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Fluorescence

Regiospecific Formation and Unusual Optical Properties of 2,5-Bis(arylethynyl)rhodacyclopentadienes: A New Class of Luminescent Organometallics

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Abstract: A series of 2,5-bis(arylethynyl)rhodacyclopentadienes has been prepared by a rare example of regiospecific reductive coupling of 1,4-(*p*-R-phenyl)-1,3-butadiynes (R=H, Me, OMe, SMe, NMe_2, CF_3, CO_2Me, CN, NO_2, $-C{\equiv}C$-(*p*-C_6H_4–$NHex_2$), $-C{\equiv}C$–(*p*-C_6H_4–CO_2Oct)) at $[RhX(PMe_3)_4]$ (**1**) (X = $-C{\equiv}C-SiMe_3$ (**a**), $-C{\equiv}C$-(*p*-C_6H_4–NMe_2) (**b**), $-C{\equiv}C-C{\equiv}C$–(*p*-C_6H_4–NPh_2) (**c**) or $-C{\equiv}C$–{*p*-C_6H_4-$C{\equiv}C$–(*p*-C_6H_4-$N(C_6H_{13})_2$)} (**d**) or Me (**e**)), giving the 2,5-bis(arylethynyl) isomer exclusively. The rhodacyclopentadienes bearing a methyl ligand in the equatorial plane (compound **1e**) have been converted into their chloro analogues by reaction with HCl etherate. The rhodacycles thus obtained are stable to air and moisture in the solid state and the acceptor-substituted compounds are even stable to air and moisture in solution. The photophysical properties of the rhodacyclopentadienes are highly unusual in that they exhibit, exclusively, fluorescence between 500–800 nm from the S_1 state, with quantum yields of $\Phi = 0.01$–0.18 and short lifetimes ($\tau = 0.45$–8.20 ns). The triplet state formation ($\Phi_{ISC} = 0.57$ for **2a**) is exceptionally slow, occurring on the nanosecond timescale. This is unexpected, because the Rh atom should normally facilitate intersystem crossing within femto- to picoseconds, leading to phosphorescence from the T_1 state. This work therefore highlights that in some transition-metal complexes, the heavy atom can play a more subtle role in controlling the photophysical behavior than is commonly appreciated.

Introduction

An immense variety of applications of metallacyclopentadienes has arisen from the investigation of their structure–property relationships. Diimine-based metallacyclopentadienes of type A (Figure 1), for example, have been found to be highly active catalysts for alkene polymerization, and systems based on nickel subsequently became well-known as Brookhart's catalysts.[1] The redox-activity of metallacyclopentadienes with diimine ligands has been explored, but more attention in this regard was given to metal complexes of type B bearing N^N-bonded 2,2′-bipyridine (bpy) and related ligands. Rhenium(I) and ruthenium(II) complexes, in particular, show great promise for electrochemical and photochemical applications, such as catalysts for the electrochemical reduction of CO_2 or in dye-sensitized solar cells as photosensitizers.[2] Remarkable progress has been achieved, with metallacyclopentadienes featuring (N^N)-bonded bpy- and C^N-bonded 2-phenylpyridyl (ppy) ligands, in the area of luminescent materials for organic light-emitting diodes (OLEDs). Second- and third-row transition-metal complexes of types B and C (Figure 1) are well-known as efficient phosphorescent triplet-state emitters.[2n, 3] The prototypical compounds $[Ru(bpy)_3]^{2+}$ and $[Ir(ppy)_3]$ and their derivatives have been extensively studied to understand the excited-state behavior and photophysical properties of organo-transition-metal compounds.[2e, 4] In general, the strong spin-orbit coupling (SOC) of the metal atom facilitates intersystem-crossing (ISC) between the excited singlet and triplet states very efficiently. The ISC can be ultrafast, that is, <20 fs, as has been measured for $[M(bpy)_3]^{2+}$ (M = Fe, Ru).[2d, 5] In addition, the spin-forbidden nature of the radiative transition between the triplet state and the ground state is removed, and thus high quantum yields of up to unity for phosphorescence are observed.[3b]

In contrast to their types A–C congeners, MC_4 metallacyclopentadienes of types D and E have been largely neglected for photophysical applications. Investigations have concentrated

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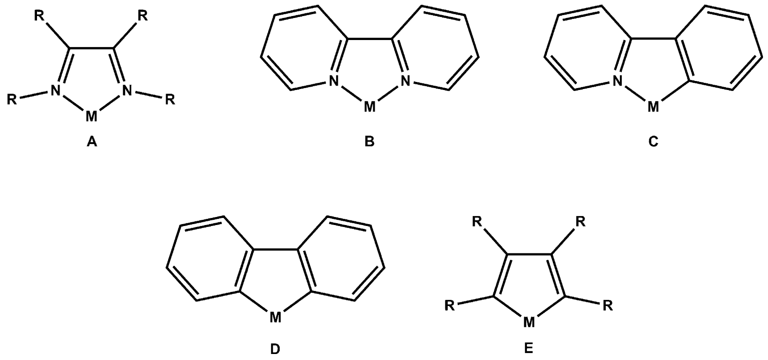


Figure 1. A) Metal–diimine complex; B) metal–bipyridine complex; C) metal-2-phenylpyridyl complex; D) metal-2,2′-biphenylene complex; E) metallacyclopentadiene.

on the catalytic activity of 2,2′-biphenylene (bph) complexes in C–C bond-forming reactions or the reduction of biphenylene.[6] Photophysical studies of only a limited number of bph complexes of Ir, Pd, and Pt have been reported; these compounds exhibit phosphorescence with quantum yields of up to $\Phi = 0.16$ and lifetimes of $\tau = 3$–14 μs.[7] Despite these promising results, limited synthetic access to bph transition-metal complexes is presumably the reason for the lack of photophysical data in the literature. Metallacyclopentadienes of type E are well-established intermediates in catalytic cyclotrimerization reactions of alkynes to benzenes and alkyne/nitrile mixtures to pyridines,[6b,8] but very little is known about their photophysical and excited-state properties.[6a] This is astonishing, because structurally related main group EC_4 systems such as boroles,[9] siloles,[10] phospholes,[11] and thiophenes[12] have attracted significant attention due to their optical and electron-transporting properties. In particular, 2,5-conjugated ring systems,[6a] such as 2,5-bis(arylethynyl)thiophenes,[13] 2,5-bis(arylethynyl)phospholes[14] and 2,5-bis(arylethynyl)siloles,[10a] are of interest. Similar to *p*-bis(phenylethynyl)benzenes (BPEBs)[15] and anthracenes (BPEAs),[15f,r,t,16] the extended conjugation gives rise to interesting linear and non-linear optical behavior.

