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

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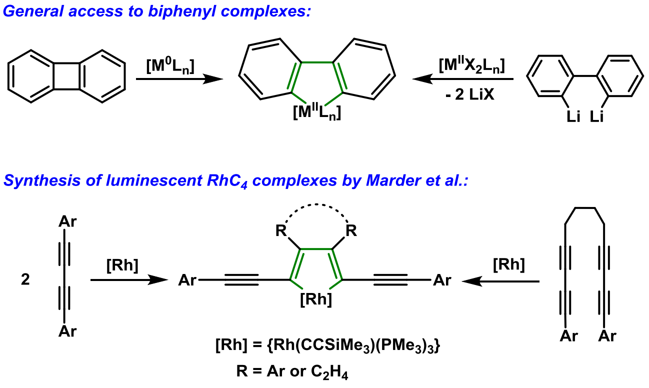
**Abstract:** Reactions of [Rh($\kappa^2$-$O$,$O$-acac)(PMe$_3$)$_2$] (acac = acetylacetonato) and $\alpha,\omega$-bis(arylbutadiynyl)alkanes afford two isomeric types of MC$_4$ metallacycles with very different photophysical properties. As a result of a [2+2] reductive coupling at Rh, 2,5-bis(arylethynyl)rhodacyclopentadienes (**A**) are formed, which display intense fluorescence ($\Phi$ = 0.07-0.54, $\tau$ = 0.2-2.5 ns) despite the presence of the heavy metal atom. Rhodium biphenyl complexes (**B**), which show exceptionally long-lived (hundreds of µs) 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$_1$→T$_n$ and T$_1$→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 [Ru(bpy)$_3$]$^{2+}$ and [Ir(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.*, MC$_{4-n}$N$_n$ (n = 0-2) compounds, is mainly limited to {M($\kappa^2$-$N$,$N$´-C$_2$N$_2$)} and {M($\kappa^2$-$N$,$C$-C$_3$N)} type complexes.

Synthesis of M(2,2'-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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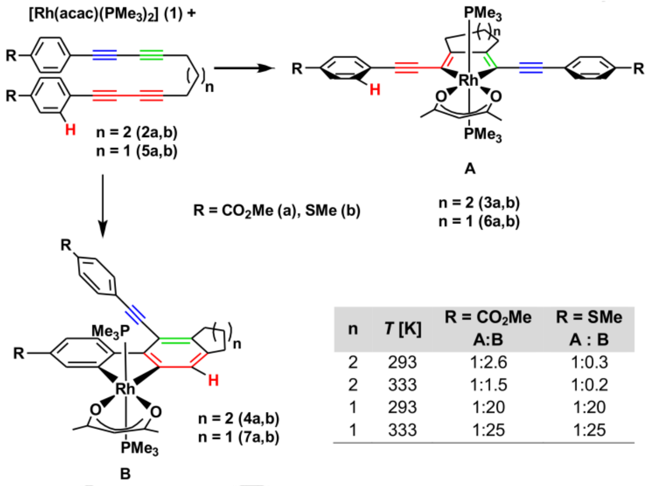
We have recently achieved the regioselective, quantitative formation of rod-like, conjugated 2,5-bis(arylethynyl)-rhodacyclopentadienes, and one iridium analogue, by reductive coupling of 1,4-diarylbuta-1,3-diynes or linked bis(diynes) Ar-C≡C-C≡C-$(CH_2)_4$-C≡C-C≡C-Ar (Scheme 1).[6] A ruthenium analogue has been reported in a purely synthetic study by Hill *et al*.[7] Such $MC_4$ metallacycles are structurally related to 2,5-bis(arylethynyl)-substituted main group heterocycles, such as siloles,[8] phospholes[9] or thiophenes,[10] which display interesting linear and non-linear optical properties. Surprisingly, our rhodacyclopentadienes exhibit highly efficient fluorescence with quantum yields of up to $\Phi_{PL}$ = 0.69,[6b, c] 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.[1c, 1h] This finding motivated us to prepare new $MC_4$ metallacycles and to investigate their photophysical properties.

## Results and Discussion

### Synthesis of rhodium 2,2´-biphenyl complexes and 2,5-bis(arylethynyl)rhodacyclopenta-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 rhodacyclopentadienes by introduction of $\pi$-electron-donating groups, such as acetylacetonato. Interestingly, the reaction of [Rh($\kappa^2$-*O*,*O*-acac)$(PMe_3)_2$][11] (**1**) 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(arylethynyl)rhodacyclopentadienes **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 ($CO_2Me$) substrate favoring isomer **B**, and the donor-substituted (SMe) substrate leading to an excess of **A**.



| n | *T* [K] | R = $CO_2Me$ A:B | R = SMe A : B |
|---|---|---|---|
| 2 | 293 | 1:2.6 | 1:0.3 |
| 2 | 333 | 1:1.5 | 1:0.2 |
| 1 | 293 | 1:20 | 1:20 |
| 1 | 333 | 1:25 | 1:25 |

**Scheme 2.** Synthesis of rhodacyclopentadienes (**A**) and rhodium biphenyl complexes (**B**).

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 ($CO_2Me$) $\alpha,\omega$-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 *in situ* solution NMR spectroscopy (Figure 1).

Isomers **A** and **B** were separated by column chromatography, crystallization and washing with hot hexane, giving analytically pure samples that were used to grow single crystals suitable for X-ray diffraction, and which were used for luminescence spectroscopy (see below). The molecular structures of **3a** and **4a** in the solid state (Figure 2) confirm the identity of these two fundamentally different classes of $MC_4$ metallacycles containing highly conjugated organic $\pi$-systems.

