

Supporting Information for:

**Benz[e]indenyl and benz[f]indenyl molybdenum compounds: Evidence of η^3 -
coordination mode.**

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Materials. The reagents were purchased from Acros Organics. Benz[f]indanone was prepared according to literature procedure.¹

Synthesis of benz[e]indanone. A suspension of AlCl₃ (22 g; 165 mmol) in carbon disulfide (100 mL) was cooled on 0 °C and treated with mixture of naphthalene (15 g; 117 mmol) and 3-chloropropionyl chloride in carbon disulfide (40 mL) dropwise. The reaction mixture was stirred for 15 min at 0°C and then for 4 h at room temperature. The reaction mixture was poured into the mixture of ice and hydrochloric acid and the product was extracted with CH₂Cl₂ (3 × 100 mL). The volatiles were vacuum evaporated, and the solid product was treated with sulfuric acid (100 mL; 98%) and heated on 90 °C for 40 min. The reaction mixture was poured into water/ice mixture and extracted with CH₂Cl₂ (3 × 100 mL). The combined organic phases were washed with brine, dried with magnesium sulfate. Volatiles were vacuum evaporated to give mixture of benz[e]indan-1-one and benz[e]indan-3-one in molar ratio 1:1.9 (determined by NMR spectroscopy). Yield: 9.3 g (51 mmol; 43.6%). Pale yellow powder. Pure isomers were isolated by column chromatography (Silica; CH₂Cl₂/hexane – 7:3). Benz[e]indan-1-one: Colorless crystals (*R_f* = 0.39). Benz[e]indan-3-one: Colorless crystals (*R_f* = 0.19). Analytical and spectroscopic data of pure isomers are in line with those published elsewhere.^{2,3}

Synthesis of benz[e]indanol. Suspension of LiAlH₄ (0.52 g; 13.7 mmol) in THF (100 mL) was cooled on 0 °C, treated with solution of crude benz[e]indanone (2.5 g; 13.7 mmol; mixture of isomers) in THF (35 mL) and stirred for 90 min at room temperature. The mixture was cooled on 0 °C and the reaction was quenched with water (1 mL added dropwise). *Caution: Hydrogen gas is produced vigorously.* The mixture was diluted with water and extracted with Et₂O (3 × 100 mL). Volatiles were vacuum evaporated and vacuum dried to give pure mixture of benz[e]indan-1-ol and benz[e]indan-3-ol. Yield: 2.14 g (11.6 mmol; 84.9%). Pale yellow powder. Analytical and spectroscopic data are in line with those published elsewhere.⁴

Synthesis of benz[e]indene (1). Benz[e]indanol (2.14 g, 11.6 mmol) was dissolved in toluene (75 mL), treated with *p*-toluenesulfonic acid (10 mg) and under reflux for 18 h. The formed water was distilled off using Dean-Stark apparatus. The solution was cooled at room temperature, washed with water (3 × 100 mL) and dried with anhydrous magnesium sulfate. Volatiles were vacuum evaporated. The crude product was dissolved in CH₂Cl₂ (100 mL) and filtered through short pad of silica. The pure mixture of 1*H*-benz[e]indene and 3*H*-benz[e]indene was obtained after vacuum evaporation of the solvent. Yield: 1.69 g (10.2 mmol; 87.7%). Pale yellow powder. Analytical and spectroscopic data are in line with those published elsewhere.⁴

Deuterium labeled benz[e]indene (1-[D]). A solution of benz[e]indene (**1**; 0.18 g, 1.08 mmol) was cooled to 0 °C, treated dropwise with a solution of *n*-BuLi in hexane (1.6 M, 1.5 mL, 2.4 mmol), and stirred for 30 min at this temperature. The mixture was cooled to –80 °C, treated dropwise with D₂O (2 mL), warmed up to room temperature, slowly poured into distilled water (50 mL) and extracted with CH₂Cl₂ (4 × 50 mL). The combined organic layer was dried with magnesium sulfate. The volatiles were vacuum evaporated. The procedure was repeated three times to give light pink product. Yield: 0.17 g (1.01 mmol; 93.1%). Analytical and spectroscopic data are in line with those published elsewhere.⁴

Synthesis of benz[f]indene (2).

The reaction was performed as described for compound **1** but with benz[f]indanone (5.00 g; 27.4 mmol). Yield: 2.68 g (16.1 mmol, 58.8 %). Analytical and spectroscopic data are in line with those published elsewhere.⁵

References

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