Synthetic access to conjugated 2,5-bis(R-ethynyl)metallacyclopentadienes should, in principle, be possible by reductive coupling of 1,3-butadiynes at a suitable transition-metal precursor complex.[6a] However, examples of reductive coupling of 1,3-butadiynes are scarce, and most of the reactions do not occur with the desired regioselectivity. Nishihara and co-workers found that in the reaction of $[CoCp(PPh_3)_2]$ (Cp = cyclopentadienyl) with diphenylbuta-1,3-diyne, an insoluble polymer was the major product, with three different regioisomeric complexes being formed only at elevated temperature (Figure 2).[17]

The problem of regioselectivity has also been observed in the reaction of $[TiCl_2Cp_2]$ with bis(trimethylsilyl)-1,3-butadiyne in the presence of Mg as reducing agent, which forms the 2,4-isomer in 65% yield.[18] Bruce and co-workers were able to isolate, although in very low yields of 4%, a mononuclear 2,5-dialkynyl ruthenacyclopentadiene from the reaction of diphenylbutadiyne with $[Ru_3(CO)_{10}(NCMe)_2]$.[19] We were able to demonstrate the regiospecific synthesis of a luminescent rhodacyclopentadiene from 1,4-di(*p*-tolyl)-1,3-butadiyne and $[Rh(C{\equiv}CSiMe_3)(PMe_3)_4]$.[20] Subsequently, Hill and co-workers observed the same regiospecificity at ruthenium, when $[Ru(CO)_2(PPh_3)_3]$ was treated with excess diphenyl-1,3-butadiyne at elevated temperature to give the 2,5-dialkynyl isomer exclusively.[21] Reductive coupling of 2,4-hexadiyne at osmium was also observed to produce the 2,5-diethynyl metallacyle. Recently, we also succeeded in preparing more rigid conjugated 2,5-bis(*p*-R-arylethynyl)rhodacyclopentadienes by treatment of $[Rh(C{\equiv}CSiMe_3)(PMe_3)_4]$ or $[Rh(\kappa^2\text{-}S,S'\text{-}S_2CNEt_2)(PMe_3)_2]$ with 1,12-diaryldodeca-1,3,9,11-tetraynes.[22] The rhodacyclopentadienes thus obtained exhibit exceptional fluorescence properties, although phosphorescence would have been expected due to the heavy atom effect. Apart from our previous two preliminary studies, none of the other reports address the optical properties of conjugated 2,5-bis(*p*-R-arylethynyl)metallacyclopentadienes.

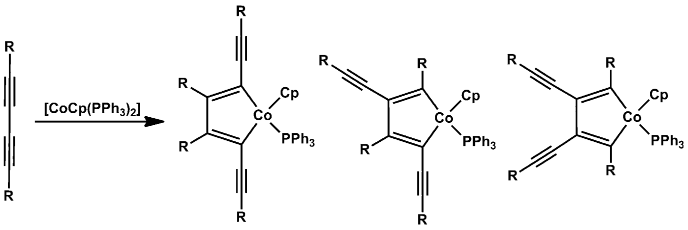


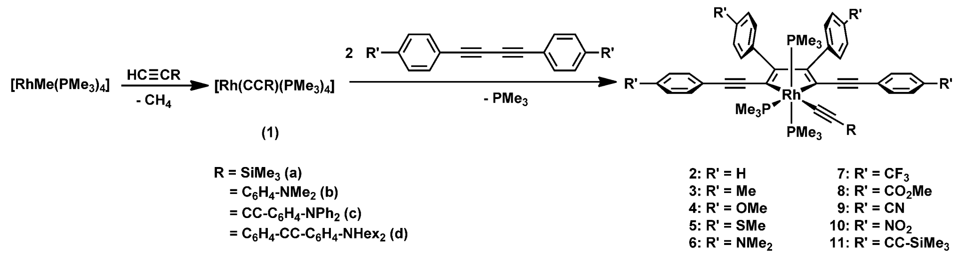
Figure 2. Reductive coupling of butadiynes at $[CoCp(PPh_3)]$, leading to the formation of three regioisomers.[17]

As part of our program of research on metal acetylides and their optical properties,[23] we examined the reactions of rhodium(I) acetylides with 1,3-diynes. We now demonstrate the applicability of our general synthetic approach to access rhodacyclopentadienes by reductive coupling of 1,4-bis(*p*-R-arylethynyl)-1,3-butadiynes, with a variety of substituents R of differing electronic donor or acceptor strength and different ligand combinations at the Rh center. The reactions occur regiospecifically, yielding the 2,5-isomer exclusively. Detailed photophysical investigations of the metallacyclopentadienes have been carried out, which show highly unusual excited-state behavior in comparison with other luminescent organometallic complexes.

Results

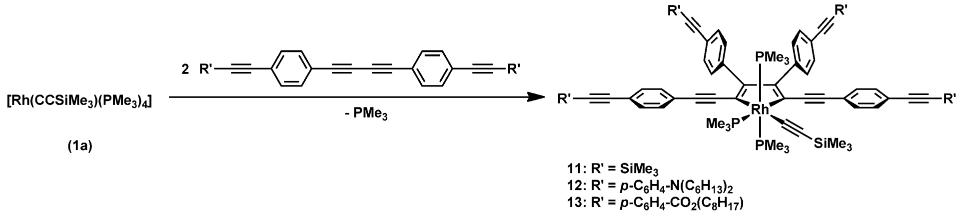
Synthesis and characterization

Treatment of $[RhMe(PMe_3)_4]$ with terminal alkynes $HC{\equiv}CR$ (R = $SiMe_3$, *p*-C_6H_4–NMe_2, $C{\equiv}C$-(*p*-C_6H_4–NPh_2),[24] *p*-C_6H_4-[$C{\equiv}C$-{*p*-C_6H_4–$N(C_6H_{13})_2$}][25]) gives the rhodium(I) compounds **1a**–**d** through C–H activation with loss of methane (Scheme 1). Subsequent reductive coupling of two equivalents of 1,4-bis(*p*-R′-phenyl)-1,3-butadiynes (R′=H, Me, OMe, SMe, $C{\equiv}CSiMe_3$, NMe_2, CF_3, CO_2Me, CN, NO_2) at room temperature in the coordination sphere of rhodium yields the rhodacyclopentadienes **2(a**–**d)**–

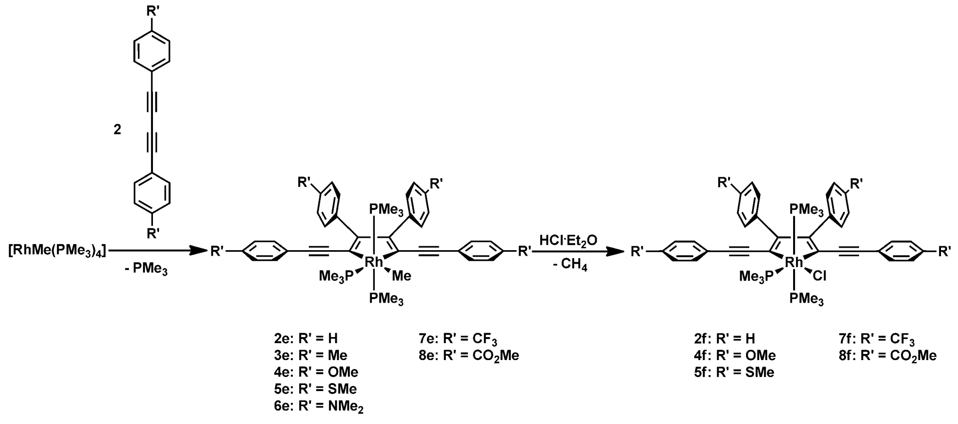


Scheme 1. Regiospecific formation of 2,5-bis(arylethynyl)rhodacyclopentadienes **2**–**10**.

