Supporting Information

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Synthesis and Structure of a Dimetallated Buckybowl: Coordination of One Cp*Ru⁺ Unit to Each Side of Corannulene

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Synthetic Details and Spectroscopic Characterization

**Figure 1S:** ¹H NMR and ¹³C NMR spectra of free corannulene (1) in CD₂Cl₂.

**Experimental Section**

**General Considerations**

*Synthesis and Characterization of [(Cp*Ru)₂(µ₂-η⁶,η⁶-C₂₀H₁₀)]₂ (X = BF₄⁻ (2a), PF₆⁻ (2b)).*

**Figure 2S:** Labeling scheme for compound 2.

**Figure 3S:** ¹H NMR Spectrum of 2a in CD₃NO₂.

**Figure 4S:** ¹³C {¹H} NMR Spectrum of 2a in CD₃NO₂.

**Figure 5S:** COSY NMR Spectrum of 2a in CD₃NO₂.

**Figure 6S:** Thermal ellipsoid drawings and numbering schemes for 2b. Ellipsoids are drawn at the 50% (top) and 30% (bottom) probability level; hydrogen atoms are omitted for clarity.
Figure 1S: $^1$H NMR (top) and $^{13}$C NMR (bottom) spectra of free corannulene (1) in CD$_2$Cl$_2$.

Experimental Section

General Considerations

All manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques. Diethyl ether and methylene chloride were purified on alumina using a Solv-Tech solvent purification system, as described by Grubbs and co-workers.$^{[1]}$ Deuterated nitromethane was purchased from Aldrich and subjected to three freeze-pump-thaw cycles before use. Corannulene$^{[2]}$ and [Cp*RuCl]$_4$$^{[3]}$ were synthesized following published methods. All other chemicals (AgBF$_4$, AgPF$_6$, 99.99+ %) were used without further purification as purchased from Aldrich. Filtrations were performed with Celite on filter paper. NMR spectra were obtained on a Bruker DRX-400 spectrometer using CD$_3$NO$_2$ as solvent, internal lock, and internal reference ($\delta = 4.33$). Electrospray ionization mass spectra were obtained on a Finnigan TSQ700 triple quadrupole mass spectrometer Finnigan MAT, San Jose, CA, fitted with a Finnigan ESI interface (Finnigan MAT, San Jose, CA). Elemental analyses were performed on a Perkin-Elmer 2400 series II CHNS/O analyzer.
Synthesis and Characterization of [(Cp*Ru)₂(μ₂-η⁶,η⁶-C₂₀H₁₀)](X)₂ (X = BF₄⁻ (2a), PF₆⁻ (2b)).

To a solution of 0.022 g (0.020 mmol) of [Cp*RuCl]₄ and 0.010 g (0.040 mmol) of corannulene (1) in 1 mL of CD₃NO₂ was added 0.081 mmol of AgBF₄ or AgPF₆. The solution was stirred at room temperature for 1 h, and the AgCl precipitate was removed by filtration. The resulting dark orange solution was evaporated to dryness under vacuum to give an oily residue of 2a or 2b, respectively. These reactions are nearly quantitative by NMR spectroscopy. The residue was washed with diethyl ether (2 × 3 mL) and dried under vacuum. After dissolving 2a or 2b in 1-2 mL of CH₂Cl₂, the resulting solution was added to ~5 ml of hexanes via cannula to give orange powders (0.034 g, 85 % yield, for 2b). ¹H NMR (400.13 MHz, CD₃NO₂, RT, 2a): δ = 8.51 (d, J(H,H) = 9 Hz, 2H, H₈,₉), 8.20 (s, 2H, H₃,₄), 8.17 (d, J(H,H) = 9 Hz, 2H, H₇,₁₀), 6.87 (d, J(H,H) = 6 Hz, 2H, H₁,₆), 6.80 (d, J(H,H) = 6 Hz, 2H, H₂,₅), 1.27 (s, Cp*, 30H).
¹³C{¹H} NMR (100.61 MHz, CD₃NO₂, RT, 2a): δ = 135.1 (C₈,₉), 132.2 (C₃,₄), 128.8 (C₇,₁₀), 98.7 (C-Ru), 98.5 (C-Ru), 96.9 (C-Ru), 96.8 (C₅Me₅), 95.6 (C-Ru), 86.9 (C₂,₅), 85.8 (C₁,₆), 9.0 (C₅Me₅), 135.6, 132.7 (C₁₅, C₁₆). MS m/z 362 ([(Cp*Ru)₂(μ₂-η⁶,η⁶-C₂₀H₁₀)]²⁺), electrospray in CD₃NO₂. Anal. Calcd for [(Cp*Ru)₂(μ₂-η⁶,η⁶-C₂₀H₁₀)](PF₆)₂·1CH₂Cl₂: C, 44.86; H, 3.86. Found: C, 45.32; H, 3.99. The presence of CH₂Cl₂ in the sample was confirmed by an ¹H NMR spectrum of the compound in CD₃NO₂.

![Figure 2S](image_url)

**Figure 2S:** Atom labeling scheme for compound 2.
Figure 3S: $^1$H NMR spectrum of 2a in CD$_3$NO$_2$. 
**Figure 4S**: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2a in CD$_3$NO$_2$.

**Figure 5S**: COSY NMR spectrum of 2a in CD$_3$NO$_2$. 
**Figure 6S:** Thermal ellipsoid drawings and numbering scheme for 2b. Ellipsoids are drawn at the 50% (top) and 30% (bottom) probability level; hydrogen atoms are omitted for clarity.