Reductive Coupling of Diynes at Rhodium Gives Fluorescent Rhodacyclpentadienes or Phosphorescent Rhodium 2,2′-Biphenyl Complexes

Carolin Sieck, Meng Guan Tay, Marie-Hélène Thibault, Robert M. Edkins, Karine Costuas, Jean-François Halet, Andrei S. Batsanov, Martin Haehnel, Katharina Edkins, Andreas Lorbach, Andreas Steffen and Todd B. Marder*

Abstract: Reactions of \([\text{Rh}(\kappa^2O,O\text{-acac})(\text{PMe}_3)_2]\) (acac = acetylacetone) and \(\alpha,\alpha\text{-bis(arylbutadiynyl)}\)alkanes afford two isomeric types of MC₄ metalloacalenes with very different photophysical properties. As a result of a [2+2] reductive coupling at Rh, 2,5-bis(aryl ethynyl)rhodacyclopentadienes (A) are formed, which display intense fluorescence (\(\Phi = 0.07-0.54\), \(\tau = 0.2-2.5\) ns) despite the presence of the heavy metal atom. Rhodium biphenyl complexes (B), which show exceptionally long-lived (hundreds of \(\mu\)s) phosphorescence (\(\Phi = 0.01-0.33\)) at room temperature in solution, have been isolated as a second isomer originating from an unusual \([4+2]\) cycloaddition reaction and a subsequent \(\beta\)-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 \(S_{2.5} \rightarrow T_{1.3}\) and \(T_1 \rightarrow S_0\). Control of the isomer distribution is achieved by modification of the bis(diynyl) 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 \(\mu\)s, which can be exploited in photocatalysis, light-emitting devices, and biological imaging. The great attention that the prototypical compounds \([\text{Ru(bpy)}_3]^{2+}\) and \([\text{Ir}(	ext{ppy})_3]\) 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. However, it is worth noting that our knowledge of the optical properties of metallocyclpentadienes, i.e., \(MC_4N_N\) \((n = 0-2)\) compounds, is mainly limited to \(\{\text{M}(\kappa^2-N,\text{N}=\text{C}_2\text{N})\}\) type complexes.

Synthesis of M(2,2′-bph) complexes (bph = biphenyl) as MC₄ 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 dhalide (Scheme 1). 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 biphényl compounds of Pd, Pt, Ir and Au. 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, metallocyclpentadienes derived from the reductive coupling of alkynes are well known intermediates in cyclotrimerization reactions of alkynes and alkynenitrile combinations, and are thus much more readily accessible. However, apart from our recent reports, nothing is known about their photophysical properties.

General access to biphenyl complexes:

\[
\begin{align*}
\text{Synthesis of luminescent RhC₄ complexes by Marder et al.:} \\
\[\text{[Rh]} = \{\text{Rh(CCS)}_3\text{(PMe}_3)_2\} \\
\text{R} = \text{Ar or C}_2\text{H}_4
\end{align*}
\]

Scheme 1. General synthetic access to transition metal biphényl complexes (top) and synthesis of luminescent 2,5-bis(aryl ethynyl)rhodacyclopta-2,4-dienes established by Marder et al. (bottom).
We have recently achieved the regioselective, quantitative formation of rod-like, conjugated 2,5-bis(arylthynyl)-rhodacorhopentadienes, and one iodine analogue, by reductive coupling of 1,4-diarylbuta-1,3-dienes or linked bis(diyynes) Ar-C≡C-C≡C-(CH2)n-C≡C-C≡C-Ar (Scheme 1).6 A ruthenium analogue has been reported in a purely synthetic study by Hill et al.7 Such MC4 metallacycles are structurally related to 2,5-bis(arylthynyl)-substituted main group heterocycles, such as siloles,8 phospholes9 or thiophenes,10 which display interesting linear and non-linear optical properties. Surprisingly, our rhodacorhopentadienes exhibit highly efficient fluorescence with quantum yields of up to \( \Phi_{FL} = 0.69 \) despite the presence of the heavy metal atom that would be expected to facilitate rapid \( S_1 \rightarrow T_n \) intersystem crossing (ISC) and thus to quench the fluorescence.11c, 11e This finding motivated us to prepare new MC4 metallacycles and to investigate their photophysical properties.

**Results and Discussion**

**Synthesis of rhodium 2,2'-biphenyl complexes and 2,5-bis(arylthynyl)rhodacorhopenta-2,4-dienes.**

We decided to examine the influence of the ligand sphere around the rhodium center on the ISC processes in the abovementioned fluorescent rhodacorhopentadienes by introduction of \( \pi \)-electron-donating groups, such as acetylacetone. Interestingly, the reaction of \([\text{Rh}(\kappa^2\mathrm{O,C}, \text{acac})\text{(PMe}_3)_2]\)12 with either \( \alpha,\omega \)-bis(arylbutadiynyl)alkane 2a or 2b in a 1:1 ratio in homogenous solution at room temperature leads to the formation of two isomers, i.e., 2,5-bis(arylthynyl)rhodacorhopentadienes A (3a,b) and rhodium biphenyl complexes B (4a,b) (Scheme 2). The product ratio depends on the temperature and on the aryl substituents, with the acceptor-substituted (CO\( \text{Me}_2 \)) substrate favoring isomer B, and the donor-substituted (SMe) substrate leading to an excess of A.