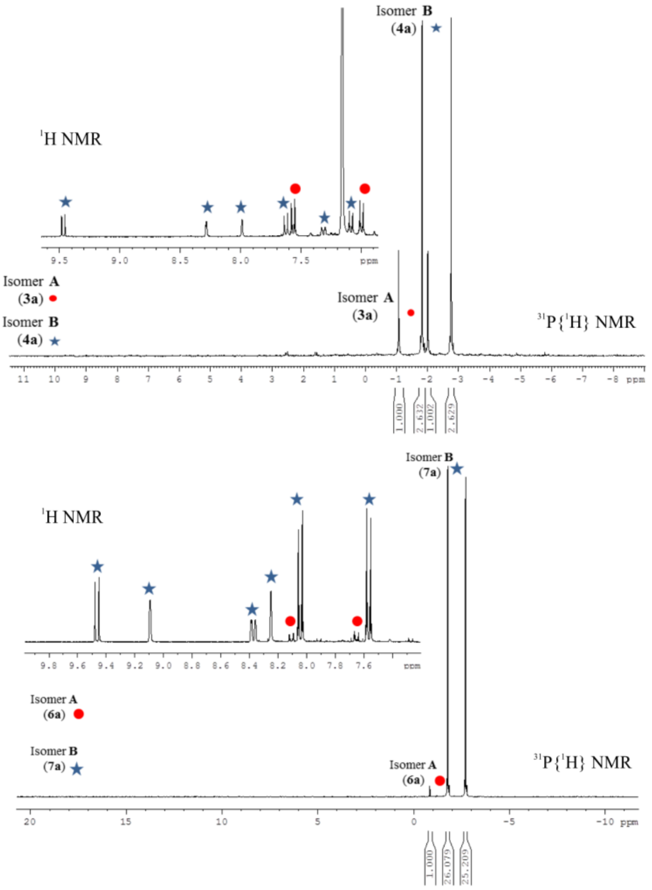


**Figure 1.** *In situ* $^{31}P\{^1H\}$ and $^1H$ NMR spectra of the reactions of $[Rh(acac)(PMe_3)_2]$ (**1**) with **2a** at 293 K (top) and with **5a** at 333 K (bottom) giving **A:B** isomer ratios of 1:2.6 and 1:25, respectively.

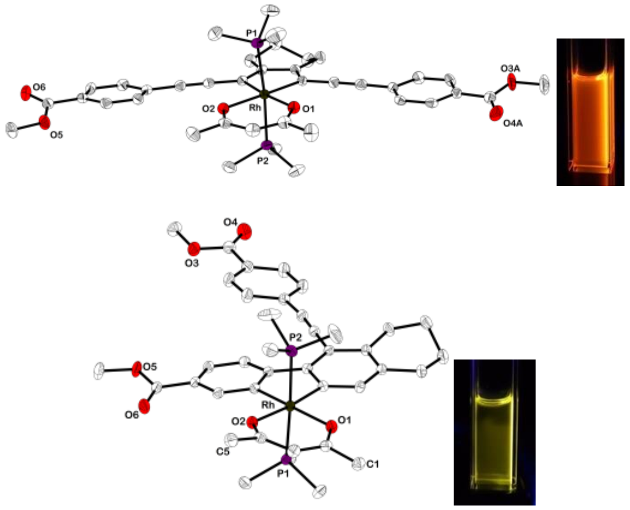
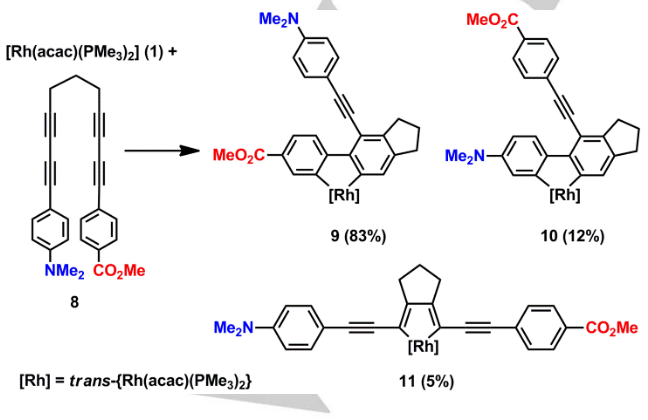


**Figure 2.** Molecular structures of **3a** (top) and **4a** (bottom) in the solid state determined by single crystal X-ray diffraction, and their respective toluene solutions under UV (365 nm) irradiation. H atoms are omitted for clarity.

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 $\alpha,\omega$-bis(arylbutadiynyl)alkanes **8** with [Rh($\kappa^2$-*O*,*O*-acac)($PMe_3$)$_2$] (**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 $\alpha,\omega$-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.



**Scheme 3.** Synthesis of rhodacyclopentadiene **11** and rhodium biphenyl complexes **9** and **10**.

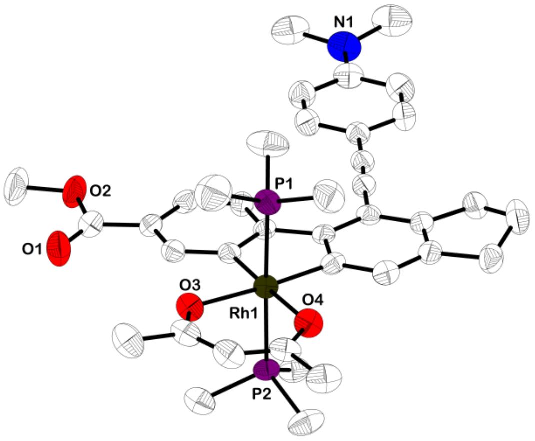


**Figure 3.** Molecular structure of **9** in the solid state determined by single crystal X-ray diffraction; H atoms are omitted for clarity.

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] diyne-alkyne cyclization occurs with a subsequent *ortho* C-H activation and $\beta$-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[12] 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 benzyne $\pi$-complex is formed as an intermediate, undergoing subsequent C-H activation of the pendant *p*-($CO_2Me$)$C_6H_4$ 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 $CO_2Me$-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 $RhC_4$ core to the phenyl moieties. The $NMe_2$/$CO_2Me$-substituted rhodacyclopentadiene **11** experiences a strong intra-ligand 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.

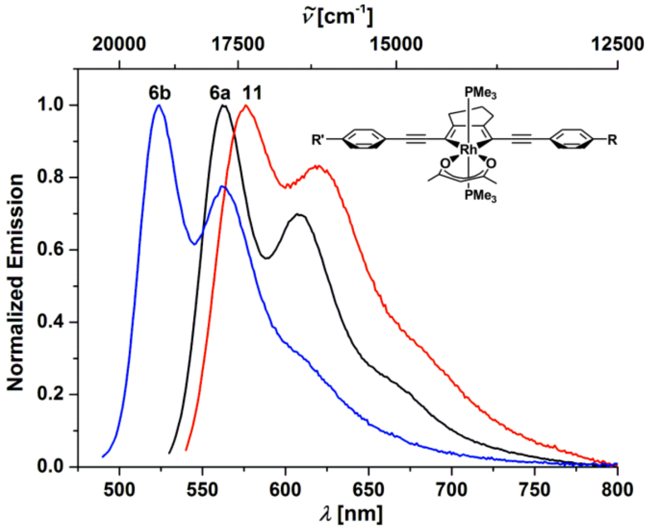


**Figure 4.** Emission spectra of rhodacyclopentadienes **6a** (black), **6b** (blue) and **11** (red) in degassed toluene solution at room temperature.

