

Supporting Information for

“Diruthenium Complexes of Axial Ferrocenylpolyynyl Ligands: the Cases of C₆Fc and C₈Fc”

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Experimental

n-BuLi and Et₃N were purchased from Aldrich, and silica gel was from Merck. CuI was from ACROS. 1-Ferrocenyl-1,3-butadiyne (FcC₄H)¹ and 1-bromo-2-triethylsilyl (BrC≡CSiEt₃)² were prepared according to the literatures. Unless specified, all syntheses were performed using standard Schlenk techniques under a nitrogen atmosphere.

Preparation of FcC₆SiEt₃. A Schlenk flask was charged with FcC₄H (0.414 g, 1.76 mmol), CuI (0.402 g, 2.12 mmol), and THF (50 mL) and cooled to -45°C. Then *n*-BuLi (2.5 M in hexane; 0.85 mL, 2.13 mmol) was added with stirring. The cold bath was removed. After 45 min, EtNH₂ (ca. 1.5 mL) was added, followed by dropwise addition of solution of BrC≡CSiEt₃ (0.460 g, 2.1 mmol) in THF (4 mL). Stirred for another 30 min, the reaction mixture was filtered through a 2 cm silica gel pad, and solvent was removed by rotary vapor. The residue was further purified by column chromatography eluted with hexanes to yield orange oil (0.380 g, 58%). Data for **1**: R_f 0.74 (THF/Hexanes=1/6). ¹H NMR (CDCl₃): 4.51 (s, 2H, Fc), 4.23 (s, 7H, Fc), 1.00 (t, 9H, Si(CH₂CH₃)₃), 0.69-0.61 (q, 6H, Si(CH₂CH₃)₃).

Preparation of FcC₈SiEt₃. To a 60 mL THF/CH₃OH (2:1, v/v) solution of FcC₆SiEt₃

(0.450 g, 1.21 mmol) was added K_2CO_3 (0.5 g), and the mixture was stirred for 20 min. The reaction mixture was filtered through a 2 cm silica gel pad, and solvent was removed by rotary vapor. The residue was immediately mixed with CuI (0.100 g, 0.53 mmol) in dry THF (40 mL), and cooled to -45°C . Then *n*-BuLi (2.5 M in hexane; 0.3 mL, 0.75 mmol) was added with stirring. The cold bath was removed. After 45 min, the mixture was cooled to -20°C , and EtNH_2 (ca. 0.5 mL) was added. A solution of $\text{BrC}\equiv\text{CSiEt}_3$ (0.430 g, 1.96 mmol) in THF (4 mL) was added dropwise. The cold bath was removed. After 30 min, the reaction mixture was filtered through a 2 cm silica gel pad, and solvent was removed by rotary vapor. The residue was further purified by column chromatography eluted with hexanes to yield orange solids (0.160 g, 33%). Data for $\text{FcC}_8\text{SiEt}_3$: R_f 0.68 (THF/Hexanes=1/6). ^1H NMR (CDCl_3): 4.55 (*t*, 2H, $\eta\text{-C}_5\text{H}_4$), 4.30 (*t*, 2H, Fc), 4.26 (*s*, 5H, Fc), 1.00 (*t*, 9H, $\text{Si}(\text{CH}_2\text{CH}_3)_3$), 0.68-0.63 (*q*, 6H, $\text{Si}(\text{CH}_2\text{CH}_3)_3$).

(1) Yuan, Z.; Stringer, G.; Jobe, I. R.; Kreller, D.; Scott, K.; Koch, L.; Taylor, N. J.;

Marder, T. B. *J. Organomet. Chem.* **1993**, 452, 115-120.

(2) Zheng, Q. L.; Bohling, J. C.; Peters, T. B.; Frisch, A. C.; Hampel, F.; Gladysz, J. A.

Chem. Eur. J. **2006**, 12, 6486-6505.

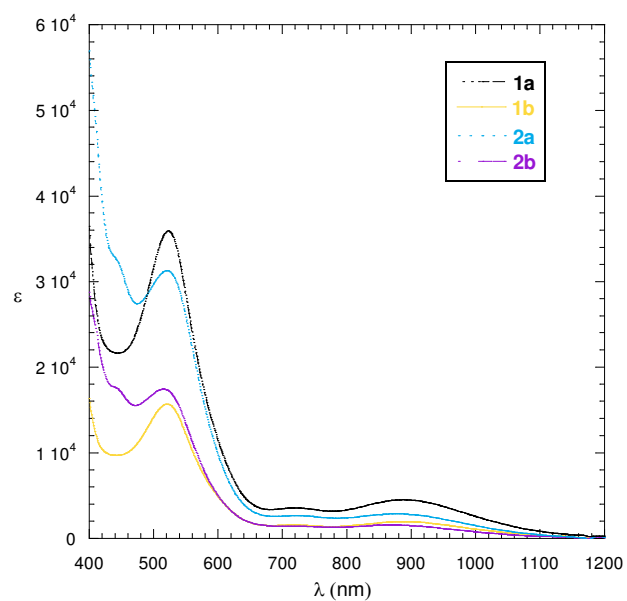


Figure S1. Vis-NIR absorption spectra of compounds **1a-2b** recorded in THF.

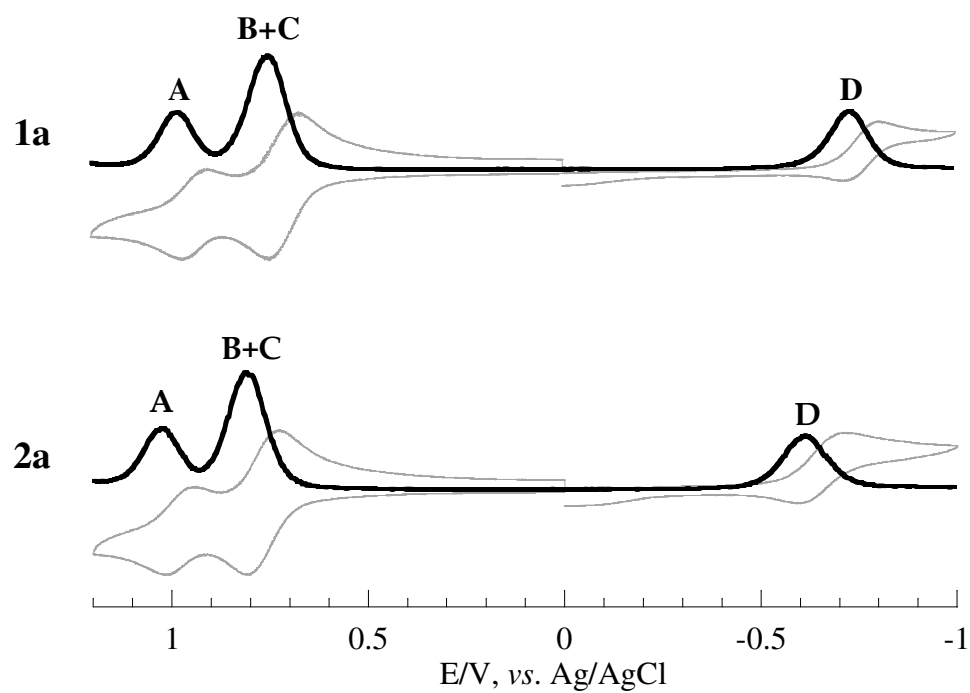


Figure S2. DPVs (bold) and CVs (gray) of $\text{Ru}_2(\text{DMBA})_4(\text{C}_{2n}\text{Fc})_2$ ($n = 3$ and 4) recorded in 0.20 M THF solution of Bu_4NPF_6 .