![Scheme 2. Synthesis of rhodacorhopentadienes (A) and rhodium biphenyl complexes (B).](image)

In contrast, simple modification of the \( \alpha,\omega \)-bis(arylbutadiynyl)alkane, i.e., changing the linker length from 4 CH\(_2\) groups in 2a,b to 3 CH\(_2\) groups in 5a and 5b, dramatically favors the formation of the rhodium biphenyl isomer B for entropic reasons, leading to an A:B ratio of 1:20 at room temperature. For these shorter chain substrates the para-substituents of the aryl rings have no influence on the isomer distribution although they do affect the reaction rate, with the acceptor-substituted (CO\( \text{Me}_2 \)) \( \alpha,\omega \)-bis(arylbutadiynyl)alkanes 2a and 5a reacting the fastest. Also remarkable is that the shorter chain substrates react much faster (complete in 3 days) than the longer ones (several weeks). It is important to note that all reactions shown in Scheme 1 occur with complete conversion of the starting materials to the two isomers A and B in 100% total yield, with no byproducts observed by \textit{in situ} solution NMR spectroscopy (Figure 1).

![Figure 1. \textit{In situ} \( ^1\text{P}[^1\text{H}] \) and \( ^1\text{H} \) NMR spectra of the reactions of \([\text{Rh}(\text{acac})\text{(PMe}_3)_2]\) with 2a at 293 K (top) and with 5a at 333 K (bottom) giving A:B isomer ratios of 1:2.6 and 1:2.5, respectively.](image)
Due to the fact that the para-substituents of the aryl moieties influence the reaction rate (see above), we were interested in the selectivity of the reaction of unsymmetrical donor/acceptor-substituted $\alpha,\alpha'$-bis(arylbutadiynyl)alkanes 8 with [Rh($\kappa^2$-O,O-\text{acac})(PMe$_3$)$_2$]$_2$ (1), as we were seeking hints on the reaction pathway that discriminates the formation of the biphenyl complexes from the [2+2+M] cycloaddition that gives the 2,5-substituted rhodacyclopentadienes. In addition, use of 8 was expected to lead to different isomers with increased charge-transfer character in their excited states in comparison to 3, 4, 6 and 7, potentially leading to materials with interesting non-linear optical properties.

The reaction of 1 with the $\alpha,\alpha'$-bis(arylbutadiynyl)alkanes 8 at 333 K gave the biphenyl complex 9 as the major product (83%), while its isomer 10 and rhodacyclopentadiene 11 are formed in 12% and 5% yield, respectively (Scheme 3). We were able to isolate pure 9 and 11, and the identity of the rhodium biphenyl complex 10 was confirmed by $^1$H and $^{31}$P($^1$H) NMR spectroscopic studies of the reaction mixture. The molecular structure of 9 obtained from single crystal X-ray diffraction is shown in Figure 3, unambiguously identifying that isomer.

Whereas the rhodacyclopentadienes of type A are the result of a “normal” [2+2] cycloaddition reaction, and thus structurally related to well established intermediates in metal-mediated alkyne cyclotrimerization,[5] the mechanism of formation of the biphenyl complexes (B) is more complicated. Formally, a [4+2]-dine-alkyne cyclization occurs with a subsequent ortho C-H activation and C-H-shift (Scheme 2). Recently, it has been demonstrated that the hexadehydro Diels-Alder (HDDA) reaction gives an aryne species, which can either be trapped directly by nucleophiles[13] or be stabilized by, e.g., Ag(I) or other Lewis acids.[13] The latter allows for a Friedel-Crafts-type electrophilic aromatic substitution to occur, leading to a hydroarylation forming biaryls. We cannot exclude that, related to the HDDA reaction, a Rh benzene $\pi$-complex is formed as an intermediate, undergoing subsequent C-H activation of the pendant $\rho$-(CO$_2$Me)$_2$C$_6$H$_4$ ring to give the Rh(III) biphenyl complexes B instead of the rhodacyclopentadienes A. However, we note that HDDA reactions usually require elevated temperatures, even in the presence of a metal complex, while formation of B is observed at or even below room temperature. We have not yet been able to clarify the kinetics (i.e., the reaction order in M and bis(diyne)) via in situ NMR spectroscopic investigations due to the limited solubility range of the starting materials, but further synthetic and mechanistic studies are currently being performed to gain more insight into the mechanism of this exciting and very unusual reaction.