The other derivatives show only marginal changes of the photophysical properties upon changing the solvent or in PMMA. Interestingly, the radiative rate constants $k_r$ of **3a,b**, **6a,b** and **11** are very similar, but the non-radiative rate constants $k_{nr}$ of donor-substituted **3b** and **6b** as well as of the donor-acceptor compound **11** are greatly enhanced in comparison to the acceptor-substituted **3a** and **6a**. No additional phosphorescence at 77 K is observed, and dioxygen has no effect on the luminescence properties of the rhodacyclopentadienes. We recently showed[6b, 14] that SOC mediated by the heavy metal atom in 2,5-bis(arylethynyl)rhoda- and iridacyclopentadienes is negligible. Below 233 K, a temperature-independent ISC process occurs inefficiently *via* pure SOC. At room temperature, a second thermally activated ISC process is the major pathway for triplet state population. However, fluorescence remains a competitive process, and those triplet states that are formed do not phosphoresce due to efficient non-radiative decay channels.

The origin of this fluorescence, despite the presence of a heavy metal atom, lies in the pure intra-ligand (IL) nature of the excited states $S_1$ and $T_1$. The HOMO and the LUMO are nearly pure $\pi$ and $\pi^*$ ligand orbitals, respectively, and the HOMO is energetically well separated by more than 1 eV from the filled Rh d orbitals (Figures 5, 6 and S32). This inhibits low-energy MLCT transitions, which could contribute to the nature of the emissive state and facilitate spin-orbit coupling (SOC), leading to a much lower triplet state density around $S_1$ than in **B** (*vide infra*), and hampering the ISC process. The absence of phosphorescence in transition metal complexes due to mainly IL character of the excited states is not unusual, even for metals heavier than Rh with more SOC, occasionally resulting in residual $S_1$ emission

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

| Cpd. | toluene | | | | | | 2-MeTHF / 297 K | | | 2-MeTHF / 77 K | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\lambda_{abs}$ [nm] | $\lambda_{em}$ [nm] | $\Phi_{PL}$ | $\tau$ | $k_r$ [s$^{-1}$] | $k_{nr}$ [s$^{-1}$] | $\lambda_{em}$ [nm] | $\Phi_{PL}$ | $\tau$ | $\lambda_{em}$ [nm] | $\tau$ |
| **3a** | 514 | 579 | 0.50 | 2.5 ns | $2.0\cdot10^{8}$ | $2.0\cdot10^{8}$ | 579 | 0.24 | 0.5 ns | 581 | 2.8 ns |
| **3b** | 481 | 534 | 0.13 | 2.0 (25%),<br>0.5 (75%) ns | $1.5\cdot10^{8}$ [a] | $9.9\cdot10^{8}$ [a] | 544 | 0.09 | 0.4 ns | 532 | 0.9 (57%),<br>2.4 (43%) ns |
| **4a** | 410 | 545 | 0.12 | 162 µs | 740 | 5430 | 544 | 0.33 | 372 µs | 540 | 537 µs |
| **4b** | 390 | 542 | 0.01 | 43 (40%),<br>119 (60%) µs | 110 [a] | 11200 | 577 | 0.02 | 81 µs | 530 | 2750 (80%),<br>3950 (20%) µs |
| **6a** | 535 | 563 | 0.54 | 1.7 ns | $3.2\cdot10^{8}$ | $2.7\cdot10^{8}$ | 570 | 0.57 | 1.7 ns | 569 | 2.1 (90%),<br>3.1 (10%) ns |
| **6b** | 503 | 522 | 0.07 | 0.3 (77%),<br>0.1 (23%) ns | $2.8\cdot10^{8}$ [a] | $3.7\cdot10^{9}$ [a] | 522 | 0.08 | 0.2 ns | 515 | 2.2 ns |
| **7a** | 377 | 540 | 0.14 | 181 µs | 770 | 4750 | 541 | 0.16 | 338 µs | 537 | 374 (97%),<br>1340 (3%) µs |
| **7b** | 382 | 535 | 0.02 | 61 (98%),<br>163 (2%) µs | 330 [a] | 16000 [a] | 534 | 0.10 | 646 µs | 527 | 1920 (73%),<br>2770 (27%) µs |
| **9** | 371 | 536 | 0.29 | 164 (12%),<br>496 (88%) µs | 640 [a] | 1560 [a] | 535 | 0.21 | 45 (34%),<br>210 (66%) µs | 534 | 680 (66%),<br>1100 (34%) µs |
| **11** | 498 | 576 | 0.22 | 0.8 ns | $2.8\cdot10^{8}$ | $9.8\cdot10^{8}$ | 651 | 0.13 | 0.5 ns | 582 | 2.2 (98%),<br>4.5 (2%) ns |

[a] Calculated from weighted average lifetimes.

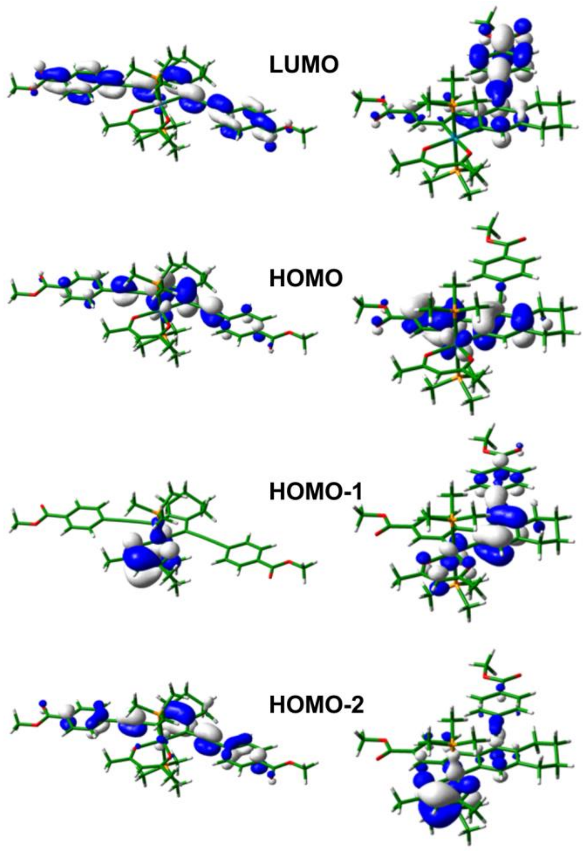


**Figure 5.** Selected molecular orbitals of rhodacyclopentadiene **3a** (left) and rhodium biphenyl complex **4a** (right). Contour values: ±0.035 [e/bohr$^3$]$^{1/2}$.

