

Metal-Organic Layers Stabilize Earth-Abundant Metal-Terpyridine Diradical Complexes for Catalytic C-H Activation

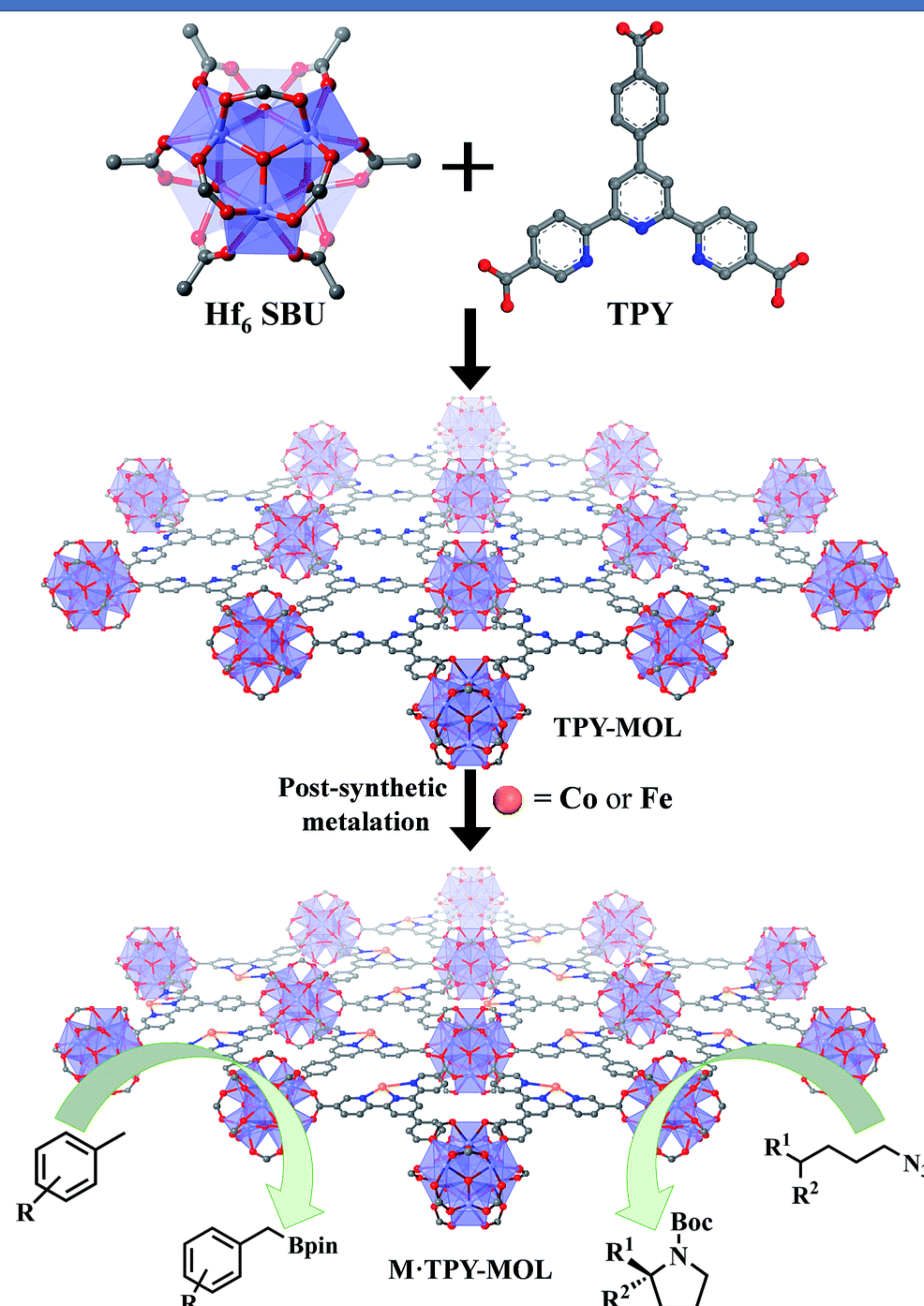
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Introduction

