

Abstract :

The complexes $\text{FcCH}=\text{C}\{1,4\text{-C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}(\text{dppe})\text{Cp}^*\}_2$ (Fc = ferrocenyl ($\text{FeCp}(\eta\text{-C}_5\text{H}_4\text{-})$); M = Fe (**1**), Ru (**2**)) were prepared from $\text{FcCH}=\text{C}\{1,4\text{-C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{CSiMe}_3\}_2$ (**3**) via a desilylation/metalation protocol in good (**2**; 65%) to excellent (**1**; 97%) yield. The iron compound **1** could also be prepared in a stepwise fashion by desilylation of **3** to give $\text{FcCH}=\text{C}\{1,4\text{-C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{CH}\}_2$ (**4**), reaction with $\text{FeCl}(\text{dppe})\text{Cp}^*$ to give the vinylidene complex $\text{FcCH}=\text{C}\{1,4\text{-C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{CH}=\text{C}=\text{Fe}(\text{dppe})\text{Cp}^*\}_2(\text{PF}_6)_2$ (**5**(PF_6)₂; 65%), and deprotonation. The cyclic voltammograms of **1** and **2** are characterized by an initial oxidation wave resulting from the overlap of two closely spaced oxidation processes, the potentials of which are sensitive to the identity of M, and a subsequent, one-electron-oxidation wave. Thus, while the dications **1**²⁺ and **2**²⁺ could be prepared by oxidation with 2 equiv of ferrocenium hexafluorophosphate and isolated as the PF_6^- salts **1**(PF_6)₂ and **2**(PF_6)₂ at low temperature, the monocations **1**⁺ and **2**⁺ could only be detected and studied as comproportionated mixtures of **1**, **1**(PF_6), **1**(PF_6)₂ and **2**, **2**(PF_6), **2**(PF_6)₂. A combination of EPR spectroscopy, IR and NIR spectroelectrochemistry, and DFT quantum chemical calculations reveal subtle distinctions in the electronic structures of **1**(PF_6)_n and **2**(PF_6)_n ($n = 0-2$). The HOMOs of **1** and **2** are more heavily distributed over the metal–diethynylbenzene arm trans to the ferrocenyl moiety. While one-electron oxidation of **1** gives **1**(PF_6), in which the spin density is similarly distributed along the branch of the molecule trans to the ferrocenyl group, the spin density in **2**(PF_6) is more extensively, but not fully, delocalized. Further analysis of the ESR, NIR, and IR spectra reveals that charges are essentially localized in **1**(PF_6) and **1**(PF_6)₂ on the IR time scale, but ground-state exchange between the $\text{Fe}(\text{dppe})\text{Cp}^*$ moieties can take place via the ferrocenyl moiety on the slower ESR time scale. For **2**(PF_6) and **2**(PF_6)₂, optical charge transfer processes between the ferrocenyl moiety and the organometallic branches can also be observed, consistent with the increased coupling between the $\text{Ru}(\text{dppe})\text{Cp}^*$ and Fc moieties that are linked by a linear conjugation pathway through the bridging-ligand backbone.