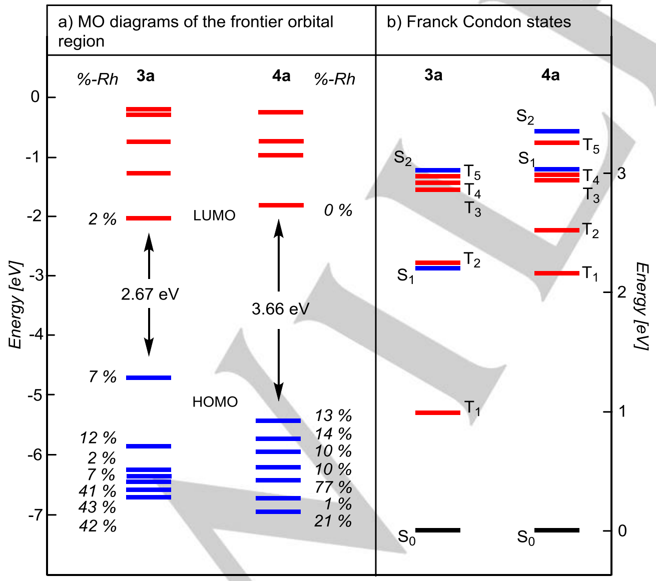


**Figure 6.** a) MO diagrams of the frontier orbital region of **3a** and **4a**. b) Calculated vertical excitations of **3a** and **4a** (blue: singlet states, red: triplet states).

despite ISC $S_1 \rightarrow T_n$ being sufficiently fast for population of $T_1$.[1c, 1e, 1h, 6b, 14-15] However, there are very few complexes which exhibit fluorescence with the efficiency displayed by our rhodacyclopentadienes,[16] which involves exceptionally slow $S_1 \rightarrow T_n$ 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 2nd row metal complexes (Figure 7),[1c, 1h, 17] 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 PLQYs 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 $T_1 \rightarrow S_0$, increasing or decreasing the rate constants for radiative and non-radiative decay.

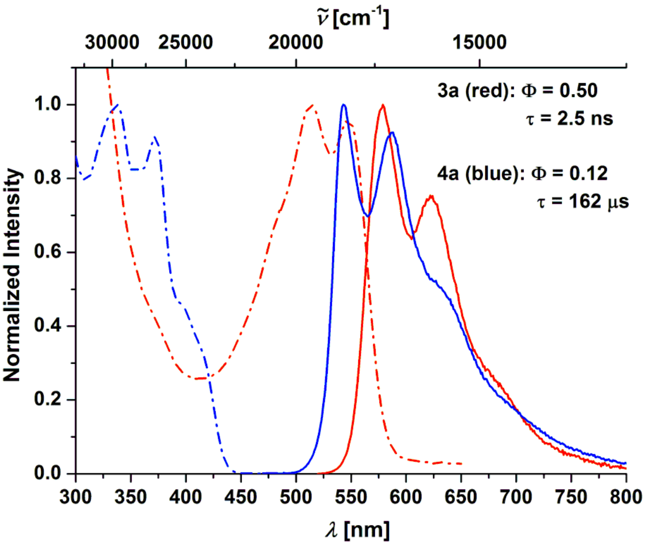


**Figure 7.** Emission (solid) and excitation (dashed) spectra of rhodium biphenyl complexes **3a** (red) and **4a** (blue) in degassed toluene solution at room temperature.

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 $NMe_2$/$CO_2Me$- and the $CO_2Me$-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,[4l] being even more efficient than known Ir- and Pt-biphenyl complexes.[4, 18]

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).[1c, 1h] Indeed, as no fluorescence is detected even at low temperature, it can be assumed that $S_1 \rightarrow T_n$ 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.

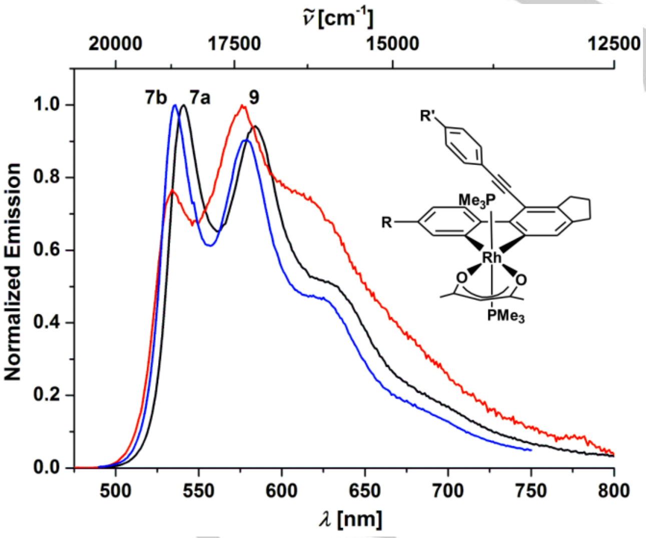


**Figure 8.** Emission spectra of rhodacyclopentadienes **7a** (black), **7b** (blue) and **9** (red) in degassed toluene solution at room temperature.

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,[19a] 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 luminophore. 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 Pd(II) porphyrin and Au(III) 2,6-diphenylpyridine complexes.[19b, c]

## 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 $\beta$-H-shift leads to a novel class of highly phosphorescent Rh(2,2'-bph) 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(arylbutadiynyl)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 dibenzometallacyclopentadienes.

