

## Supporting Information

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Electronic and Magnetic Couplings in Free and  $\pi$ -Coordinated 1,4-Diethynynaphthalene  
Bridged  $[\text{Cp}^*(\text{dppe})\text{Fe}]^{n+}$  ( $n = 0, 1$ ) Units

### 1. Synthesis of the Heterotrinnuclear Iron(II)/iron(II)/Ruthenium(II) complex **5B**[PF<sub>6</sub>].

The heterotrimetallic complex **5H<sub>2</sub>**[PF<sub>6</sub>]<sub>3</sub> was obtained upon reaction of the bis(vinylidene) **4H<sub>2</sub>**[PF<sub>6</sub>]<sub>2</sub> with  $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3][\text{PF}_6]$  in dichloromethane from 0 °C to 12 °C. For reaction times ranging from 45 min to 24 h, the yield were 60 %. The optimal yield of 82 % requires an intermediate drying and dissolution cycle in order to remove the acetonitrile by-product. This cycle consists of the following four steps: (1) the filtration of the reaction solution through a celite plugged canula filter, leaving the unreacted and insoluble  $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3][\text{PF}_6]$  starting material behind; (2) the evaporation of the filtrate at room temperature to remove the dichloromethane and the acetonitrile side-product; (3) the dissolution of the residue in dichloromethane, and (4) the transfer by canula of this solution into the initial reaction flask. Even upon optimization, NMR and high resolution MS revealed that the crude product contains the target complex **5H<sub>2</sub>**[PF<sub>6</sub>]<sub>3</sub> and 10-15 % of the starting material **4H<sub>2</sub>**[PF<sub>6</sub>]<sub>2</sub>. The bisvinylidene salts **5H<sub>2</sub>**[PF<sub>6</sub>]<sub>3</sub> and **4H<sub>2</sub>**[PF<sub>6</sub>]<sub>2</sub> are separable either by partial precipitation or by crystallization, and column chromatography is unsuitable as well. These facts precluded rigorous spectroscopic and structural characterization of the trimetallic bisvinylidene **5H<sub>2</sub>**[PF<sub>6</sub>]<sub>3</sub>. However, it was established on the basis of <sup>1</sup>H NMR spectra that

the reaction is regiospecific with complexation occurring only on the unsubstituted ring of the naphthyl moiety, never on either the competing dppe phenyls or the 1,4-substituted naphthyl ring. In related work, sterics were shown to play a decisive role in the regioselectivity of the  $\text{Cp}^*\text{Ru}^+$  arenophile towards 1-substituted naphthalenes in the absence of large electronic donor interactions.<sup>1, 2</sup>

Despite the inseparability of the salts **5H<sub>2</sub>[PF<sub>6</sub>]<sub>3</sub>** and **4H<sub>2</sub>[PF<sub>6</sub>]<sub>2</sub>**, analytically pure samples of the daughter trimetallic acetylene **5B[PF<sub>6</sub>]**, were prepared from their mixture via deprotonation with potassium tert-butoxide in MeOH/THF solution as illustrated in Scheme 1. The brown solution underwent an immediate color change to greenish blue and was allowed to react at room temperature over the course of 2h. Upon completion, the solvent was evaporated, and the residue was extracted with cold dichloromethane and precipitated from a minimum of pentane. The regiopure product **5B[PF<sub>6</sub>]** was isolated as a dark brown powder in 61 % yield, based on **4H<sub>2</sub>[PF<sub>6</sub>]<sub>2</sub>**. Dry samples of this trimetallic complex display good thermal stability in air for a period of months. In contrast with the related  $[\text{Cp}^*(\text{dppe})\text{Fe}-\text{C}\equiv\text{C}-(\eta^6\text{-1-naphthyl})\text{RuCp}^*][\text{PF}_6]$  monoiron derivative previously described, the formation of the **5A[PF<sub>6</sub>]** isomer is not observed for the diiron species (for definition of regioisomers A and B see Chart 1), most certainly for steric reasons.<sup>2</sup>

Alternatively, treatment of the bis(acetylide) complex **4** with  $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3][\text{PF}_6]$  in dichloromethane produced a mixture of heterotrimetallic complexes **5A[PF<sub>6</sub>]** and **5B[PF<sub>6</sub>]** in the 3:1 ratio evaluated on the basis of the intensity of the IR  $\nu_{(\text{C}\equiv\text{C})}$  bands at 1914 and 2004  $\text{cm}^{-1}$ . All attempts to separate derivatives **5A[PF<sub>6</sub>]** and **5B[PF<sub>6</sub>]** failed and therefore, the characterization of the trimetallic bisacetylide **5A[PF<sub>6</sub>]** could not be completed.

Satisfactory mass spectra and microanalysis were obtained for **5B[PF<sub>6</sub>]**. Upon complexation to  $\text{Cp}^*\text{Ru}^+$ ,  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts attributed to the complexed aromatic ring of **5H<sub>2</sub>[PF<sub>6</sub>]<sub>3</sub>** and **5B[PF<sub>6</sub>]** move upfield, as usual for  $\text{Cp}^-$  and  $\text{Cp}^*\text{Ru}^+ \eta^6$  aromatic

compounds ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ).<sup>3</sup> For example, the  $^1\text{H}$  NMR spectroscopy reveals that the unsubstituted **B** ring accommodates the arenophile in both of these compounds because the four **B** ring naphthyl protons are shifted upfield for **5H<sub>2</sub>[PF<sub>6</sub>]<sub>3</sub>** (6.17 - 5.98) and **5B[PF<sub>6</sub>]** (6.23 - 5.72) versus the organoiron starting materials. The arenophile in these two compounds is also observed *via* the presence of one and two sharp singlets in the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra, respectively.

Furthermore, the dppe phosphorus nuclei resonate as an AB system in the  $^{31}\text{P}$  NMR spectra of **5H<sub>2</sub>B[PF<sub>6</sub>]<sub>3</sub>** ( $^2J_{\text{p-p}} = 82$  Hz) and **5B[PF<sub>6</sub>]** ( $^2J_{\text{p-p}} = 281$  Hz), whereas the corresponding organoiron species, **4H<sub>2</sub>[PF<sub>6</sub>]<sub>2</sub>** and **4**, are each characterized by a singlet (see above). The AB system doublet is further split into a smaller doublet, because the heterotrinnuclear species are planar chiral. Therefore, the enantiotopic phosphorus atoms of each diastereomer within the racemic mixtures is distinguishable by 33 and 34 Hz, respectively. The bulky arenophile also introduces coalescence into the spectra, which explains the disappearance of the dppe ethylene peaks in the  $^1\text{H}$  NMR spectrum of **5H<sub>2</sub>[PF<sub>6</sub>]<sub>3</sub>**. The shortening and broadening of iron ligand signals were also observed in mono-Fe(II)/Ru(II) naphthyl sandwich complexes described previously.<sup>2</sup>

## References

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