Photophysical and DFT/TD-DFT studies.

Isomers A exhibit intense visible fluorescence with $\Phi_{PL} = 0.01$-0.54 and emission lifetimes of a few nanoseconds in toluene and 2-MeTHF solutions, as well as in the solid state and in PMMA films at room temperature (Figure 4 and Table 1, and ESI). The CO$_2$Me-substituted compounds 3a and 6a show significantly higher $\Phi_{PL}$ and a bathochromic shift in the absorption and emission spectra in comparison to their SMe-substituted congeners 3b and 6b, due to a more pronounced charge-transfer from the Rh$_2$ core to the phenyl moieties. The NMe$_2$/CO$_2$Me-substituted rhodacyclopentadiene 11 experiences a strong intraligand charge-transfer, resulting in an emission with $\lambda_{max} = 576$ nm, $\lambda_{max} = 600$ nm and $\lambda_{max} = 651$ nm in toluene.
PMMA and 2-MeTHF, respectively. Interestingly, at 77 K in 2-MeTHF the bathochromic shift of the emission in comparison to toluene solutions at 297 K is negligible, which suggests that the CT in more polar environments at room temperature is accompanied by a significant geometrical reorganization in the excited state, which is hampered at low temperatures in the glassy matrix.

Figure 4. Emission spectra of rhodacyclopentadienes 6a (black), 6b (blue) and 11 (red) in degassed toluene solution at room temperature.

Table 1. Selected photophysical data of compounds 3, 4, 6, 7 (all a,b), 9 and 11 recorded under oxygen-free conditions.

<table>
<thead>
<tr>
<th>Cpd.</th>
<th>λ_{em} [nm]</th>
<th>λ_{on} [nm]</th>
<th>Φ_{PL}</th>
<th>τ [s]</th>
<th>κ_{r} [s^-1]</th>
<th>κ_{nr} [s^-1]</th>
<th>2-MeTHF / 297 K</th>
<th>λ_{em} [nm]</th>
<th>τ [s]</th>
<th>2-MeTHF / 77 K</th>
<th>λ_{em} [nm]</th>
<th>τ [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>514</td>
<td>579</td>
<td>0.50</td>
<td>2.5 ns</td>
<td>2.0 \times 10^6</td>
<td>2.0 \times 10^8</td>
<td>579</td>
<td>0.24</td>
<td>0.5 ns</td>
<td>581</td>
<td>2.8 ns</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>481</td>
<td>534</td>
<td>0.13</td>
<td>2.0 (25%), 0.5 (75%) ns</td>
<td>1.5 \times 10^8</td>
<td>9.9 \times 10^8</td>
<td>544</td>
<td>0.09</td>
<td>0.4 ns</td>
<td>532</td>
<td>0.9 (57%), 4.4 (43%) ns</td>
<td></td>
</tr>
<tr>
<td>4a</td>
<td>410</td>
<td>545</td>
<td>0.12</td>
<td>162 µs</td>
<td>740</td>
<td>5430</td>
<td>544</td>
<td>0.33</td>
<td>372 µs</td>
<td>540</td>
<td>537 µs</td>
<td></td>
</tr>
<tr>
<td>4b</td>
<td>390</td>
<td>542</td>
<td>0.01</td>
<td>43 (40%), 119 (60%) µs</td>
<td>110 (6%)</td>
<td>11200</td>
<td>577</td>
<td>0.02</td>
<td>81 µs</td>
<td>530</td>
<td>2750 (80%), 3950 (20%) µs</td>
<td></td>
</tr>
<tr>
<td>6a</td>
<td>535</td>
<td>563</td>
<td>0.54</td>
<td>1.7 ns</td>
<td>3.2 \times 10^6</td>
<td>2.7 \times 10^8</td>
<td>570</td>
<td>0.57</td>
<td>1.7 ns</td>
<td>569</td>
<td>2.1 (90%), 3.1 (10%) ns</td>
<td></td>
</tr>
<tr>
<td>6b</td>
<td>503</td>
<td>522</td>
<td>0.07</td>
<td>0.3 (77%), 0.1 (23%) ns</td>
<td>2.8 \times 10^6</td>
<td>3.7 \times 10^8</td>
<td>522</td>
<td>0.08</td>
<td>0.2 ns</td>
<td>515</td>
<td>2.2 ns</td>
<td></td>
</tr>
<tr>
<td>7a</td>
<td>377</td>
<td>540</td>
<td>0.14</td>
<td>181 µs</td>
<td>770</td>
<td>4750</td>
<td>541</td>
<td>0.16</td>
<td>338 µs</td>
<td>537</td>
<td>374 (97%), 1340 (3%) µs</td>
<td></td>
</tr>
<tr>
<td>7b</td>
<td>382</td>
<td>535</td>
<td>0.02</td>
<td>61 (99%), 163 (2%) µs</td>
<td>330 (6%)</td>
<td>16000 (3%)</td>
<td>534</td>
<td>0.10</td>
<td>646 µs</td>
<td>527</td>
<td>1920 (73%), 2770 (27%) µs</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>371</td>
<td>536</td>
<td>0.29</td>
<td>164 (12%), 496 (88%) µs</td>
<td>640 (4%)</td>
<td>1560 (1%)</td>
<td>535</td>
<td>0.21</td>
<td>45 (34%), 210 (66%) µs</td>
<td>534</td>
<td>680 (66%), 1100 (34%) µs</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>496</td>
<td>576</td>
<td>0.22</td>
<td>0.8 ns</td>
<td>2.8 \times 10^8</td>
<td>9.8 \times 10^8</td>
<td>651</td>
<td>0.13</td>
<td>0.5 ns</td>
<td>582</td>
<td>2.2 (98%), 4.5 (2%) ns</td>
<td></td>
</tr>
</tbody>
</table>