## Experimental Section

**General considerations:** The syntheses of $\alpha,\omega$-bis(arylbutadiynyl)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 photophysical 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 VNMRS-700 ($^1$H, 700 MHz; $^{13}$C{$^1$H}, 176 MHz; $^{31}$P{$^1$H}, 283 MHz), Bruker Avance-500 ($^1$H, 500 MHz; $^{13}$C{$^1$H}, 126 MHz; $^{31}$P{$^1$H}, 202 MHz), Bruker Avance-400 ($^1$H, 400 MHz; $^{13}$C{$^1$H}, 101 MHz) or Bruker Avance III 300 ($^1$H, 300 MHz; $^{13}$C{$^1$H}, 101 MHz; $^{31}$P{$^1$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 LTQ 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 biphenyl complexes (4a, 4b, 7a, 7b, 9, 10) and rhodacyclopentadienes (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**), (**8** 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 ($Al_2O_3$), eluting with hexane and THF (2:1). The rhodium biphenyl complexes **4a**, **4b**, **7a**, **7b**, **9** and **10** were recrystallized from THF and washed with hot hexane, both steps several times, to obtain spectroscopically 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 (4.1%). $^1$H NMR (500 MHz, $C_6D_6$, r.t., ppm) *δ*: 9.52 (d, *J* = 8 Hz, 1 H, $CH_{arom}$), 9.10 (s, 1 H, $CH_{arom}$), 8.37 (d, *J* = 8 Hz, 1 H, $CH_{arom}$), 8.05 (d, *J* = 8 Hz, 2 H, $CH_{arom}$), 8.04 (s, 1 H, $CH_{arom}$), 7.57 (d, *J* = 8 Hz, 2 H, $CH_{arom}$), 5.13 (s, 1 H, CH), 3.62 (s, 3 H, $CH_3$), 3.62 (s, 3 H, $CH_3$), 3.48 (m, 2 H, $CH_2$), 3.24 (m, 2 H, $CH_2$), 2.91 (m, 2 H, $CH_2$), 1.89 (s, 3 H, $CH_3$), 1.88 (s, 3 H, $CH_3$) 1.70 (m, 2 H, $CH_2$), 0.57 (vt, $J_{P\text{-}H}$ = 3 Hz, 18 H, $PMe_3$). $^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$, r.t., ppm) *δ*: 188.4, 187.7, 168.2, 166.3, 166.0, 163.1 (dt, $^1J_{Rh\text{-}C}$ = 10 Hz, $^2J_{P\text{-}C}$ = 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, 99.2, 93.8, 51.6, 51.3, 30.9, 28.8, 28.7, 24.3, 23.7, 10.6 (vt, $J_{C\text{-}P}$ = 14 Hz). Due to the low intensity, the $^1J_{Rh\text{-}C}$ and $^2J_{P\text{-}C}$ coupling of the second quat. carbon atom could not be determined. $^{31}$P{$^1$H} NMR (121 MHz, $C_6D_6$, r.t., ppm) *δ*: -2.2 (d, $J_{Rh\text{-}P}$ = 113 Hz, 2 P). Elem. Anal. Calcd. (%) for $C_{38}H_{47}O_6P_2Rh$: C, 60.31; H, 6.10. Found: C, 60.42; H, 6.17. MS (MALDI-TOF) *m/z*: 776 [M$^+$], 677 [M - acac]$^+$.

**4b:** Stirring at room temperature for 14 days. Yellow solid. Isolated yield: 0.02 g (3.5%). $^1$H NMR (500 MHz, $C_6D_6$, r.t., ppm) *δ*: 9.47 (d, *J* = 8 Hz, 1 H, $CH_{arom}$), 8.29 (m, 1 H, $CH_{arom}$), 7.98 (s, 1 H, $CH_{arom}$), 7.56 (d, *J* = 8 Hz, 2 H, $CH_{arom}$), 7.56 (s, 1 H, $CH_{arom}$), 7.32 (d, *J* = 8 Hz, 1 H, $CH_{arom}$) 7.00 (d, *J* = 8 Hz, 2 H, $CH_{arom}$), 5.12 (s, 1 H, CH), 3.34 (m, 2 H, $CH_2$), 2.94 (m, 2 H, $CH_2$), 2.32 (s, 3 H, $CH_3$), 1.90 (s, 3 H, $CH_3$), 1.89 (s, 3 H, $CH_3$) 1.84 (s, 3 H, $CH_3$), 1.74 (m, 2 H, $CH_2$), 0.60 (vt, $J_{P\text{-}H}$ = 3 Hz, 18 H, $PMe_3$). $^{13}$C{$^1$H} NMR (176 MHz, $C_6D_6$, r.t., ppm) *δ*: 187.9, 187.7, 167.0 (dt, $^1J_{Rh\text{-}C}$ = 10 Hz, $^2J_{P\text{-}C}$ = 31 Hz), 160.7 (dt, $^1J_{Rh\text{-}C}$ = 10 Hz, $^2J_{P\text{-}C}$ = 31 Hz), 151.2, 150.5, 139.1, 134.3, 133.9, 132.8, 131.9, 130.3, 128.4, 127.9, 126.6, 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, $J_{C\text{-}P}$ = 14 Hz) $^{31}$P{$^1$H} NMR (202 MHz, $C_6D_6$, r.t., ppm) *δ*: -2.26 (d, $J_{Rh\text{-}P}$ = 114 Hz, 2 P). Elem. Anal. Calcd. (%) for $C_{37}H_{47}O_2P_2RhS_2$: C, 59.04; H, 6.29; S, 8.52. Found: C, 59.44; H, 6.42; S, 8.56. MS (MALDI-TOF) *m/z*: 676 [M - $PMe_3$]$^+$.

**7a:** Stirring at 60°C for 2 days. Yellow solid. Isolated yield: 0.24 g (9%) $^1$H NMR (300 MHz, $C_6D_6$, r.t., ppm) *δ*: 9.46 (d, *J* = 8 Hz, 1 H, $CH_{arom}$), 9.10 (m, 1 H, $CH_{arom}$), 8.38 (d, *J* = 8 Hz, 1 H, $CH_{arom}$), 8.25 (s, 1 H, $CH_{arom}$), 8.04 (d, *J* = 8 Hz, 2 H, $CH_{arom}$), 7.57 (d, *J* = 8 Hz, 2 H, $CH_{arom}$), 5.13 (s, 1 H, CH), 3.62 (s, 3 H, $CH_3$), 3.48 (s, 3 H, $CH_3$), 3.25 (m, 2 H, $CH_2$), 3.01 (m, 2 H, $CH_2$), 1.99 (m, 2 H, $CH_2$), 1.89 (s, 3 H, $CH_3$), 1.88 (s, 3 H, $CH_3$) 0.57 (vt, $J_{P\text{-}H}$ = 3 Hz, 18 H, $PMe_3$). $^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$, r.t., ppm) *δ*: 188.4, 187.7, 168.2, 166.3, 165.4 (dt, $^1J_{Rh\text{-}C}$ = 10 Hz, $^2J_{P\text{-}C}$ = 31 Hz), 158.5, 148.9, 143.3, 140.6, 133.4, 131.5, 129.8, 129.8, 129.4, 128.4, 126.6, 124.6, 123.1, 113.4, 99.3, 96.9, 93.8, 67.8, 51.6, 51.3, 33.9, 33.4, 30.1, 28.7, 25.0, 10.6 (vt, $J_{C\text{-}P}$ = 14 Hz). Due to the low intensity, the $^1J_{Rh\text{-}C}$ and $^2J_{P\text{-}C}$ coupling of the second quat. carbon atom could not be determined. $^{31}$P{$^1$H} NMR (121 MHz, $C_6D_6$, r.t., ppm) *δ*: -2.0 (d, $J_{Rh\text{-}P}$ = 113 Hz, 2 P). Elem. Anal. Calcd. (%) for $C_{38}H_{45}O_6P_2Rh$: C, 59.85; H, 5.95. Found: C, 59.81; H, 6.12. MS (MALDI-TOF) *m/z*: 761 [M - H]$^+$, 662 [M - acac]$^+$.

