

Reductive Coupling of Diynes at Rhodium Gives Fluorescent Rhodacyclopentadienes or Phosphorescent Rhodium 2,2'-Biphenyl Complexes

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Abstract: Reactions of $[\text{Rh}(\kappa^2\text{-O,O-acac})(\text{PMe}_3)_2]$ (acac = acetylacetonato) and α,ω -bis(arylbutadiynyl)alkanes afford two isomeric types of MC_4 metallacycles with very different photophysical properties. As a result of a [2+2] reductive coupling at Rh, 2,5-bis(arylethynyl)rhodacyclopentadienes (**A**) are formed, which display intense fluorescence ($\Phi = 0.07\text{--}0.54$, $\tau = 0.2\text{--}2.5$ ns) despite the presence of the heavy metal atom. Rhodium biphenyl complexes (**B**), which show exceptionally long-lived (hundreds of μs) phosphorescence ($\Phi = 0.01\text{--}0.33$) at room temperature in solution, have been isolated as a second isomer originating from an unusual [4+2] cycloaddition reaction and a subsequent β -H-shift. We attribute the different photophysical properties of isomers **A** and **B** to a higher excited state density and a less stabilized T_1 state in the biphenyl complexes **B**, allowing for more efficient intersystem-crossing $S_1 \rightarrow T_n$ and $T_1 \rightarrow S_0$. Control of the isomer distribution is achieved by modification of the bis(diyne) linker length, providing a fundamentally new route to access photoactive metal biphenyl compounds.

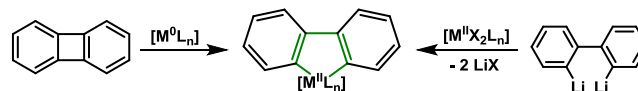
Introduction

Transition metal complexes of 2,2'-bipyridine (bpy) and 2-phenylpyridine (ppy), or derivatives thereof, usually exhibit triplet

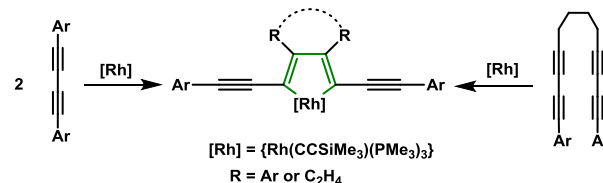
excited states with lifetimes of a few μs , which can be exploited in photocatalysis, light-emitting devices, and biological imaging.^[1] The great attention that the prototypical compounds $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ir}(\text{ppy})_3]$ have received for their employment in solar energy conversion and OLEDs, respectively, and the resulting progress in those areas impressively underlines the importance and potential of such compounds.^[2] However, it is worth noting that our knowledge of the optical properties of metallacyclopentadienes, *i.e.*, $\text{MC}_{4-n}\text{N}_n$ ($n = 0\text{--}2$) compounds, is mainly limited to $\{\text{M}(\kappa^2\text{-N,N'-C}_2\text{N}_2)\}$ and $\{\text{M}(\kappa^2\text{-N,C-C}_3\text{N})\}$ type complexes.

Synthesis of $\text{M}(2,2'\text{-bph})$ complexes (bph = biphenyl) as MC_4 analogues can be achieved, *e.g.*, by insertion of a low-valent, electron-rich transition metal fragment into a C-C bond of biphenylene or *via* reaction of a 2,2'-dilithiated biphenyl with a metal dihalide (Scheme 1).^[3] These methods clearly limit the range of accessible substituted 2,2'-bph complexes, and hence photophysical studies have been performed on only a small number of transition metal biphenyl compounds of Pd, Pt, Ir and Au.^[4] These few examples exhibit phosphorescence with quantum yields of 0.01–0.16, but attempts to improve their performance have not been reported. In contrast, metallacyclopentadienes derived from the reductive coupling of alkynes are well known intermediates in cyclotrimerization reactions of alkynes and alkyne/nitrile combinations,^[5] and are thus much more readily accessible. However, apart from our recent reports,^[6] nothing is known about their photophysical properties.

General access to biphenyl complexes:



Synthesis of luminescent RhC_4 complexes by Marder *et al.*:



Scheme 1. General synthetic access to transition metal biphenyl complexes (top) and synthesis of luminescent 2,5-bis(arylethynyl)rhodacyclopenta-2,4-dienes established by Marder *et al.* (bottom).

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