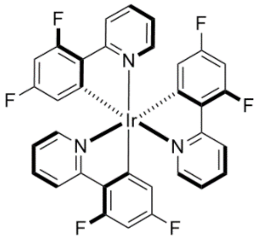
Ir(dFppy)$_3$



[387859-70-3] $C_{33}H_{18}F_6IrN_3$ MW 762.74

Alternate names: Tris[2-(4,6-difluorophenyl)pyridinato-C2,*N*]iridium(III), Tris[2-(2,4-difluorophenyl)pyridine]iridium(III)

Physical data: Yellow solid at room temperature. Soluble in *N*-methyl 2-pyrrolidinone, tetrahydrofuran, dichloromethane, and *N,N*-dimethylformamide. Not soluble in water.[1]

Preparative Methods: Tris-cyclometallation with 2-(2,4-difluorophenyl)pyridine and IrCl$_3$ at 205 ^{0}C in H_2O at 97% yield.[2]

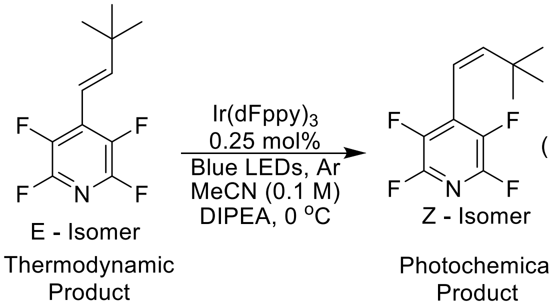
Purification: preparation of catalyst generally results in pure product. Further purification possible through flash chromatography (dry loaded) using hexane:ethyl acetate on a silica column.[3]

Handling and storage: generally considered bench stable and air and moisture insensitive as a solid.

Introduction. Ir(dFppy)$_3$ is a unique photocatalyst in that it has both a high triplet state energy (60 vs. 55 kcal/mol for Ir(dFppy)$_3$ and Ir(ppy)$_3$, respectively) and yet its excited state redox potentials are comparatively diminished when compared to Ir(ppy)$_3$. Specifically, $E_{1/2}$ (Ir+ /Ir*) = -1.23 vs. -1.97 and $E_{1/2}$ (Ir*/Ir-) = 0.39 vs. 0.55 vs. Ag/AgCl, for Ir(dFppy)$_3$ and Ir(ppy)$_3$.[4] The combination of high triplet state energy and diminished excited state redox potentials has frequently led to its superior photocatalytic performance by favoring energy transfer pathways over redox reactivity. The use of this particular photocatalyst often allows for selective energy transfer reactivity, and displays greater toleration of redox sensitive functional groups. The two fluorine substituents attached to the arenes serve to blue shift the emission energy while not significantly increasing the steric volume of the photocatalyst, another factor that was shown to be important in the rate of the energy transfer process involving this family of related iridium-based dyes[5]. As such, Ir(dFppy)$_3$ has been shown to be an excellent catalyst for reactions that involve energy transfer as well as select examples of redox reactions in which substrates or products are redox sensitive.

Energy Transfer reactions:

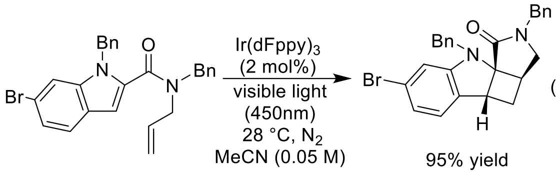
Contrathermodynamic alkene isomerizations.



(1)

Conjugated aryl- and heteroaryl-alkenes have triplet state energies that are lowered compared to non-conjugated alkenes. In the case of acyclic alkenes, the deconjugated alkene isomer is favored at the photostationary state due to its higher triplet state energy. In a study of the rate of isomerization as a function of photocatalyst structure, Ir(dFppy)$_3$ proved exceedingly effective, giving essentially all Z-isomer.[5]

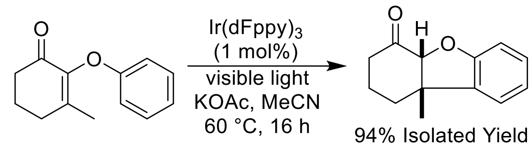
Cyclization reactions of excited alkenes