**7b:** Stirring at 60°C for 5 days. Yellow solid. Isolated yield: 0.15 g (7%). $^1$H NMR (500 MHz, $C_6D_6$, r.t., ppm) *δ*: 9.42 (d, *J* = 8 Hz, 1 H, $CH_{arom}$), 8.28 (m, 1 H, $CH_{arom}$), 8.20 (m, 1 H, $CH_{arom}$), 7.56 (d, *J* = 8 Hz, 2 H, $CH_{arom}$), 7.32 (d, *J* = 8 Hz, 1 H), 6.99 (d, *J* = 8 Hz, 2 H, $CH_{arom}$), 5.12 (s, 1 H, CH), 3.34 (m, 2 H, $CH_2$), 3.05 (m, 2 H, $CH_2$), 2.34 (s, 3 H, $CH_3$), 2.03 (m, 2 H, $CH_2$), 1.89 (s, 3 H, $CH_3$), 1.88 (s, 3 H, $CH_3$) 1.84 (s, 3 H, $CH_3$), 0.60 (vt, $J_{P\text{-}H}$ = 3 Hz, 18 H, $PMe_3$). $^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$, r.t., ppm) *δ*: 187.9, 187.7, 166.4 (dt, $^1J_{Rh\text{-}C}$ = 10 Hz, $^2J_{P\text{-}C}$ = 31 Hz), 162.9 (dt, $^1J_{Rh\text{-}C}$ = 11 Hz, $^2J_{P\text{-}C}$ = 31 Hz), 151.1, 149.6, 142.6, 139.2, 139.1, 134.2, 131.9, 130.4, 129.1, 126.5, 124.1, 121.6, 120.6, 112.6, 99.1, 97.0, 91.2, 33.9, 33.5, 30.0, 28.7, 28.6, 25.1, 16.1, 15.0, 10.6 (vt, $J_{C\text{-}P}$ = 14 Hz). $^{31}$P{$^1$H} NMR (121 MHz, $C_6D_6$, r.t., ppm) *δ*: -2.26 (d, $J_{Rh\text{-}P}$ = 114 Hz, 2 P).Elem. Anal. Calcd. (%) for $C_{36}H_{45}O_2P_2RhS_2$: C, 58.53; H, 6.14; S, 8.68. Found: C, 58.85; H, 6.16; S, 8.47. MS (MALDI-TOF) *m/z*: 738 [M$^+$].

**9:** Stirring at 60°C for 5 days. Yellow solid. Isolated yield: 0.26 g (8%). $^1$H NMR (500 MHz, $C_6D_6$) δ: 9.74 (d, *J* = 8 Hz, 1 H, $CH_{arom}$), 9.09 (m, 1 H, $CH_{arom}$), 8.43 (m, 1 H, $CH_{arom}$), 8.20 (d, *J* = 8 Hz, 2 H, $CH_{arom}$), 7.73 (d, *J* = 8 Hz, 1 H), 6.44 (d, *J* = 8 Hz, 2 H, $CH_{arom}$), 5.12 (s, 1 H, CH), 3.39 (m, 2 H, $CH_2$), 3.62 (s, 3 H, $CH_3$), 3.04 (m, 2 H, $CH_2$), 2.41 (s, 6 H, $CH_3$), 2.02 (m, 2 H, $CH_2$), 1.89 (s, 3 H, acac-$CH_3$), 1.88 (s, 3 H, $CH_3$), 0.58 (vt, $J_{P\text{-}H}$ = 3 Hz, 18 H, $PMe_3$). $^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$) δ: 188.3, 187.6, 168.3, 164.9 (dt, $^1J_{Rh\text{-}C}$ = 11 Hz, $^2J_{P\text{-}C}$ = 31 Hz), 159.2, 159.1, 150.2, 142.5, 140.5, 133.2, 132.8, 128.4, 126.2, 124.6, 123.2, 115.2, 112.6, 112.4, 99.2, 88.7, 67.8, 51.2, 39.8, 34.0, 33.6, 28.7, 28.6, 25.8, 25.1, 10.6 (vt, $J_{C\text{-}P}$ = 14 Hz). Due to the low intensity, the $^1J_{Rh\text{-}C}$ and $^2J_{P\text{-}C}$ coupling could not be determined. $^{31}$P{$^1$H} NMR (121 MHz, $C_6D_6$) δ: -2.23 (d, $J_{Rh\text{-}P}$ = 113 Hz, 2 P). Elem. Anal. Calcd. (%) for $C_{38}H_{48}NO_4P_2Rh$: C, 61.05; H, 6.47; N, 1.87. Found: C, 61.30; H, 6.76; N, 1.67. MS (MALDI-TOF) *m/z*: 747 [M$^+$], 648 [M - acac]$^+$. Compound **10** was identified by $^1$H and $^{31}$P{$^1$H} NMR spectroscopy in the product mixture. $^1$H NMR (300 MHz, $C_6D_6$, r.t., ppm) *δ*: 9.29 (d, *J* = 8 Hz, 1 H, $CH_{arom}$), 8.23 (s, 1 H, $CH_{arom}$), 8.05 (m, 2 H, $CH_{arom}$), 7.73 (d, *J* = 8 Hz, 2 H, $CH_{arom}$), 7.64 (d, *J* = 8 Hz, 2 H), 5.17 (s, 1 H, CH), 3.45 (s, 3 H, $CH_3$), 3.33 (m, 2 H, $CH_2$), 3.09 (m, 2 H, $CH_2$), 2.90 (s, 6 H, $CH_3$), 2.75 (m, 2 H, $CH_2$), 1.92 (s, 3 H, $CH_3$), 1.91 (s, 3 H, $CH_3$), 0.67 (vt, $J_{P\text{-}H}$ = 3 Hz, 18 H, $PMe_3$). $^{31}$P{$^1$H} NMR (121 MHz, $C_6D_6$, r.t., ppm) *δ*: -2.13 (d, $J_{Rh\text{-}P}$ = 115 Hz, 2 P).