[a] Calculated from weighted average lifetimes.
selected molecular orbitals of rhodacyclopentadiene 3a (left) and rhodium biphenyl complex 4a (right). Contour values: ±0.035 [e/bohr$^3$]$	ext{1/2}$.

Figure 6. a) MO diagrams of the frontier orbital region of 3a and 4a. Calculated vertical excitations of 3a and 4a (blue: singlet states, red: triplet states).

Figure 7. Emission (solid) and excitation (dashed) spectra of rhodium biphenyl complexes 3a (red) and 4a (blue) in degassed toluene solution at room temperature.

Unlike in the solid state, the biphenyl complexes B are chemically sensitive to dioxygen in solution, thus we ensured rigorous exclusion of O$_2$. In contrast to rhodacyclopentadienes A, the para-substituents of the phenyl rings barely influence the absorption and emission spectra (Figure 8). However, we found that, again, the acceptor-substituted compounds show higher $\Phi_{PL}$. Interestingly, the NMe$_2$/CO$_2$Me- and the CO$_2$Me-substituted biphenyl complexes 9 and 4a are, to the best of our knowledge, among the most efficient phosphorescing Rh complexes as well as among the most efficient metal biphenyl triplet emitters to date, being even more efficient than known Ir- and Pt-biphenyl complexes.

Despite ISC S$_1$→T$_n$ being sufficiently fast for population of T$_1$, however, there are very few complexes which exhibit fluorescence with the efficiency displayed by our rhodacyclopentadienes, which involves exceptionally slow S$_1$→T$_n$ ISC on the timescale of nanoseconds rather than in a few picoseconds or faster.

In stark contrast, the unusual biphenyl complexes B display purely phosphorescence, as expected of 2$^{nd}$ row metal complexes (Figure 7), with quantum yields of up to 0.29 for 9 in toluene and up to 0.33 for 4a in 2-MeTHF, and emission lifetimes on the 10’s – 100’s of microsecond timescale (Tables 1 and S2) at room temperature. We note that the PLOYs and lifetimes in PMMA differ for some of the isomers B from the data obtained in solution. We exclude aggregation from being responsible for this phenomenological observation due to the superimposition of the emission spectra (see ESI). Apparently, the interaction of B with the surrounding matrix leads to changes in the Franck-Condon factors for the vertical transition T$_1$→S$_0$, increasing or decreasing the rate constants for radiative and non-radiative decay.

Unlike in the solid state, the biphenyl complexes B are chemically sensitive to dioxygen in solution, thus we ensured rigorous exclusion of O$_2$. In contrast to rhodacyclopentadienes A, the para-substituents of the phenyl rings barely influence the absorption and emission spectra (Figure 8). However, we found that, again, the acceptor-substituted compounds show higher $\Phi_{PL}$. Interestingly, the NMe$_2$/CO$_2$Me- and the CO$_2$Me-substituted biphenyl complexes 9 and 4a are, to the best of our knowledge, among the most efficient phosphorescing Rh complexes as well as among the most efficient metal biphenyl triplet emitters to date, being even more efficient than known Ir- and Pt-biphenyl complexes.
The fundamentally different photophysical properties of B in comparison with A may arise from the energetic proximity of the filled frontier molecular orbitals in B, which are mixtures of ligand $\pi$ and metal d orbitals (Figures 5, 6 and S33). As a result, a number of triplet excited states with some MLCT contribution can efficiently connect the S$_1$ state with the emitting T$_1$ state (see Figure 6 and TD-DFT results in the ESI). Indeed, as no fluorescence is detected even at low temperature, it can be assumed that S$_1\rightarrow$T$_{1r}$ ISC must be faster than both fluorescence and non-radiative decay from S$_1$, and, therefore, $\Phi_{ISC} = 1$ (vide infra). This contrasts with the behavior of the isomeric rhodacyclopentadienes (e.g., 3, 6, 11) for which we have previously shown that the unusually slow ISC occurs on a timescale that is competitive with fluorescence (vide supra).