10 (a–**d)**. It is striking that the reactions occur quantitatively and regiospecifically in all cases, forming the 2,5-bis(*p*-R′-phenyl)-ethynyl isomer exclusively as confirmed by in situ ^{31}P{^{1}H} NMR spectroscopy. We observed that *p*-R′-phenyl-1,3-butadiynes with donor substituents react slower than the acceptor-substituted diynes, which may be due to diminished π-backbonding from the electron-rich Rh^{I} center in the precursor bis(diyne) complexes. We also prepared compounds **11**–**13** with longer conjugated chains in the *para* position of the phenyl rings for exploration of liquid-crystal behavior and the influence of conjugation on the photophysics (Scheme 2). However, no evidence for liquid-crystal phase behavior was observed using transmitted polarized light microscopy.

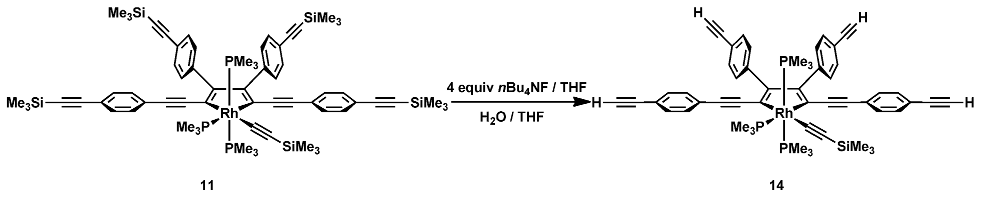


Scheme 2. Synthesis of 2,5-bis(arylethynyl)rhodacyclopentadienes **11**–**13** with conjugated groups at the *para*-position of the phenyl substituents.



Scheme 3. Synthesis of methyl- (**2 e**–**8 e**) and chloro- (**2 f**, **4 f**, **5 f**, **7 f**, and **8 f**) substituted 2,5-bis(arylethynyl)rhodacyclopentadienes.

[RhMe(PMe$_3$)$_4$] also reacts directly with two equivalents of 1,4-bis(*p*-R′-phenyl)-1,3-butadiynes (R′ = H, Me, OMe, SMe, CF$_3$, CO$_2$Me) to give the corresponding rhodacyclopentadienes **2 e**–**8 e** bearing a methyl ligand in the equatorial plane, although higher reaction temperatures of 80 °C for 3–12 h are required for full conversion (Scheme 3). We note that for compounds **3 e** and **6 e**, small amounts of **3 f** (13 %) and **6 f** (15 %), respectively, are found in the single crystals used for X-ray diffraction (see below), presumably a result of the reaction of the butadiynes with residual [Rh(PMe$_3$)$_4$][Cl], the precursor to [RhMe(PMe$_3$)$_4$]. However, the amount of the impurities in the bulk material of **3 e** and **6 e** must be very small, that is, less than 1 %, because they were not detected by NMR spectroscopy or elemental analysis, indicating analytically pure compounds. The relatively larger amount of **3 f** and **6 f** in the single crystals is most likely due to their lower solubility than **3 e** and **6 e**, which leads to enrichment during the crystallization process. The intentional reaction with [Rh(PMe$_3$)$_4$][Cl] as precursor was only successful when (p-CF$_3$–C$_6$H$_4$)-C≡C-C≡C-(p-C$_6$H$_4$–CF$_3$) was employed in a fourfold excess with prolonged heating at 80 °C for four days, leading to moderate yields of the desired conjugated 2,5-isomer **7 f** containing an equatorial chloride ligand. The low reactivity of [Rh(PMe$_3$)$_4$][Cl] also indicates that the content of **3 f** and **6 f** must be very small in the samples we prepared of **3 e** and **6 e**. Attempts to accelerate the reaction in a microwave reactor failed due to the fact that three different isomers were formed according to ^{31}P{^{1}H} NMR spectroscopy and mass spectrometry. However, addition of HCl·Et$_2$O to **2 e** and **4 e**–**8 e** converts the Rh-methyl-substituted rhodacyclopentadienes to their corresponding chloro analogues quantitatively (Scheme 3). The chemical stability of the rhodacyclopentadienes is underlined by the fact that selective removal of the four SiMe$_3$ groups at the peripheral C$_6$H$_4$–C≡C–SiMe$_3$ positions of **11** is possible with *n*-Bu$_4$NF in THF, whereas the –C≡C–SiMe$_3$ ligand on the Rh center remains intact, yielding **14** (Scheme 4). Compounds **2 a**/



Scheme 4. Deprotection of **11** with nBu$_4$NF to give **14**.

b–**10 a**/**b** are exceedingly robust and insensitive to air and moisture in the solid state, whereas the acceptor-substituted rhodacylopentadienes **7 a**/**b**–**10 a**/**b** are stable to air and moisture for months in THF or toluene solution. However, the complexes with longer conjugated substituents, either as R or R′ (**2 c**/**d**–**10 c**/**d** and **11**–**14**), are rather sensitive to air and moisture, and **6 d** and **14** also appear to be photochemically unstable.