For ease of isolation of spectroscopically pure rhodacyclopentadienes (**3a, 3b, 6a, 6b, 11**), a different reaction procedure was developed: one equivalent of [Rh(acac)(P(*p*-tolyl)$_3$)$_2$], 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, $PMe_3$ (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, $C_6D_6$, r.t., ppm) $\delta$: 8.13 (d, $J$ = 8 Hz, 4 H, $CH_{arom}$), 7.68 (d, $J$ = 8 Hz, 4 H, $CH_{arom}$), 5.13 (s, 1 H, CH), 3.47 (s, 6 H, $CH_3$), 2.91 (m, 4 H, $CH_2$), 1.91 (s, 6 H, $CH_3$), 1.66 (m, 4 H, $CH_2$), 0.88 (vt, $J$ = 4 Hz, 18 H, $PMe_3$). $^{13}C\{^1H\}$ NMR (126 MHz, $C_6D_6$, r.t., ppm) $\delta$: 187.1, 166.5, 158.4, 140.3 (dt, $^1J_{Rh\text{-}C}$ = 10 Hz, $^2J_{P\text{-}C}$ = 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 (vt, $J_{C\text{-}P}$ = 14 Hz). $^{31}P\{^1H\}$ NMR (161 MHz, $C_6D_6$, r.t., ppm) $\delta$: -0.50 (d, $J_{Rh\text{-}P}$ = 113 Hz, 2 P). Elem. Anal. Calcd. (%) for $C_{39}H_{47}O_6P_2Rh$: C, 60.31; H, 6.10. Found: C, 60.15; H, 6.10. MS ($ES^+$) *m/z* = 776 [$M^+$], 700 [$M - PMe_3$]$^+$, 677 [M - acac]$^+$.

**3b:** Red solid. Isolated yield: 0.01 g (2.2%). $^1H$ NMR (400 MHz, $C_6D_6$, r.t., ppm) $\delta$: 7.62 (d, $J$ = 8 Hz, 4 H, $CH_{arom}$), 7.08 (d, $J$ = 8 Hz, 4 H, $CH_{arom}$), 5.17 (s, 1 H, CH), 2.96 (m, 4 H, $CH_2$), 1.97 (s, 6 H, $CH_3$), 1.93 (s, 6 H, $CH_3$), 1.69 (m, 4 H, $CH_2$), 0.96 (vt, $J_{P\text{-}H}$ = 4 Hz, 18 H, $PMe_3$). $^{13}C\{^1H\}$ NMR (126 MHz, $C_6D_6$, r.t., ppm) $\delta$: 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 (vt, $J_{C\text{-}P}$ = 14 Hz) Due to the low intensity, the $^1J_{Rh\text{-}C}$ and $^2J_{P\text{-}C}$ coupling could not be determined. $^{31}P\{^1H\}$ NMR (161 MHz, $C_6D_6$, r.t., ppm) $\delta$: -0.41 (d, $J_{Rh\text{-}P}$ = 114 Hz, 2 P). Elem. Anal. Calcd. (%) for $C_{37}H_{47}O_2P_2RhS_2$: C, 59.04; H, 6.29. Found: C, 59.60; H, 6.08. MS ($ES^+$) *m/z* = 752 [$M^+$], 676 [$M - PMe_3$]$^+$, 653 [M - acac]$^+$.

**6a:** Red solid. Isolated yield: 0.03 g (9%). $^1H$ NMR (300 MHz, $C_6D_6$, r.t., ppm) $\delta$: 7.58 (d, $J$ = 8 Hz, 4 H, $CH_{arom}$), 7.18 (br. s, 4 H, $CH_{arom}$), 5.07 (s, 1 H, CH), 2.71 (m, 4 H, $CH_2$), 2.27 (s, 6 H, $CH_3$), 2.10 (m, 2 H, $CH_2$), 1.76 (s, 6 H, $CH_3$), 0.95 (vt, $J_{P\text{-}H}$ = 3 Hz, 18 H, $PMe_3$). $^{13}C\{^1H\}$ NMR (126 MHz, $C_6D_6$, r.t., ppm) $\delta$: 186.4, 156.5, 144.6, 132.9, 129.6, 128.4, 98.2, 30.9, 30.5, 28.3, 21.4, 12.5 (vt, $J_{C\text{-}P}$ = 14 Hz). Due to the low intensity, the $^1J_{Rh\text{-}C}$ and $^2J_{P\text{-}C}$ coupling could not be determined. Two carbon signals were not observed. $^{31}P\{^1H\}$ NMR (121 MHz, $C_6D_6$, r.t., ppm) $\delta$: -3.0 (d, $J_{Rh\text{-}P}$ = 113 Hz, 2 P). Elem. Anal. Calcd. (%) for $C_{38}H_{45}O_6P_2Rh$: C, 59.85; H, 5.95. Found: C, 59.55; H, 5.97. MS (MALDI-TOF) *m/z*: 762 [$M^+$], 663 [M - acac]$^+$.

**6b:** Red solid. Isolated yield: 0.06 g (16%). $^1H$ NMR (300 MHz, $C_6D_6$, r.t., ppm) $\delta$: 7.60 (d, $J$ = 8 Hz, 4 H, $CH_{arom}$), 7.05 (br. s, 4 H, $CH_{arom}$), 5.15 (s, 1 H, CH), 2.74 (m, 4 H, $CH_2$), 2.19 (m, 2 H, $CH_2$), 1.96 (s, 6 H, $CH_3$), 1.92 (s, 6 H, $CH_3$), 1.03 (vt, $J_{P\text{-}H}$ = 3 Hz, 18 H, $PMe_3$). $^{13}C\{^1H\}$ NMR (126 MHz, $C_6D_6$, r.t., ppm) $\delta$: 186.3, 165.9, 136.8, 131.0, 126.4, 124.0, 107.0, 98.5, 94.9, 30.1, 29.9, 28.2, 15.0, 10.7 (vt, $J_{C\text{-}P}$ = 14 Hz). Due to the low intensity, the $^1J_{Rh\text{-}C}$ and $^2J_{P\text{-}C}$ coupling could not be determined. $^{31}P\{^1H\}$ NMR (121 MHz, $C_6D_6$, r.t., ppm) $\delta$:-1.14 (d, $J_{Rh\text{-}P}$ = 114 Hz, 2 P). Elem. Anal. Calcd. (%) for $C_{36}H_{45}O_2P_2RhS_2$: C, 58.53; H, 6.14; S, 8.68. Found: C, 58.92; H, 6.19 S, 8.23. MS (MALDI-TOF) *m/z*: 738 [$M^+$].