(2)

This visible light mediated photocatalytic [2+2] reaction proceeds through an energy transfer process in which the Ir(dFppy)$_3$ is the preferred catalyst due to its high triplet state energy and low redox potential which presumably prevented any undesired redox chemistry from occurring on the electron rich indole and indoline ring systems.[6] Related aniline derivavtives have undergo alpha C–H functionalization in the presence of more oxidizing photocatalysts.[7]

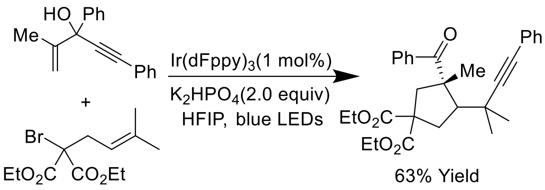
Visible light photocatalytic 6π heterocyclization



(3)

Similar to the previous reactions (1 and 2), this reaction (3) proceeds through an energy transfer mechanism in which the excited Ir(dFppy)$_3$ donated its energy to the aryloxy enone which possessed a TSE of approximately 60 kcal/mol. Indeed, Ir(dFppy)$_3$ proved to be the most effective catalyst with complete conversion of the starting material, even outperforming other high energy photocatalysts such as [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (60.1Kcal/mol).[6] The reaction is believed to initially form the trans-fused product via a conrotatory 6-π electrocyclization (not shown) which ultimately epimerizes to the thermally favored cis-fused product.[8]

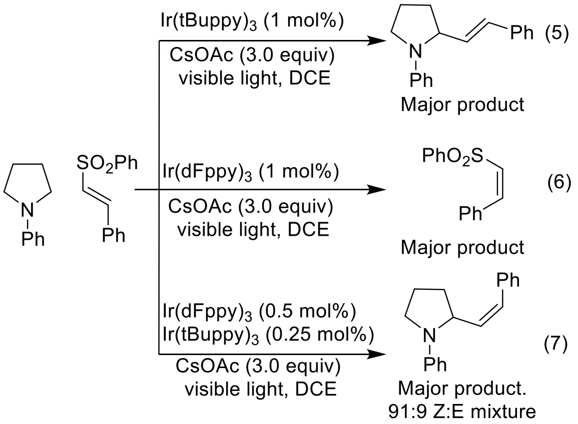
SET reactions:



(4)

Even though Ir(dFppy)$_3$ is commonly used in energy transfer reactions, it can still be an effective catalyst for single electron transfer reactions. For instance, Ir(dFppy)$_3$ was found to be the optimal catalyst for the annulation-alkynylation of alkenes reaction (4). This reaction appears to take place via oxidative quenching of the photocatalyst by the bromomalonate derivative which is supported by Stern-Volmer analysis. Other more oxidizing photocatalysts such as [Ir(dF(CF$_3$)ppy)$_2$(bpy)]PF$_6$ gave poorer results.[9]

Mixed photocatalyst systems:



In one study of selectable E/Z alkene synthesis Ir(dFppy)$_3$ was highlighted. In an example of synergistic photocatalysis, two photocatalysts-Ir(dFppy)$_3$ and fac-Ir(tBuppy)$_3$, were combined to accomplish what neither could do effectively on its own (equations 5-7).[5]

While the sterically bulky Ir(tBuppy)$_3$ underwent efficient redox initiated C–H vinylation it was very inefficient for energy transfer/contra-thermodynamic isomerization (equation 5). In contrast, Ir(dFppy)$_3$ efficiently isomerized the vinylation reagent rather than engaging in the redox mediated vinylation reaction (equation 6). However, combining both photocatalysts together allowed both photocatlytic processes to occur. Namely, the Ir(tBuppy)$_3$ gave rise to give the kinetic and thermodynamic E-product via a redox process, which was subsequently isomerized by Ir(dFppy)$_3$ to yield the Z-product as the major product (equation 7). Effectively, the concerted use of both photocatalysts expanded the synthetic scope of the coupling reaction by allowing access to either isomer.

With its high triplet state energy that can be accessed using visible light, its relatively small steric volume, and its diminished redox potentials, it is likely that Ir(dFppy)$_3$, will continue to find applications in energy transfer reactions, especially those which contain other redox sensitive functional groups.

References

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