10 mL). The resulting solid was solved in acetone and dried over anhydrous MgSO₄. Evaporation of the solvent and addition of *n*-hexane afforded complex **1** as a white solid (3.14 g, 74.8 %). Mass spectrum (ES-) *m/z* = 597 ([Au(3,5-C₆F₃Cl₂)₂]⁺). Elemental

analysis (%) calcd. For $C_{28}H_{36}AuF_6Cl_4N$: C 40.07, H 4.32, N 1.67; Found: C 40.11, H 4.58, N 1.71. ^{19}F NMR (282 MHz, $CDCl_3$): δ -89.14 (s, 4F, F_o), -119.11 (s, 2F, F_p). FT-IR (Nujol mulls): $\nu = 882\text{ cm}^{-1}$ (NBu_4^+), $\nu = 1587, 1562, 1047, 775\text{ cm}^{-1}$ (3,5- $C_6F_3Cl_2$). $\Lambda_M = 92\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$.

(NBu_4)₂[Au(3,5- $C_6F_3Cl_2$)₂Ag₄(μ - CF_3CO_2)₅] (2): To a solution of $NBu_4CF_3CO_2$ (0.074 g, 0.2 mmol) and $AgCF_3CO_2$ (0.177 g, 0.8 mmol) in dichloromethane was added complex **1** (0.168 g, 0.2 mmol) and the solution immediately turned yellow. After 30 min. of stirring the solution was concentrated in vacuum to ca. 5 mL and diethyl ether (20 mL) was added to precipitate complex **2** as a yellow solid (0.376 g, 90.4 %). Elemental analysis (%) calcd. For $C_{54}H_{72}AuAg_4F_{21}Cl_4N_2O_{10}$: C 31.20, H 3.50, N 1.35; Found: C 31.27, H 3.54, N 1.37. ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.96 (s, 15F, $CF_3CO_2^-$), δ -83.42 (s, 4F, F_o), -109.50 (s, 2F, F_p). FT-IR (Nujol mulls): $\nu = 887\text{ cm}^{-1}$ (NBu_4^+), $\nu = 1588, 1557, 1057, 793\text{ cm}^{-1}$ (3,5- $C_6F_3Cl_2$), $\nu = 1652, 1210\text{ cm}^{-1}$ ($CF_3CO_2^-$). $\Lambda_M = 208\text{ cm}^{-1}\text{cm}^2\text{mol}^{-1}$.