Crystal and molecular structure

Representations of the general atom and ring numbering for the following discussion are shown in Figures 3 and 4 using **2 a** and **3 d** as examples. Selected bond lengths and angles are given in Tables 1 and 2. More details and pictorial presentations are given in the Supporting Information (Figures S13–S25, the Supporting Information). In all cases, the Rh coordination is distorted octahedral. The metallacycle (*i*) is planar, with bond length alternation consistent with a rhodacyclopentadiene structure. In the σ-ethynyl derivatives, the endocyclic Rh–C(2) and Rh–C(5) bond lengths are similar, indicating comparable *trans*-influence of the phosphine and σ-ethynyl ligands. Replacement of the σ-ethynyl with a σ-methyl ligand causes lengthening of the *trans* Rh–C(2) bond, which, in **8 e**, is 0.05 Å longer than Rh–C(5). In contrast, replacement of σ-ethynyl with a chloro ligand (in **5 f**, **7 f**, **8 f**) makes the Rh–C(2) bond significantly shorter than Rh–C(5), by 0.04 Å or more. The *trans*-influences of the σ-ligands thus agree with their electronegativities, that is, 3.0 (Cl), 3.1 (C sp), 2.4 (Me), and σ-donating properties. The Rh–C(2) bond lengths in **3 e/f** and **6 e/f** are much longer (ca. 0.06 Å) than in pure **5 f**, **7 f**, or **8 f**, and they are similar to those bearing strong σ-donors, which is consistent with only a very small amount of the methyl ligand being replaced by the chloro ligand. The degree of π-electron delocalization in the rhodacyclopentadiene can be estimated by the ratio $\Delta = 2d_1/(d_2+d'_2)$ (see Figure 3 and Table 2) between the length of the nominally single (d_1) and nominally double bonds (d_2, d'_2). In the present complexes, Δ ranges from 1.055 to 1.072 Å, compared to 1.058 in previously reported **3 a**[20] and 1.047–1.059 in four cyclohexano-rhodacyclopentadiene analogues.[22] This indicates greater delocalization than in related 2,5-bis(arylethynyl)siloles (mean $\Delta = 1.122(16)$ Å for seven structures)[10a] or in carbocyclic cyclopentadienes (mean $\Delta = 1.094(9)$ Å for the 23 most accurate low-temperature structures in the CSD[26]).

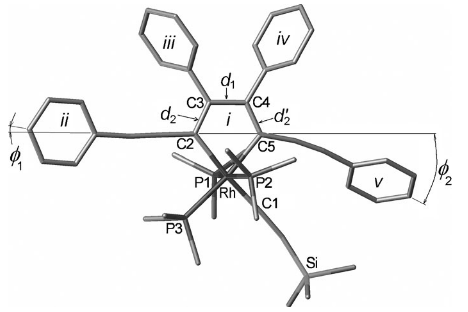


Figure 3. Molecular structure of **2 a** in the solid state, showing atom and ring numbering. Hydrogen atoms omitted for clarity.

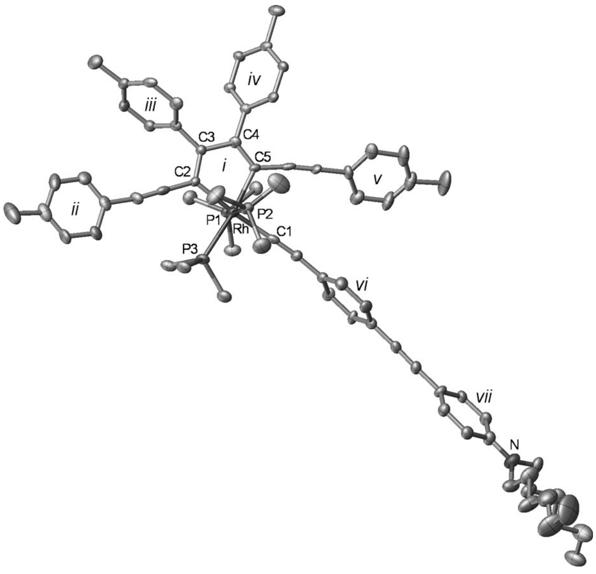


Figure 4. Molecular structure of **3 d** in the solid state, showing atom and ring numbering. Hydrogen atoms omitted for clarity.

Arene rings *iii* and *iv* are inclined to the rhodacyclopentadiene plane substantially (by 43 to 64°). The corresponding angle for ring *ii* varies widely, notwithstanding the same intramolecular environment, and must be attributed to the effect of crystal packing. This, in turn, suggests that variable orientation of ring *v* may also be due to intermolecular interactions, rather than steric repulsion between this moiety and the σ-ligand. Indeed, it is noteworthy that ring *v* is almost always tilted towards the latter, through bending of the ethynyl group, whereas for the 2-ethynylarene substituent, such bending is much smaller and usually occurs perpendicularly to the metallacycle plane, rather than within this plane.

Arene ring *vi* in **2 b**, **3 b**, and **3 d** (both independent molecules), **4 d** and **7 d** forms a large dihedral angle with ring *i*. The twist between rings *vi* and *vii* is substantial in **3 d** and **7 d**. In **4 d**, this twist is small, but the ligand rod is substantially bent; whereas the Rh–C(1) bond is tilted out of plane *i* by 4°, for the C(55)–N bond this angle increases to 55°. For comparison, the corresponding angles equal only 2.0 and 7.4° in molecule *I*, or

Table 1. Selected bond lengths [Å].

	Rh–P(1)	Rh–P(2)	Rh–P(3)	Rh–Cl(1)	Rh–C(1)	Rh–C(2)	Rh–C(5)	C(2)–C(3)	C(3)–C(4)	C(4)–C(5)	Δ[a]
2a	2.3230(5)	2.3180(5)	2.3763(6)		2.041(2)	2.095(2)	2.100(2)	1.377(2)	1.463(2)	1.374(2)	1.064(2)
2b	2.3149(7)	2.3044(6)	2.3632(6)		2.042(2)	2.085(2)	2.091(2)	1.381(3)	1.462(3)	1.368(3)	1.064(3)
3b	2.3113(12)	2.3136(13)	2.3550(7)		2.042(4)	2.091(4)	2.072(4)	1.373(5)	1.462(6)	1.363(6)	1.069(6)
3d[c]	2.320(3)	2.308(3)	2.364(2)		2.028(9)	2.067(7)	2.093(8)	1.362(11)	1.464(12)	1.368(11)	1.072(12)
3e/3f	2.3164(7)	2.3011(6)	2.3550(7)	2.255(2)[b]		2.103(2)	2.083(2)	1.379(3)	1.464(3)	1.377(3)	1.062(3)
4d	2.3316(13)	2.3079(14)	2.3798(13)		2.052(5)	2.082(4)	2.099(4)	1.385(6)	1.456(6)	1.370(6)	1.057(6)
5a[c]	2.325(4)	2.317(6)	2.369(3)		2.05(2)	2.09(1)	2.08(1)	1.37(3)	1.45(2)	1.37(2)	1.06(2)
5f	2.3301(8)	2.3302(8)	2.4137(7)	2.4802(7)		2.030(2)	2.071(3)	1.375(3)	1.456(3)	1.372(3)	1.060(3)
6a	2.3071(4)	2.3113(4)	2.3765(4)		2.0451(16)	2.0976(15)	2.0874(14)	1.376(2)	1.466(2)	1.374(2)	1.066(2)
6e/6f	2.3088(13)	2.3049(13)	2.3544(13)	2.201(4)[b]		2.087(4)	2.078(4)	1.381(6)	1.461(5)	1.374(6)	1.061(6)
7a	2.3223(4)	2.3248(4)	2.3729(4)		2.037(2)	2.093(2)	2.083(2)	1.380(2)	1.462(2)	1.372(2)	1.063(2)
7d	2.3188(14)	2.3244(14)	2.3634(14)		2.039(5)	2.073(4)	2.092(5)	1.384(7)	1.452(7)	1.372(2)	1.055(7)
7f	2.3225(8)	2.3440(7)	2.3962(9)	2.4670(7)		2.038(3)	2.072(3)	1.362(4)	1.458(3)	1.369(4)	1.068(4)
8e[c]	2.3108(9)	2.3107(8)	2.347(1)		2.165(3)	2.128(3)	2.077(3)	1.374(4)	1.470(4)	1.370(4)	1.071(4)
8f	2.3255(6)	2.3431(6)	2.4015(6)	2.4490(5)		2.034(2)	2.079(2)	1.379(3)	1.458(3)	1.369(3)	1.061(3)
9a	2.3249(8)	2.3199(7)	2.3660(7)		2.036(2)	2.098(2)	2.072(3)	1.380(3)	1.455(3)	1.372(3)	1.057(3)