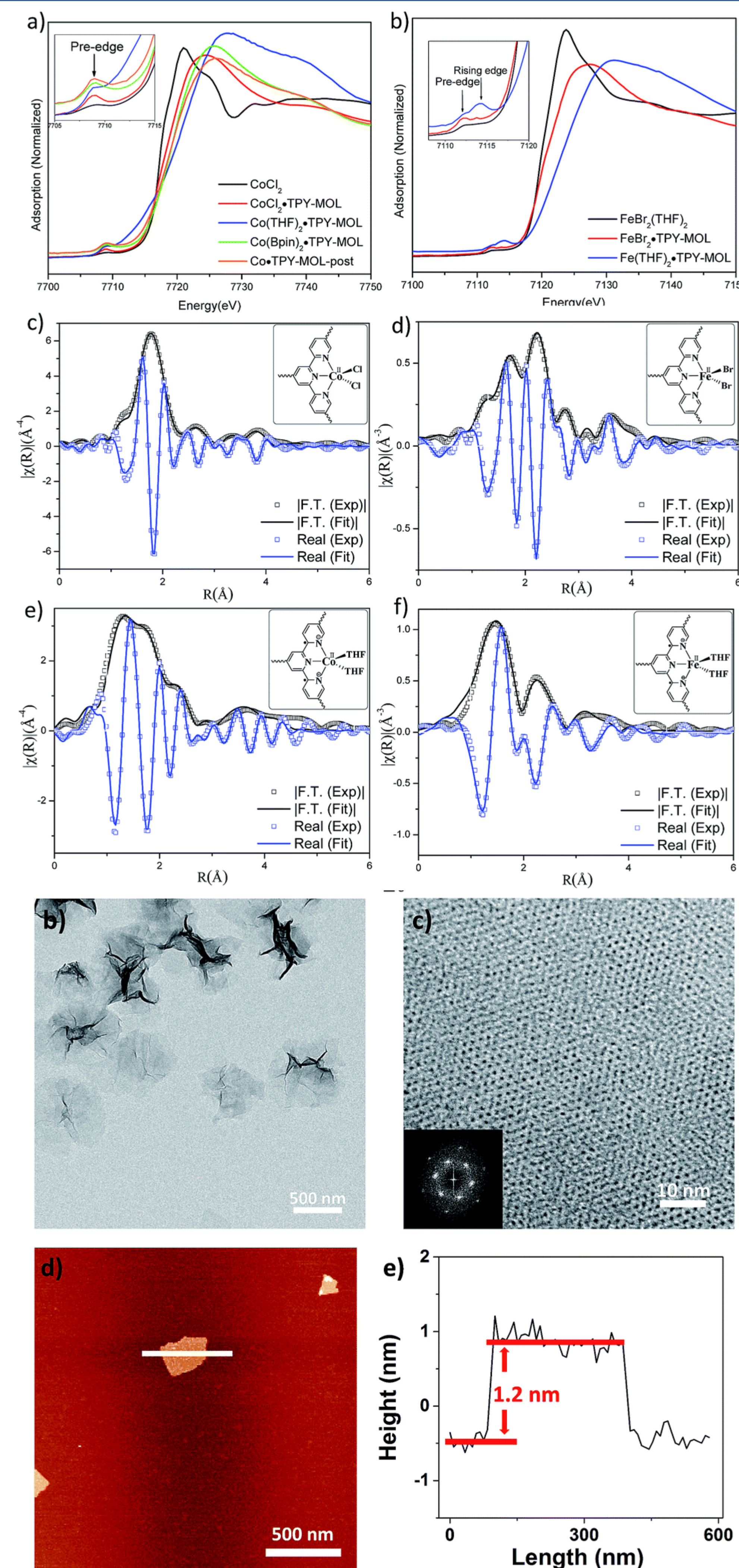
The production of fine and commodity chemicals often employs homogenous precious metal catalysts. These catalysts are susceptible to bimetallic decomposition which leads to reduced catalytic performance. To avoid this issue, bulky ligands are used to sterically protect the catalysts. However, this strategy impedes access to the metal species by the substrate. Furthermore, the recapture and reuse of the catalyst is often difficult due to its homogeneous nature. Consequently, for the sustainable production of fine chemicals, the synthesis of solid, earth-abundant metal catalysts is crucial.

Research in the catalysis subgroup of the Lin lab features metal-organic frameworks (MOFs) as supports for earth-abundant metal catalysts. Metal cations coordinate to the MOF via bridging organic linkers or the inorganic nodes. The high dispersion of the metal ions prevents bimetallic decomposition. Evidence has shown that these solid, single-site catalysts can be recycled and reused without a loss of activity. The site isolation and unique steric properties created by the MOF channels allows a wide range of substrates to be transformed while achieving high activity and product selectivity. Hydrogenation, C-H activation, and other reactions have been catalyzed by Ti, Mn, Co, Ru, Rh, Ir, Fe, and Pd coordinated to linkers possessing BINOL, salen, BINAP, diene, bipyridine, terpyridine, nacnac, and salicylaldimine functionalities, among others.

