Synthesis, Molecular Structure, Properties, and Electronic Structures of Cp(dppe)FeC C-TTFMe3 PF6 (n) (n = 0, 1): Electronic Coupling between the Inorganic and Organic Electrophores

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Résumé en anglais	Sequential treatment of trimethylsilylethynyl-TTF (TTFMe3) 3a dissolved in methanol with potassium fluoride, the chloro complex Cp(dppe)FeCl (8; Cp = eta(5)-C-5(CH3)(5), dppe = 1,2-bis-(diphenylphosphino)ethane) in the presence of ammonium hexafluorophosphate, and finally with KOBu provided Cp(dppe)FeC equivalent to C-TTFMe3 (I), which was isolated in 69% yield as an air- and moisture-sensitive orange powder. The X-ray crystal structure, IR, cyclic voltammetry (CV), UV-vis, Mossbauer, and DFT data obtained for 1 show that only weak interactions take place between the iron center and the TTFMe3 core and that the latter acts as a rather poor electron donor vis-a-vis the organometallic group. When reacted with 1.0 equiv of [(C5H5),Fe][PF6] in tetrahydrofuran (THF) at -60 degrees C, 1 gives the thermally stable radical cation 1[PF6], which was isolated in a pure form as a purple powder (77%). The Fe-III derivative was characterized by the same spectroscopic methods as 1 complemented by FIRMS and elemental analyses also obtained for neutral 1. All experimental and theoretical data obtained for 1[PF6] indicate that after one-electron oxidation the relaxation of the molecular structure is characterized by an increase of the Fe C carbon bond order, the localization of the positive charge on the iron nuclei, and the delocalization of the spin density on the whole molecule. In the radical cation, the interaction between the iron center and the TTFMe3 fragment is much stronger than in the neutral species, and a good electronic communication characterized by a rather large electronic coupling for a class II MV system takes place (H-ab = 320 cm(-1) determined from the analysis of the NI R spectrum). Furthermore, the dicationic species 1[PF6](2) was in situ generated and characterized by IR, NIR, and EPR spectroscopies.
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