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Supporting Information

Silver(I) and Gold(I) Carbene Complexes of Cyclic Tetra- and Hexadentate Polycarbene Ligands

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Supplementary material

Synthesis of [**2**]$(Br)_2$

200 mg (0.24 mmol) of the tetraimidazolium salt H_4-**1**$(Br)_4$ and 113 mg (0.48 mmol) Ag_2O were suspended in 20 mL of water. The suspension was stirred at room temperatureand protected from light for 16 h and afterwards warmed to 35°C for one hour. After cooling the resulting suspension was filtrated twice through Cellite to remove the AgBr and insoluble residues. Removal of the solvent without warming gave [**2**]$(Br)_2$ as brownish solid. Yield: 130 mg (60%).

Synthesis of [**2**]$(PF_6)_2 \cdot 2AgPF_6$

The same procedure as described above was followe using H_4-**1**$(PF_6)_4$ as imidazolium source and acetonitrile as solvent. The compound can be recrystalized from acetonitrile/ diethyether and was isolated as pale brown powder. Yield: 139 mg (60%).

Synthesis of [**3**]$(PF_6)_2$

150 mg of [**2**]$(PF_6)_2 \cdot 2PF_6$ were dissolved in 10 mL of acetonitrile. To this solution were added 4.4 eq (128 mg) of solid [AuCl(SMe_2)]. The solution turns purple within 3 minutes and a grey solid starts to precipitate. The mixture was stirred at room temperature for 12 h and filtered through Cellite at least three times to remove all purple solids. The resulting solution was dropped slowly into 40 mL of diethyl ether. Upon addition a white solid precipitates that was collected by filtration, washed with diethyl ether and dried in vacuo. Yield: 76 mg (65%).

Synthesis of [**4**]$(PF_6)_3$

200 mg (0.18 mmol) H_4-**1**$(PF_6)_4$ and 47 mg (0.18 mmol) $AgPF_6$ were dissolved in 20 mL of acetonitrile. To this solution were added 10 mg (0.40 mmol) of sodium hydride. The reaction mixture was stirred over night at room temperature, filtered through Cellite and poured into 50 mL of diethyl ether. The resulting white precipitate was collected by filtration and recrystallized from acetonitrile/diethyl ether. Yield: 86 mg (45%). Single crystals suitable for an X-ray analysis were obtained by slow diffusion of diethyl ether into a saturated solution of the compound in acetonitrile.

Synthesis of [**5**]$(PF_6)_3$

[**5**]$(PF_6)_3$ was prepared following the procedure described for [**3**]$(PF_6)_2$ using 70 mg (0.0067 mmol) of [**4**]$(PF_6)_3$ and 20 mg (0.0067 mmol) of [AuCl(SMe_2)] in 10 mL of acetonitrile. The reaction mixture turns orange. After filtration and removal of the solvent a pale yellow solid was obtained. Recrystallization from acetonitrile/diethyl ether gave [**5**]$(PF_6)_3$ as white needles. Yield: 36 mg (48%). Single crystals suitable for an X-ray analysis were obtained by slow diffusion of diethyl ether into a saturated solution of the compound in acetonitrile.