[a] $\Delta = 2d_{C(3)-C(4)}/(d_{C(2)-C(3)}+d_{C(4)-C(5)})$. [b] Positions of C(1) and Cl(1) unresolved. [c] Average for two (**3d**, **8e**) or eight (**5a**) independent molecules.

Table 2. Angles [°] between ring planes and vectors.

	i/*ii*	*i*/*iii*	*i*/*iv*	*i*/*v*	*i*/*vi*	*vi*/*vii*	ϕ_1	ϕ_2
2a	11.0	64.0	58.6	58.3			9.8	28.7
2b	12.0	50.5	53.4	15.3	83.7		5.9	11.7
3b	5.2	56.8	61.4	22.4	49.3		2.6	19.1
3d[a]	16.8	60.5	47.0	38.0	81.1	40.5	14.7	22.4
	21.0	60.6	48.3	41.5	88.9	38.4	10.4	15.0
3e/3f	19.8	53.6	49.5	51.1			8.4	25.4
4d	4.9	58.2	53.4	7.0	49, 40[b]	12, 5[b]	1.0	32.0
5a[a]	4.1,	57.4	45.9	9.5			5.3,	11.2
A	7.6[b]						10.6[b]	
B	2.2	62.6	47.0	20.1			10.9	17.8
C	1.0, 8.0[b]	58.6	46.7	12.8			10.3, 6.0[b]	6.7
D	3.0, 7.0[b]	58.4	45.6	8.0			11.2, 7.0	11.3
E	3.1	64.7	48.5	15.9			9.5	16.8
F	3.3	62.3	46.1	6.2			10.1	9.8
G	5.6	62.1	49.0	10.9			11.7	10.9
H	2.9	62.9	49.7	15.4			8.9	15.9
5f	19.6	56.4	50.6	11.9			9.3	29.2
6a	18.5	55.0	43.3	14.5			11.8	22.7
6e/6f	39.8	52.4	44.1	27.5			1.3	15.4
7a	18.3	53.1	46.9	65.1			2.2	18.6
7d	16.5	63.3	51.7	28.4	73.4	35.9	11.0	26.8
7f	24.0	55.7	50.0	10.4, 9.2[b]			13.6	20.3, 12.2[b]
8e[a]	72.1	45.1	54.7	39.6			16.7	5.0
	71.6	44.3	55.9	21.9			16.7	2.4
8f	19.9	51.1	52.6	41.1			5.4	26.1
9a	6.4	49.3	56.6	14, 24, 38[b]			2.5	20, 20, 16[b]

[a] Symmetrically independent molecules. [b] Alternative positions of disordered ligands.

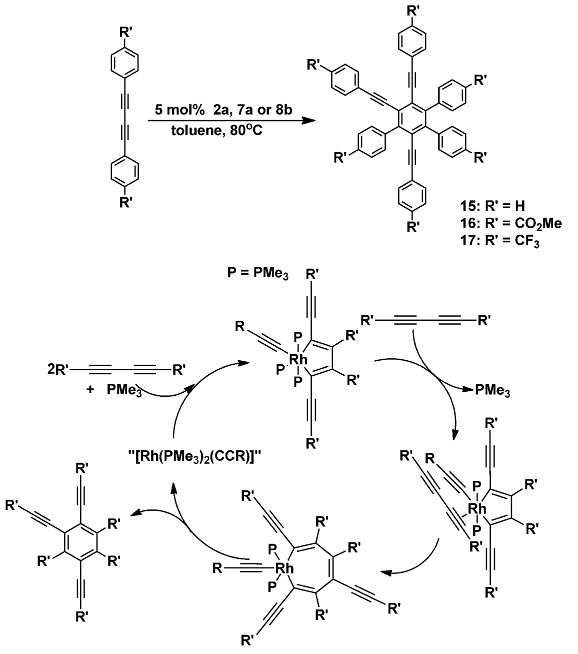
2.0 and 10.3° in molecule *II* of **3d**, and 2.3 and 12.6° in **7d** (although the angles between the Rh–C(1) and C(55)–N bonds are larger, being 15.5, 15.4, and 22.0°) in which the dihedral angle *i*/*vi* is close to 90°.

Cyclotrimerization reactions

Metallacyclopentadienes are well-known as intermediates in cyclotrimerization reactions of alkynes as discussed in the introduction,[6b,8] motivating us to investigate the reactivity of our compounds with respect to their use as catalyst precursors. Addition of excess bis(*p*-R′-phenyl)-1,3-butadiyne (R′ = H, CO_2Me, CF_3) to the respective rhodacyclopentadienes with −C≡C−$SiMe_3$ (**2a** and **7a**) or −C≡C−(*p*-C_6H_4−NMe_2; **8b**) ligands gave the 1,2,4-tris(*p*-R′-phenylethynyl)-3,5,6-tris(*p*-R′-phenyl)benzene derivatives **15**–**17** as the sole products, but only under forcing conditions, that is, *T* = 80 °C for three weeks and with low turnover numbers of three to seven (Scheme 5). Single crystals of **15** suitable for X-ray diffraction experiments were obtained, and the molecular structure is shown in Figure 5. The regiospecificity of the cyclotrimerization reaction, giving rare examples of 1,2,4-tris(arylethynyl)benzenes, can be explained by the catalytic cycle, which involves the regiospecific regeneration of the key 2,5-bis(arylethynyl)rhodacyclopentadiene intermediate. The low catalytic activity may well be related to the limited phosphine (PMe_3) dissociation from the Rh^{III} rhodacyclopentadienes, a factor which contributes to their stability.

