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Synthesis, characterization, molecular structure and computational study of tetrahedral pentamethylcyclopentadienyl iridacycle complexes with α,β-conjugated Schiff base ligands

Abstract

Due to the excellent catalytic activities and phosphorescent properties that iridium complexes display, iridium chemistry has been of great interest for scientific investigation over the past 30 years. Iridium metallacycle analogues (also known as an iridacycles) bearing phenylpyridine (ppy) ligands have been well reported on, whilst complexes with R-phenyl-(3-R-phenylallylidene)amine, which is an α,β-conjugated Schiff base ligand, have not had the same attention, despite the fact that both ligands share a similar coordination mode. In this research, four pentamethylcyclopentadienyl iridacycle complexes, Ir1a-Ir1d, with different α,β-conjugated Schiff base ligands were synthesized from a di-μ-chloro-dichloro-bis-(η^5-pentamethylcyclopentadienyl)diiridium(III) precursor. The iridacycle complexes were characterized using spectroscopic techniques and the molecular structures of Ir1ab-Ir1d were determined using X-ray crystallography. The X-ray results revealed that the iridacycle complexes have a tetrahedral geometry, the iridium centre being coordinated through the N[dbnd]C[sbnd]C_α[dbnd]C_β moiety of the α,β-conjugated Schiff base ligand. Computational calculations with the B3LYP method and with LanL2DZ basis sets indicated that the HOMO-LUMO energy gaps Ir1b-Ir1d were in the range 3.31–3.36 eV. The OMe substituent at the C terminal has a greater impact on the HOMO energy level than the one at the N terminal.

Keywords

Crystal data; Cyclometallation; DFT calculations; Iridacycle; Schiff base