However, the very small values of the radiative rate constants $k_{r}$ = 110-770 s$^{-1}$ of 4, 7 and 9 in toluene indicate that the nature of the T$_1$ state is purely $^3$IL with weak SOC mediated by the Rh atom. This was further confirmed by luminescence measurements on those compounds in 2-MeTHF (Table 1). For example, compound 9 shows lifetimes of $\tau_{av} = 154$ µs and $\tau_{av} = 823$ µs at room temperature and at 77 K, respectively. The increase in emission lifetime upon cooling from 298 K, at which temperature the quantum yield has been determined to be $\Phi_{PL} = 0.21$, to 77 K by a factor of five indicates a phosphorescence quantum yield of unity and thus supports 100% ISC with $\Phi_{ISC} = 1$. Thus, their phosphorescence efficiency in solution at room temperature is even more impressive, as non-radiative coupling of the excited state with the ground state with energy loss to the environment on a sub-ms timescale typically precludes phosphorescence. Instead, the rigidity of the organic $\pi$-system allows the ligand-based triplet excited state to exist in solution for up to ca. 500 µs for 9 in toluene, and even up to 646 µs for 7b in 2-MeTHF, and to emit with exceptional quantum yields for biphenyl complexes of 0.29 and 0.33 for 9 and 4a, respectively.

![Figure 8. Emission spectra of rhodacyclopentadienes 7a (black), 7b (blue) and 9 (red) in degassed toluene solution at room temperature.](image-url)

The exceptional long lifetimes and small radiative rate constants of the rhodium biphenyl complexes in comparison to other $^3$IL emitters of, e.g., Pt(II) or Au(III)[19] presumably are a result of the long conjugation of the organic ligand $\pi$-system. According to our TD-DFT studies, the T$_1$ state involves charge transfer from the biphenyl ligand into the arylethynyl moiety away from the rhodium atom, which reduces SOC of the metal center that would be necessary for fast phosphorescence. Such long-lived triplet excited states can be very useful for application in color tunable OLEDs,[19b] in which at high voltages the emissive excited state of a low-energy emitter must have a long lifetime in order to become saturated by energy transfer from a short-lived high-energy lumiphore. The latter then mainly determines the color of the OLED, whereas at low voltages the low-energy emitter is dominant. Also, long-lived excited states are of interest for photocatalysis, energy up-conversion and non-linear optics, as has been shown recently, e.g., for $\text{Pd(II)}$ porphyrin and Au(III) 2,6-diphenylpyridine complexes.[19c, d]

**Conclusions**

In conclusion, we report a very unusual reaction which produces two isomeric metallacycles with fundamentally different photophysical properties. Whereas unusual fluorescent 2,5-bis(arylethynyl)rhodacyclopentadienes are obtained from a known type of reductive coupling of two alkyne moieties, a highly unusual [4+2] coupling reaction with subsequent C-H-shift leads to a novel class of highly phosphorescent Rh(2,2'-bpy) complexes. The exceptional luminescence performance of the latter compounds, i.e., lifetimes in solution of up to 646 µs and, for biphenyl complexes, unusually high quantum yields of up to 0.33[4, 18, 19] clearly demonstrates the potential of this class of materials. We also show that control over the isomer distribution is possible by simple modification of the $\alpha$-$\omega$-bis(arylethynyl)alkane linker length, providing a new synthetic methodology to access a range of dibenzo-metallacyclopentadienes. We are currently carrying out experimental and theoretical studies of the reaction mechanism in order to understand the factors leading to isomers A and B, and exploring applications of the new long-lived triplet states of the dibenzo-metallacyclopentadienes.