Photophysical studies

The optical properties of compounds **2a**–**10a** and **11**–**14** are summarized in Table 3, whereas absorption and emission spec-



Scheme 5. Synthesis of 1,2,4-tris(arylethynyl)-3,5,6-tri(aryl)benzenes **15**–**17** by using **2a**, **7a** or **8b** as a catalyst (top) and proposed catalytic cycle (bottom).

tra of selected compounds are presented in Figure 6 (see also Figures S1–S4, the Supporting Information). Intense bands in the UV–visible absorption spectra with maxima at $\lambda_{abs}=453$–517 nm and extinction coefficients of $\varepsilon=21\,000$–$35\,000$ dm^3 mol^{-1} cm^{-1} are observed for the rhodacyclopentadienes bearing a $-C{\equiv}C-SiMe_3$ ligand in the equatorial plane. All compounds exhibit emission in the visible region ($\lambda_{em}=496$–590 nm) with small Stokes shifts of about 1870–2390 cm^{-1} and modest photoluminescence quantum yields of $\Phi_{PL}=0.01$–0.18. We note that compound **10a** has the highest quantum yield, although in organic molecules the n→π* transition of

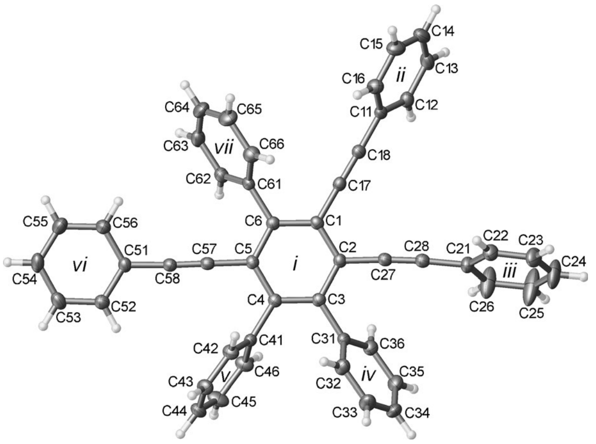


Figure 5. Molecular structure of **15** in the solid state, with hydrogen atoms omitted for clarity, and ellipsoids drawn at 50 % probability. Dihedral angles: *i*/*ii* 62.4, *i*/*iii* 66.5, *i*/*iv* 62.2, *i*/*v* 75.5, *i*/*vi* 5.9, and *i*/*vii* 61.9°.

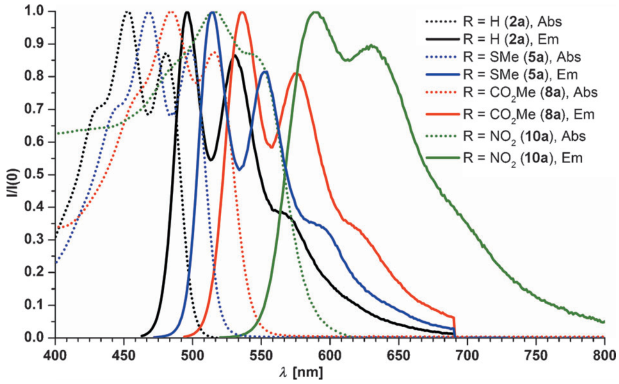


Figure 6. Normalized absorption (Abs) and emission (Em) spectra of **2a**, **5a**, **8a**, and **10a** recorded in degassed toluene at room temperature with excitation at their respective absorption maxima.

Table 3. Selected photophysical data of 2,5-bis(arylethynyl)rhodacyclopentadienes bearing a $-C{\equiv}C-SiMe_3$ ligand in the equatorial plane (**a**). All data were recorded in degassed toluene at RT.

Compound	λ_{max} (abs) [nm]	ε [mol^{-1} cm^{-1} dm^3]	λ_{max} (em) [nm]	Stokes shift [cm^{-1}]	Φ_{PL}	τ_f [ns]	Φ_Δ[a]
2a (R=H)	453	26 000	496	1910	0.15	0.87	0.57
3a (R=Me)	454	25 000	496	1870	0.12	0.66	
4a (R=OMe)	454	23 000	497	1910	0.09	0.45	
5a (R=SMe)	468	35 000	515	1950	0.10	0.55	0.50
6a (R=NMe$_2$)	466		516	2080			
7a (R=CF$_3$)	464	23 000	510	1940	0.08	0.56	
8a (R=CO$_2$Me)	485	21 000	536	1960	0.16	0.98	0.45
9a (R=CN)	482	30 000	533	1990	0.08	0.54	
10a (R=NO$_2$)	517	22 000	590	2390	0.18	1.21	
11 (R=CCTMS)	484	33 000	534	1930	0.03		
12 (R=CC(C$_6$H$_4$)NHex$_2$)	494	48 000	549	2030	0.01	0.06 (27 %) 1.64 (73 %)	
13 (R=CC(C$_6$H$_4$)CO$_2$Oct)	500	40 000	556	2010	0.02	0.10 (47 %) 0.86 (53 %)	
14 (R=CCH)	478		526	1910			

[a] Quantum yield for $^1O_2$ formation in O_2-saturated solutions.

the nitro group often tends to quench luminescence. Both the absorption and the emission occur with a vibrational progression of about 1300 cm^{-1}. In addition, the absorption and emission maxima shift bathochromically with the Hammett constants of the *para* substituents R′ on the aryl rings (σ_p), a behavior that is also found in structurally related 2,5-bis(phenylethynyl)thiophenes (BPETs).[13] Electron-withdrawing *para* substituents have a more pronounced effect than electron-donating ones on the energy gap between the ground state S_0 and the emissive excited state.

During the photophysical investigation of this class of luminescent metallacyclopentadienes, we observed that the emission occurs with a lifetime of $\tau = 0.45$–1.21 ns (Table 3), leading us to conclude that the observed luminescence is fluorescence resulting from the S_1 state, similar to the related, more rigid rhodacycles that we previously discussed in a preliminary report.[22] This is highly unusual for octahedral, late organo-transition-metal complexes, as the spin-orbit coupling (SOC) of the metal atom would be expected to facilitate very fast intersystem crossing (ISC) to the triplet state T_1 on the timescale of femto- to picoseconds (10^{-14}–10^{-10} s).[2d,3b,5] Therefore, the excited singlet state S_1 is normally too short lived to observe fluorescence, and either non-radiative decay or phosphorescence from the T_1 state with emission lifetimes of micro- to milliseconds would be expected. Singlet oxygen sensitization experiments were carried out for **2a**, **5a**, and **8a** and quantum yields for the formation of singlet oxygen (Φ_Δ) were found to be in the range 0.45–0.61, thus suggesting similar quantum yields for the ISC (Table 3).

The ISC from the S_1 to the T_1 state in compounds **2a**–**10a** occurs several orders of magnitude slower (10 ns) than one would expect, leading to unusually long-lived emitting S_1 states. Introducing longer conjugated substituents at the *para* position of the phenyl rings (see compounds **11**–**14**) leads to a bathochromic shift in absorption as well as in emission, and also drastically increases the values of the extinction coefficients. The short nanosecond emission lifetimes suggest that the general photophysical excited-state behavior is very similar to that of **2a–10a**, although the low quantum yields of 0.01–0.03 show that effective radiationless decay occurs, presumably due to additional vibrational modes.

