

## 2,5-Bis(*p*-R-arylethynyl)rhodacyclopentadienes Show Intense Fluorescence: Denying the Presence of a Heavy Atom\*\*

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The photophysics and photochemistry of transition-metal compounds are of great interest, particularly since such materials have been exploited for a wide range of applications including photocatalysis, photosynthesis and photosynthetic model compounds, artificial light-harvesting antenna systems for solar energy conversion, sensing and imaging, supra-molecular photochemically driven machines, multiphoton-absorption materials, probes for monitoring biological processes, and the fabrication of high-performance organic light-emitting diodes (OLEDs).<sup>[1]</sup> A full understanding of the excited-state behavior of organometallic compounds is crucial for the design of new materials for all of these applications. An attractive feature of this class of compounds is that subtle changes in the ligand environment or metal can be used to tune the properties, thereby allowing the control required for a particular application. Diimine complexes of Ru<sup>II</sup>, Re<sup>I</sup>, and Pt<sup>II</sup> have been extensively studied.<sup>[2]</sup> Recently there has also been considerable interest in the photophysics of C<sup>N</sup> cyclometalated complexes, particularly Ir<sup>III</sup>,<sup>[1,3]</sup> and both the diimine and C<sup>N</sup> cyclometalated complexes can exhibit highly emissive triplet excited states.

Mononuclear metal complexes usually show very rapid conversion from singlet into triplet excited states, which is attributed to the “heavy-atom effect”. The heavy-atom effect is the promotion of intersystem crossing (ISC) processes by the spin-orbit coupling (SOC) of the metal atom. These effects can begin to be observed with elements as light as sulphur ( $z = 16$ ).<sup>[4]</sup> For example, the formation of the <sup>3</sup>MLCT (MLCT = metal-to-ligand charge transfer) excited state of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (bpy = 2,2'-bipyridine) occurs on a timescale of

less than 20 fs.<sup>[5]</sup> The precise factors governing the singlet-to-triplet excited state interconversion have recently been questioned by observations which have shown that formation of the <sup>3</sup>MLCT state of the first-row complex [Fe(bpy)<sub>3</sub>]<sup>2+</sup> occurs in less than 20 fs, whereas the second-row complexes [Re(X)(CO)<sub>3</sub>(bpy)]<sup>+</sup> (X = Cl, Br, I) show a much slower interconversion (ca. 100 fs).<sup>[6]</sup> Furthermore, the order was found to be Cl (85 fs) < Br (128 fs) < I (152 fs), which is contrary to that predicted by the simplistic consideration of the effect of the heavy atom. Tetrahedral [Pt(binap)<sub>2</sub>] (binap = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) and [Cu[bis(diimine)]]<sup>+</sup> complexes have been shown to have unusually long-lived <sup>1</sup>MLCT states of  $\tau = 3$  ps and  $\tau = 15$  ps, respectively, attributed to a distortion towards a square-planar geometry which reduces the mixing of the <sup>1,3</sup>MLCT states.<sup>[7]</sup>

Our long-standing interest in rhodium-acetylide compounds<sup>[8]</sup> and luminescent bis(arylethynyl)arenes<sup>[9]</sup> led us to the development of a high-yielding, one-pot synthesis of a 2,5-bis(phenylethynyl)rhodacyclopentadiene, which we reported to be luminescent.<sup>[10]</sup> Our subsequent investigations, reported herein, indicate that this new class of luminescent rhodium complexes shows unprecedented excited-state behavior. Our luminescence spectroscopic studies are supported by picosecond time-resolved IR (TRIR) vibrational spectra of the ground and excited states as a means by which to obtain accurate kinetic data on the processes involved. Herein we demonstrate that despite the presence of the second-row transition metal the compounds show remarkable photo-physical properties: specifically, long-lived, highly emissive singlet excited states. This new class of material challenges our understanding of the behavior of excited electronic states and the role of the heavy atom in intersystem-crossing processes.

The reaction of [Rh(C≡CSiMe<sub>3</sub>)(PMe<sub>3</sub>)<sub>3</sub>] (**1**) with the bis(diyne)s **2a–d** leads to the formation of the metallacyclic complexes **3a–d** (Scheme 1, top), which have been unambiguously characterized by <sup>1</sup>H and <sup>31</sup>P NMR and IR spectroscopy, mass spectrometry, elemental analysis, and by single-crystal X-ray diffraction studies on **3a–c** (Figure 1). In situ NMR spectroscopic studies show that the reactions occur quantitatively, and the products have been isolated in 23–82% yield after several recrystallizations, to ensure high purity for photophysical studies. The photophysical data are summarized in Table 1 and Table 2.

Compounds **3a–d** absorb light with extinction coefficients of 15 000–44 000 L mol<sup>-1</sup> cm<sup>-1</sup> and emit in the visible region (Figure 2). A vibrational progression typical of aromatic stretching modes (ca. 1360 cm<sup>-1</sup>) is observable in the absorp-

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