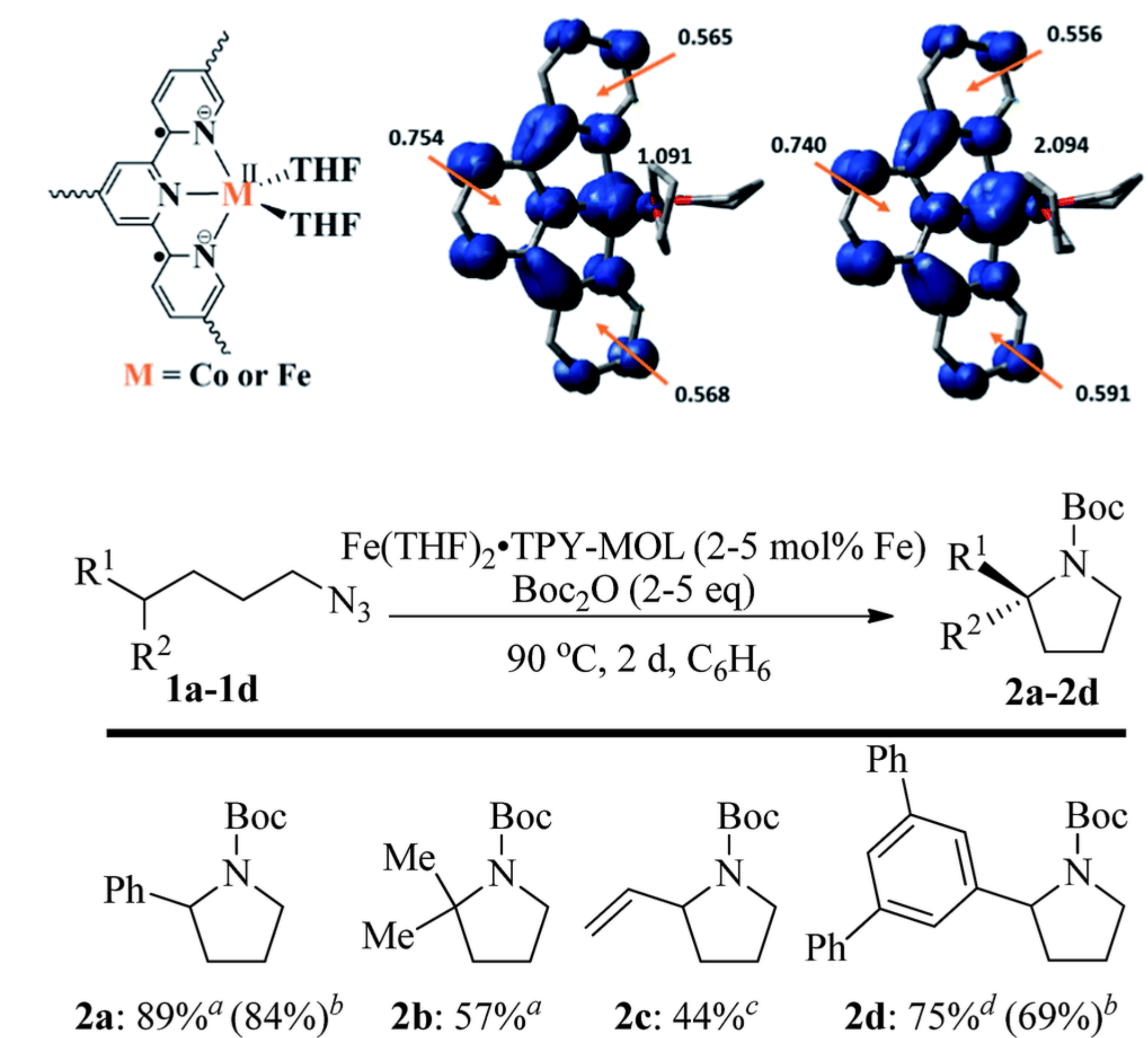
Objectives



Results



Results



Conclusions

- The MOL catalysts achieve site isolation without the need for bulky ligands.
- These MOLs have unique electronic properties capable of stabilizing a Co(II)/Fe(II)-terpyridine dianion diradical complex.
- MOLs achieve 20-50 times higher TON for C-H activation and intramolecular amination reactions compared to homogeneous analogs.
- MOLs are selective for challenging C_{sp}³-H activation and amination.

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