To understand the role of the σ-donor ligand in the metallacyclopentadiene plane and of the rhodium atom in the photophysical behavior of the excited states, the $-C\equiv C-SiMe_3$ moiety was substituted by several ligands with different conjugation lengths and varying σ/π-donor strengths. Compounds **2b**/**d**–**4b**/**d**, **5d**, **7b**/**d**–**8b**/**d**, and **9d** bearing the conjugated donor ligands $-C\equiv C-(p\text{-}C_6H_4-NMe_2)$ (**b**) and $-C\equiv C-(p\text{-}C_6H_4)-C\equiv C-(p\text{-}C_6H_4-N(C_6H_{13})_2)$ (**d**) show almost identical absorption and emission spectra with very similar extinction coefficients and fluorescence lifetimes to **2a**–**10a** and **11**–**14** (Table 3 and the Supporting Information). We attribute the negligible influence of these ligands on the photophysical properties of the compounds to the fact that the aryl rings are significantly rotated out of co-planarity with the metallacycle (see Table 2) and, thus, conjugation between the rhodium atom and the substituent on the acetylide ligands is not increased. For this reason, rhodacyclopentadiene **3c** with $-C\equiv C-C\equiv C-(p\text{-}C_6H_4-NPh_2)$[24] as a ligand was synthesized, in which the two alkynyl groups were initially anticipated to ensure co-planarity of the aryl rings. However, despite the additional alkyne unit, the absorption and emission spectra of **3c** are similar to **3a**/**b** and **3d**. A molecular modeling study showed that steric hindrance between the *p*-phenylene *ortho*-hydrogen atoms of the $-C\equiv C-C\equiv C-(p\text{-}C_6H_4-NPh_2)$ ligand and the adjacent aryl ring on the diethynylmetallacycle again prevents the desired co-planarity. A more pronounced effect was expected by replacing the acetylide with the more strongly σ-donating methyl ligand in **2e**–**8e**, which should increase electron density at the metal center and thus increase the metal-to-ligand charge transfer (MLCT) character of the emitting excited state, consequently leading to higher ISC rates. Indeed, the maxima of the absorption and emission of compounds **2e**, **4e**, **6e**, and **8e** show a very small bathochromic shift of about 350 cm^{-1} compared with **2a**, **4a**, **6a**, and **8a** and the fluorescence quantum yield is reduced to below 0.01 (Table 4). However, the singlet oxygen sensitization experiments indicate a quantum yield for the ISC of only 0.38–0.64, identical within the experimental error to the $-C\equiv C-SiMe_3$-substituted compounds **2a**, **5a**, and **8a**. The lower photoluminescence quantum yield presumably results from non-radiative decay through C–H vibrational and/or $Rh-CH_3$ rotational modes. No isotope effect on the quantum yield was found by replacing CH_3 with CD_3 (**d³–2a**), suggesting very efficient non-radiative decay pathways in compounds **2e**–**8e**. We also investigated the influence of the chloride ligand with weak σ/π-donor properties, but surprisingly, the general photophysical behavior of compounds **2f**, **4f**, **5f**, and **8f** was rather similar to that of their $-C\equiv C-SiMe_3$ analogues. Small

Table 4. Selected photophysical data of 2,5-bis(arylethynyl)rhodacyclopentadienes bearing a Me ligand (**e**) or a chloride ligand (**f**) in the equatorial plane. All data were recorded in degassed toluene at RT.

Compound	λ_{max} (abs) [nm]	ε [$mol^{-1} cm^{-1} dm^3$]	λ_{max} (em) [nm]	Φ_{PL}	τ_f [ns]	Φ_Δ[a]
2e (R=H)	460	24000	505	<0.01	1.47 (9%) <1.0 (91%)	0.64
4e (R=OMe)	458	17000	505	<0.01	8.20 (86%) 2.05 (14%)	
5e (R=SMe)	474		527	<0.01	2.30 (83%) <1.0 (17%)	
6e ($R=NMe_2$)[b]	474	40000	523			
8e ($R=CO_2Me$)	492	22000	545	<0.01	1.00 (36%) <1.0 (64%)	0.38
2f (R=H)	463	20000	505	<0.01	2.80 (9%) <1.0 (91%)	0.65
4f (R=OMe)	461	27000	508	<0.01	3.38 (36%) ≪1.0 (64%)	0.62
5f (R=SMe)	471		522		1.82 (28%) <1.0 (72%)	0.21
8f ($R=CO_2Me$)	488	26000	543	0.22	1.20	0.55

[a] Quantum yield for $^1O_2$ formation in O_2-saturated solutions. [b] Analytically pure bulk material (see above).

redshifts of about 350–480 cm^{-1} (ca. 6–10 nm) of the absorption and emission maxima were observed, and the fluorescence quantum yields strongly depend on the aryl substituents, ranging from below 0.01 for R′=H to 0.22 for $R'{=}CO_2Me$ (Table 4). However, the ISC process occurs on the same timescale as observed for all other compounds (10^{-8} s), according to our singlet oxygen sensitization experiments. The emission of the rhodacyclopentadienes is not very sensitive to solvent effects, as compounds **2 f**, **4 a**, and **4 f** exhibit a slight hypsochromic shift in MeCN, whereas the acceptor-substituted compounds **8 e/f** display an emission shift in MeCN to lower energies by about 14 and 9 nm, respectively (see the Supporting Information). This suggests some CT character of the emission.

To ensure that the observed fluorescence does not result from traces of organic products resulting from diyne cyclotrimerization reactions, we recorded the absorption, emission, and excitation spectra of the highly substituted benzene derivatives **15**–**17**. Their absorption maxima all lie in the UV region (Table 5 and Figure 7) and intense blue fluorescence (Φ_f= 0.37–0.61) was observed in all cases. As the observed photophysical properties of these potential side products differ substantially from those of **2**–**14**, we can be sure that the observed photoluminescence originates from the organometallic complexes and not from an organic impurity such as free diyne or cyclotrimerized products.

Table 5. Photophysical data of 1,2,4-tris(phenylethynyl)-3,5,6-trisphenylbenzene derivatives **15**–**17**. All data were recorded in degassed toluene at RT.