**Experimental Section**

**General considerations:** The syntheses of $\alpha$-$\omega$-bis(arylethynyl)alkanes and 1 are described in the ESI. All other starting materials were purchased from commercial sources and used without further purification. Inhibitor-free anhydrous 2-MeTHF was purchased from Sigma Aldrich. All other solvents for synthetic reactions and for photographic measurements were of HPLC grade, further treated to remove trace water using an Innovative Technology Inc. Pure-Solv Solvent Purification System and deoxygenated using the freeze-pump-thaw method. All reactions were performed under an argon atmosphere in an Innovative Technology Inc. glovebox or using standard Schlenk techniques. $^1$H, $^{13}$C($^1$H) and $^{31}$P($^1$H) NMR spectra were
measured on a Varian VNRMS-700 (1 H, 700 MHz; 13C(1)H, 176 MHz; 31P(1)H, 283 MHz), Bruker Avance-500 (1 H, 500 MHz; 13C(1)H, 126 MHz; 31P(1)H, 202 MHz), Bruker Avance-400 (1 H, 400 MHz; 13C(1)H, 101 MHz) or Bruker Avance III 300 (1 H, 300 MHz; 13C(1)H, 101 MHz; 31P(1)H, 121 MHz) NMR spectrometer. Mass spectra were recorded on a Bruker Daltonics autoflex II LRF mass spectrometer operating in the MALDI mode, unless stated otherwise. The mass spectra of 2a and 2b were obtained using an Applied Biosystem Voyager-DE STR MALDI ToF mass spectrometer. The mass spectra of 3a and 3b were obtained in ESI mode using a Thermo-Finnigan LTO FT mass spectrometer operating in positive ion mode. Elemental analyses were performed on a Leco CHNS-932 Elemental Analyzer. The elemental analysis for compounds 2a, 2b, 3a and 3b were performed on an Exeter Analytical CE-440 analyzer.

General procedure for the synthesis of rhodium biphienyl complexes (4a, 4b, 7a, 7b, 9, 10) and rhodacyclopendadienes (3a, 3b, 6a, 6b, 11):

One equivalent of 1 and one equivalent of the corresponding bis(diyne) (2a for 3a, 4a), (2b for 3b, 4b), (5a for 6a, 7a), (5b for 6b, 7b) for 9, 10, 11 were suspended in THF (10 mL) and the reaction mixture was stirred. For specific reaction temperatures and reaction times, see below. Then, the volatiles were removed in vacuo to give isomers A and B in 100% total yield as demonstrated in Figure 1. The product mixture was dissolved in THF and separation was achieved via column chromatography (Al2O3) eluting with hexane and THF (2:1). The rhodium biphienyl complexes 4a, 4b, 7a, 7b, 9 and 10 were recrystallized from THF and washed with hot hexane, both steps several times, to obtain spectrosopically pure samples, and to ensure that trace impurities are not present which might influence the photophysical characterization. The yields given below are the isolated single crystalline samples, after several purification steps, used for luminescence spectroscopy.

4a: Stirring at room temperature for 14 days. Yellow solid. Isolated yield: 0.09 g (41%).

1H NMR (500 MHz, CD3OD, r.t., ppm) δ: 9.52 (s, J = 8 Hz, 1 H, CHarom), 9.10 (s, 1 H, CHarom), 8.37 (d, J = 8 Hz, 1 H, CHarom). 8.05 (d, J = 8 Hz, 2 H, CHarom), 8.04 (s, 1 H, CHarom), 7.57 (d, J = 8 Hz, 2 H, CHarom), 5.13 (s, 1 H, CH), 3.62 (s, 3 H, CH3), 3.62 (s, 3 H, CH3), 3.48 (m, 2 H, CH2), 3.24 (m, 2 H, CH2), 2.91 (m, 2 H, CH2), 1.89 (s, 3 H, CH3), 1.88 (s, 3 H, CH3), 1.70 (m, 2 H, CH2), 0.57 (vt, J = 3 Hz, 18 H, PMe3).

13C(1)H NMR (126 MHz, CD3OD, r.t., ppm) δ: 188.4, 187.7, 186.2, 166.3, 166.0, 163.1 (dt, J = 1H, c = 10 Hz, 3J, c = 31 Hz), 158.7, 149.9, 134.7, 134.5, 134.2, 133.3, 131.4, 130.1, 129.7, 129.5, 128.4, 126.6, 124.5, 123.5, 116.5, 99.3, 93.8, 51.6, 51.3, 30.8, 28.6, 24.7, 23.7, 10.8 (vt, J = 14 Hz). Due to the low intensity, the J13H,13ch coupling of the second quat. carbon atom could not be determined.

31P(1)H NMR (121 MHz, CD3OD, r.t., ppm) δ: -2.2 (d, J = 113 Hz, 2 P).


4b: Stirring at room temperature for 14 days. Yellow solid. Isolated yield: 0.02 g (35%).

1H NMR (500 MHz, CD3OD, r.t., ppm) δ: 9.47 (d, J = 8 Hz, 1 H, CHarom), 8.29 (m, 1 H, CHarom), 7.98 (s, 1 H, CHarom), 7.76 (d, J = 8 Hz, 2 H, CHarom), 7.56 (d, J = 8 Hz, 2 H, CHarom), 7.56 (s, 1 H, CH), 5.62 (s, 1 H, CH), 5.62 (s, 1 H, CH), 2.94 (m, 2 H, CH2), 2.32 (m, 2 H, CH2), 1.90 (s, 3 H, CH3), 1.89 (s, 3 H, CH3), 1.84 (s, 3 H, CH3), 1.74 (m, 2 H, CH2), 0.60 (vt, J = 3 Hz, 18 H, PMe3).

