

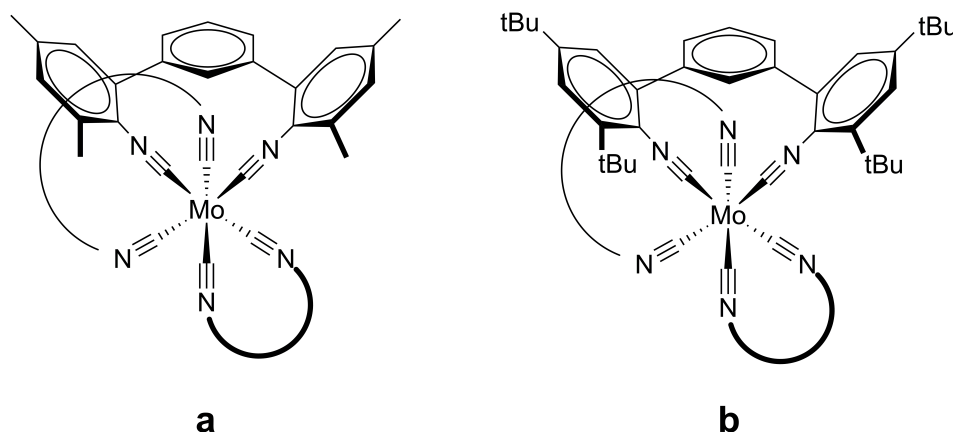
**A New Class of Photoredox Catalysts:
Robust Mo(0) Complexes as Earth-Abundant [Ru(bpy)₃]²⁺ Analoga**

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One of the best established classes of photosensitizers and photoredox catalysts are complexes derived from the ruthenium(II) tris(2,2'-bipyridine) complex. These compounds are chemically robust, exhibit MLCT absorptions in the visible spectral range, and their redox and photophysical properties are readily tunable by altering their ligands. [1]

Cr(0), Mo(0) and W(0) complexes with monodentate aromatic isonitrile ligands have been reported as isoelectronic analoga of these ruthenium complexes, but they are prone to photoinduced ligand dissociation. [2-3]



We recently reported on the first homoleptic Mo(0) complex with chelating isonitrile ligands (Fig. a).[4] Our complex is isoelectronic to [Ru(bpy)₃]²⁺ and has similar optical spectroscopic properties, while offering much more reduction power than the ruthenium(II) parent compound. The chelating ligands make the complex rather robust and permit unusually challenging photoredox chemistry to take place. The application potential of the complex was put in evidence by employing it as a photocatalyst for an acyl-cyclopropane rearrangement reaction giving a 2,3-dihydrofuran compound in good yields.

The ligand was modified in order to optimize the excited states lifetimes as well as the chemical robustness of the complex (Fig. b). The new complex outperforms [Ru(bpy)₃]²⁺ in terms of reducing power, excited-state lifetime, and luminescence quantum yield by far.

Our Mo(0) complexes are strongly reducing, chemically robust alternatives to [Ru(bpy)₃]²⁺. They can be considered a new class of exceptionally strong photoreductants based on earth abundant metals.

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