**11:** Red solid. Isolated yield: 0.19 g (21%). $^1H$ NMR (300 MHz, $C_6D_6$, r.t., ppm) $\delta$: 8.11 (d, $J$ = 8 Hz, 2 H, $CH_{arom.}$), 7.72 (d, $J$ = 8 Hz, 2 H, $CH_{arom.}$), 7.67 (d, $J$ = 8 Hz, 2 H, $CH_{arom.}$), 6.52 (d, $J$ = 8 Hz, 2 H, $CH_{arom.}$), 5.16 (s, 1 H, acac-CH), 3.47 (s, 3 H, $CH_3$), 2.75 (m, 4 H, $CH_2$), 2.42 (s, 6 H, $CH_3$), 2.20 (m, 2 H, $CH_2$), 2.20 (s, 3 H, $CH_3$), 1.93 (s, 3 H, $CH_3$), 1.03 (vt, $J_{Rh\text{-}P}$ = 3 Hz, 18 H, 2 $PMe_3$). $^{13}C\{^1H\}$ NMR (126 MHz, $C_6D_6$, r.t., ppm) $\delta$: 186.7, 186.6, 168.6, 166.6, 164.1 (dt, $^1J_{Rh\text{-}C}$ = 11 Hz, $^2J_{P\text{-}C}$ = 31 Hz), 149.5, 132.6, 132.3, 130.7, 129.9, 128.4, 127.7, 115.4, 112.6, 110.1, 106.6, 99.6, 98.9, 92.4, 51.4, 39.9, 30.6, 30.4, 30.3, 30.1, 28.6, 28.5, 11.1 (vt, $J_{C\text{-}P}$ = 14 Hz). Due to the low intensity, $^1J_{Rh\text{-}C}$ and $^2J_{P\text{-}C}$ coupling could not be determined. $^{31}P\{^1H\}$ NMR (121 MHz, $C_6D_6$, r.t., ppm) $\delta$: -1.18 (d, $J_{Rh\text{-}P}$ = 114 Hz, 2 P). Elem. Anal. Calcd. (%) for $C_{38}H_{48}NO_4P_2Rh$: C, 61.05; H, 6.47; N, 1.87. Found: C, 61.78; H, 6.34; N, 1.84. MS (MALDI-TOF) *m/z*: 747 [$M^+$].

In order to determine an accurate isomer ratio, NMR experiments were conducted. One equivalent of **1** and one equivalent of the corresponding bis(diyne) were dissolved in toluene (20 mL) and the reaction mixture was stirred at room temperature. For $^1H$ and $^{31}P\{^1H\}$ NMR, 0.6 mL of the reaction solution was transferred to a Young's NMR tube and the solvent was removed *in vacuo*, then $C_6D_6$ (0.6 mL) was added. Isomer ratios of 1:2.6 for compounds **3a** and **4a**, 1:0.3 for **3b**, **4b**; 1:20 for **6a**, **7a** and **6b**, **7b** were observed. The same procedure was performed for the reaction at 60 °C to give the isomers **3a** and **4a** in a ratio of 1:1.5, 1:0.2 for **3b**, **4b**; 1:25 for **6a**, **7a** and **6b**, **7b**.

**Single-crystal X-ray diffraction:** Single-crystals suitable for X-ray diffraction were selected, coated in perfluoropolyether oil, and mounted on MiTeGen sample holders. Diffraction data were collected on Bruker 3-circle diffractometers with CCD area detectors, SMART 1000 (**3a**, **3b**, **4a**), SMART APEX (**6b**, **9**), and 4-circle diffractometers with CCD area detectors, Apex II (**2b**, **4a**, **6a**, **7b**, **11**), and D8 QUEST with CMOS area detector PHOTON 100 (**7a**), using Mo-$K_\alpha$ radiation monochromated by graphite (**3a**, **3b**, **4a**, **6b**, **9**) or multi-layer focusing mirrors (**6a**, **7a**, **7b**, **11**). The crystals were cooled using Cryostream open-flow $N_2$ gas cryostats. The structures were solved using direct methods (SHELXS, for **3a**, **3b**, **4a**),[20] or the intrinsic phasing method (ShelXT)[21] and Fourier expansion technique, or by using the olex2.solve algorithm.[22] 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 $F^2$ of all data using the programs SHELXL[20] and OLEX2.refine.[23] The program DIAMOND was used for graphical representation.[24] General color code: carbon (white), sulfur (yellow), oxygen (red), phosphorus (purple), rhodium (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 FLSP920 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 solution-state emission spectra. 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 $10^{-6}$ 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 FLSP920 spectrometer described above.[25]

**Lifetime measurements:** The luminescence lifetimes were measured on the FLSP920 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 ($\lambda_{ex}$ = 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 $T_g$.

**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 *iso*-surface spin-density representations and the calculated absorption spectra were generated using the GaussView 5.0 program.[28]

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**Keywords:** luminescence • metallacycle • dibenzo • OLED • intersystem crossing

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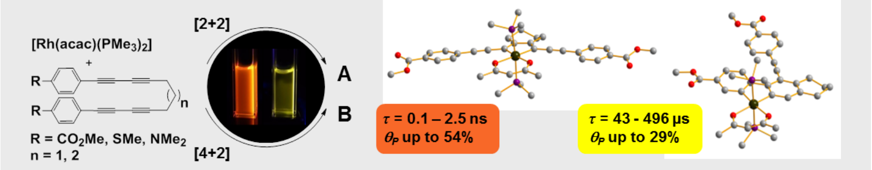

The Light at the End of the Cycle: We report a combination of novel reactivity of bis(diynes) at rhodium centers with the unusual photophysical properties of the two isomeric products formed. Thus, reactions of alkyl-linked bis(diynes) at Rh(I) gives either fluorescent rhodacyclopentadienes *via* 2+2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

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**Reductive Coupling of Diynes at Rhodium Gives Fluorescent Rhodacyclopentadienes or Phosphorescent Dibenzorhodacyclopentadienes**