13C(1)H NMR (176 MHz, CD3OD, r.t., ppm) δ: 187.9, 187.7, 187.0 (dt, J = 1H, c = 10 Hz, 3J, c = 31 Hz), 186.7 (dt, J = 1H, c = 10 Hz, 3J, c = 131 Hz), 151.2, 150.5, 139.1, 134.3, 133.9, 132.8, 131.9, 130.3, 128.4, 127.9, 125.6, 124.5, 121.7, 120.5, 115.8, 99.4, 99.1, 91.2, 30.9, 28.8, 28.7, 28.6, 24.4, 23.9, 16.1, 15.0, 10.7 (vt, J = 14 Hz).

31P(1)H NMR (202 MHz, CD3OD, r.t., ppm) δ: -2.28 (d, J = 113 Hz, 2 P).

For ease of isolation of spectroscopically pure rhodacyclopendadienes (3a, 3b, 6a, 6b, 11), a different reaction procedure was developed: one equivalent of [Rh(acac)(P(toly)-tmeda)], which was prepared via a modification of the synthesis for compound 1, and one equivalent of the corresponding bis(diyne) (2a for 3a), (2b for 3b), (5a for 6a), (5b for 6b), (8 for 11), were suspended in THF (10 mL) at 60 °C and stirred for...
5 days. Once the reaction was complete, PMe3 (excess) was added in situ to the reaction mixture, which was stirred at 60 °C for 2 d. Then, the volatiles were removed in vacuo and the product was recrystallized from THF and washed with hot hexane to give 3a, 3b, 6a, 6b and 11, respectively. The yields given below are those of single-crystalline material used for spectroscopic investigations obtained after several purification steps to ensure the absence of any trace impurities, such as free phosphine, which might influence the photophysical measurements.

3a: Red solid. Isolated yield: 0.07 g (3.5%). 1H NMR (700 MHz, CD2Cl2, r.t., ppm): δ 8.13 (d, J = 8 Hz, 4 H, CH2=), 7.68 (d, J = 4 Hz, 4 H, CH=), 5.13 (s, 1 H, CH), 3.47 (s, 6 H, CH3), 2.91 (m, 4 H, CH2), 1.91 (s, 6 H, CH3), 1.66 (m, 4 H, CH2), 0.88 (v, J = 4 Hz, 18 H, PMe3). 11C (H) NMR (126 MHz, CD2Cl2, r.t., ppm) δ: 187.1, 166.5, 158.4, 140.3 (dt, 3JPC = 10 Hz, 4JPC = 31 Hz), 132.2, 131.0, 130.0, 128.3, 110.0, 99.0, 98.0, 51.5, 30.7, 28.5, 24.9, 10.9 (v, JPC = 14 Hz). 31P (H) NMR (161 MHz, CD2Cl2, r.t., ppm) δ: 6.50 (d, JPH = 113 Hz, 2 P). Elem. Anal. Calcld. (%) for C31H32P3O3: C, 60.15; H, 6.10. Found: C, 60.15; H, 6.10. MS (ES') m/z = 776 [M]+, 700 [M - PMe3]+, 677 [M - acac]+.

3b: Red solid. Isolated yield: 0.01 g (2.2%). 1H NMR (400 MHz, CD2Cl2, r.t., ppm): δ 7.62 (d, J = 8 Hz, 4 H, CH2=), 7.08 (d, J = 4 Hz, 4 H, CH=), 5.17 (s, 1 H, CH), 2.96 (m, 4 H, CH2), 1.97 (s, 6 H, CH3), 1.93 (s, 6 H, CH3), 1.69 (m, 4 H, CH2), 0.96 (v, JPH = 4 Hz, 18 H, PMe3). 11C (H) NMR (126 MHz, CD2Cl2, r.t., ppm) δ: 186.8, 156.5, 137.1, 131.4, 126.8, 124.4, 109.7, 98.8, 94.7, 30.9, 28.6, 25.1, 15.4, 10.9 (v, JPC = 14 Hz). Due to the low intensity, the 3JPC- and 4JPC-coupling could not be determined. The crystals were cooled using Cryostream open-flow N2 gas cryostat. The structures were solved using direct methods (SHELXS, for 3a, 3b, 4a) or the intrinsic phasing method (SHELXT) and Fourier expansion technique, or by using the olex2.solve algorithm. All non-H atoms were refined anisotropically, with the exception of highly disordered groups. H atoms were refined isotropically using a riding model. All structures were refined by full-matrix least squares against F2 for all data using the programs SHELXL and OLEX2.refine. The program DIAMOND was used for graphical representation. General color code: carbon (white), sulfur (yellow), oxygen (red), phosphorus (purple), iodine (dark green), nitrogen (blue), Crystal data and experimental details are listed in Table S1; full structural information has been deposited with the Cambridge Structural Database, CCDC 1419146 to 1419156.

General photophysical measurements: UV-visible absorption spectra were obtained on an Agilent 1100 Series Diode Array spectrophotometer using standard 1 cm path length quartz cells. Emission spectra were recorded on an Edinburgh Instruments FLS980 spectrometer, equipped with a 450 W Xenon arc lamp, double monochromators for the excitation and emission pathways, and a red-sensitive photomultiplier tube (R928-P PMT) as the detector. All spectra were fully corrected for the spectral response of the instrument. Unless otherwise mentioned, the longest-wavelength absorption maximum of the compound in the respective solvent was chosen as the excitation wavelength for the emission measurements. The emission spectra are independent of the excitation wavelength, and the absorption and excitation spectra are comparable across the measured range. All solutions used in photophysical measurements had a concentration lower than 6 x 10–5 M to minimize inner filter effects during photoluminescence measurements. Films of (poly(methylmethacrylate)) (PMMA) were produced by drop-casting from chloroform solutions with a concentration of 0.1 wt%.

Fluorescence quantum yield measurements: The emission quantum yields were measured using a calibrated integrating sphere from Edinburgh Instruments combined with the FLS980 spectrometer described above.

Lifetime measurements: The luminescence lifetimes were measured on the FLS980 spectrometer using either a μF900 pulsed 60 W Xenon
microsecond flashlamp, with a repetition rate of 100 Hz, and a multichannel scaling module, or with a picosecond pulsed laser diode ($\lambda_{em} = 420$ or 376 nm) and a time-correlated single-photon counting (TCSPC) unit. The emission was collected at right angles to the excitation source with the emission wavelength selected using a double grated monochromator and detected by a R928-P PMT. Very short lifetimes for compounds 6a, 6b and 11 were recorded using an Edinburgh Instruments FLS980 spectrometer equipped with a high speed photomultiplier tube positioned after a single emission monochromator. Data were collected to 10 000 counts in the peak channel and were fitted over >1 000 channels. The instrument response function (IRF) was measured using a scattering sample (LUDOX) and setting the emission monochromator at the wavelength of the excitation beam. The resulting intensity decay is a convolution of the luminescence decay with the IRF, and iterative reconvolution of the IRF with one or two decay function(s) and non-linear least squares analysis was used to analyze the convoluted data. A bi-exponential decay fit was chosen only when the fit was significantly better than with a single function. The quality of all decay fits was judged to be satisfactory, based on the calculated values of the reduce $\chi^2$ and Durbin-Watson parameters and visual inspection of the weighted residuals.

Low temperature photoluminescence spectroscopy: Low temperature measurements were performed in an Oxford Instruments Optistat DN $N_2$ cryostat controlled by an Oxford Instruments Mercury iTC temperature controller. Samples were allowed to equilibrate at 77 K before measurements were conducted. 2-MeTHF solutions were observed to form clear glasses below $T_p$.

Computational details: DFT calculations were carried out using the Gaussian 09 program.[26] The geometric structures were fully optimized without any symmetry constraints using the MPW1PW91 functional with the LANL2DZ ECP basis set. This basis set was augmented by polarization functions for all atoms except hydrogens.[27] Harmonic vibrational frequency calculations were performed to verify that the optimized geometries represent energy minima. TD-DFT calculations were performed at the ground-state geometry for the 30 lowest-lying excited singlet and 5 lowest-lying triplet states using the previously employed functional and basis sets. The isosurface spin-density representations and the calculated absorption spectra were generated using the GaussView 5.0 program.[28]

Acknowledgements

We thank the DFG for support. A.S. thanks the DAAD and the EU (Marie-Curie FP7). M.-H.T., thanks the FORNT Quebec, Canada and R.M.E. and A.L. thank the Alexander von Humboldt Foundation for postdoctoral fellowships. M.G.T thanks Universiti Malaysia Sarawak, Malaysia, for a Ph.D. scholarship. Part of this work was conducted within the scope of the CNRS Associated European Laboratory “Molecular Materials and Catalysis (MMC)” involving the Department of Chemistry of Durham University and the Institut des Sciences Chimiques de Rennes of the University of Rennes 1, and within the Collaborative Research Network “Solar Technologies go Hybrid” of the Bavarian State Ministry of Science, Research, and the Arts.

Keywords: luminescence • metalacycle • dibenzo • OLED • intersystem crossing


The Light at the End of the Cycle: We report a combination of novel reactivity of bis(diynes) at rhodium centers with the unusual photophysical properties of the two isomeric products formed. Thus, reactions of alkyl-linked bis(diynes) at Rh(I) gives either fluorescent rhodacyclopentadienes via 2+2 coupling (normal reactivity, unusual photophysical behavior), or phosphorescent dibenzorhodacyclopentadienes via a 4+2 coupling (unusual reactivity, unexpectedly long-lived luminescence).