Compound	λ_{max} (abs) [nm]	λ_{max} (em) [nm]	Φ_{PL}
15 (R=H)	314, 342, 366	393	0.37
16 ($R{=}CO_2Me$)	330, 354, 381	395 414	0.61
17 ($R{=}CF_3$)	315, 342, 366	384	0.50

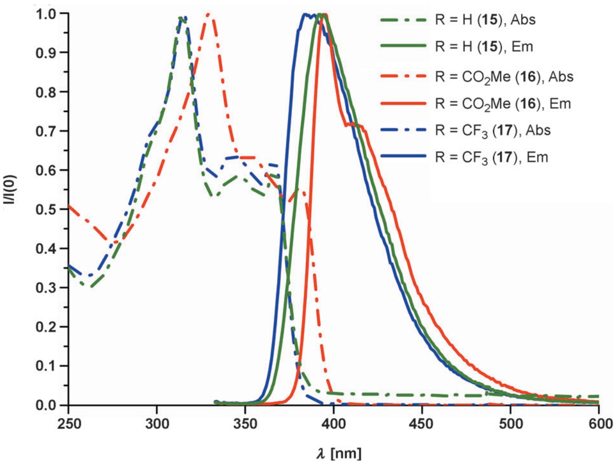


Figure 7. Absorption (Abs) and emission (Em) spectra of **15**–**17** recorded in degassed toluene at room temperature with excitation at their respective absorption maximum.

In our preliminary study on the absorption and emission properties of **3 a**, we erroneously assigned the high-energy bands at 366 and 384 nm to arise from emission from the rhodium complex.[20] We would like to correct this assignment, because further studies showed that the high-energy emission arose from an organic trace impurity in the starting material.

Cyclovoltammetric measurements

The one-electron oxidation potentials for compounds **2 a/b** and **2 e/f**, bearing different σ-donor ligands at the rhodium center, as well as for **5 a** and **8 a** with –SMe and $-CO_2Me$ as electron-donating and electron-accepting *para* substituents at the aryl rings, respectively, have been measured and are listed in Table 6. The one-electron reduction potentials were outside the measuring window and are thus not available. Using **2 a** as a benchmark for comparison, the following general trends are observed: substitution of $C{\equiv}C{-}SiMe_3$ for stronger σ-donor ligands at the rhodium atom, such as $C{\equiv}C{-}C_6H_4{-}NMe_2$ (**2 b**) or Me (**2 e**), leads to a lower oxidation potential, whereas the weaker σ-donor Cl lowers the HOMO energy and increases the oxidation potential slightly. Interestingly, the electron-donating –SMe group in the *para* position of the aryl rings (**5 a**) has a very similar effect as the $C{\equiv}C{-}C_6H_4{-}NMe_2$ ligand at the rhodium atom in **2 b**. The most pronounced effect is observed with the electron-accepting group $-CO_2Me$ in the *para* position of the aryl rings (**8 a**), greatly increasing the oxidation potential by about 0.17 V. Our results lead us to conclude that the highest occupied molecular orbital (HOMO), which is predominantly responsible for the oxidation potential, has some metal contribution, but it is mainly located at the π-system of the organic ligand. Thus, one would expect that the photophysical properties are also dominated by the ligand π-system, in agreement with our experimental results (see above).

Table 6. Cyclic voltammetric and spectroscopic data for **2 a/b**, **2 e/f**, **5 a**, and **8 a**.

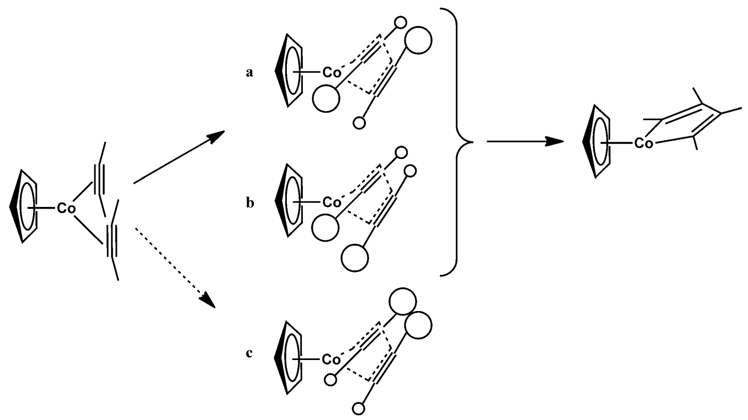
Compound	Rh–X	R	$E_{1/2}$ [V][a]	λ_{max} (abs) [nm]	λ_{max} (em) [nm]	HOMO [eV][b]
2 a	$CC{-}SiMe_3$	H	0.53	453	496	−4.74
2 b	$CC{-}Ph{-}NMe_2$	H	0.49	455	500	−4.70
2 e	Me	H	0.44	460	505	−4.65
2 f	Cl	H	0.58	463	505	−4.79
5 a	$CC{-}SiMe_3$	SMe	0.48	468	515	−4.69
8 a	$CC{-}SiMe_3$	CO_2Me	0.71	485	536	−4.92

[a] All potentials are reported versus $[FeCp^*_2]/[FeCp^*_2]^+ = 0.00$ V, from 0.1 M nBu_4NPF_6/MeCN solutions at ambient temperature at a carbon working electrode. [b] $E_{HOMO} = -e[(E_{ox}-E_{1/2(Fc)})+4.8\ V]$.

Discussion

Synthesis

The formation of the 2,5-bis(arylethynyl)rhodacyclopentadienes reported herein occurs regiospecifically in all cases, yielding the 2,5-bis(arylethynyl) isomer exclusively. Other metallacyclopentadienes constructed by the reductive coupling of butadiynes at titanocenes or cobaltocenes appear to obey Wakatsuki's rule, according to which the carbon atoms with the sterically most demanding substituents at the alkyne form the σ-bond with the transition-metal center.[27] As can be seen from Scheme 6, the reason lies in the nature of the possible transition states **a**–**c**, with the highest steric hindrance in **c**, which is thus the least favored transition state. Whether a parallel (**a**) or antiparallel arrangement (**b**) of the alkynes is preferred, remains unclear. However, Rosenthal et al. concluded for their five-membered 2,4-alkynyl-titanacyclopentadiene, produced by reacting [TiCl$_2$Cp$_2$] with bis(trimethylsilyl)-1,3-butadiyne in the presence of Mg as reducing agent, that the explanation for the observed regiochemistry is the reduced steric interference resulting from the SiMe$_3$ group and the alkynyl group in the β-positions of the metallacyclopentadiene ring, resulting in a transition state similar to (**a**).[18a] Thus, it is not necessary for the SiMe$_3$ substituents to take advantage of the free lateral sectors in the central plane of the bent metallocene unit.



Scheme 6. Transition states **a**–**c** according to Wakatsuki for the formation of metallacyclopentadienes by reductive coupling of alkynes.[27]

Apart from our initial results with these Rh systems,[20] the only comparable example for the synthesis of octahedral metallacyclopentadienes is that of the related ruthenacyclopentadiene [Ru{κ^2-*C,C′*-CR=CPhCPh=CR}(CO)$_2$(PPh$_3$)$_2$] (R = C≡CPh) reported by Hill et al.[21] They proposed that the regioselectivity resulting in the observed formation of the 2,5-bis(phenylethynyl)isomer is electronic in origin, because the transition state leading to the final product is sterically unfavorable. In contrast to the Ru complexes containing CO ligands as strong π-acceptors, our rhodium systems involve rather strong σ-donors including PMe$_3$ ligands, which are only weak π-acceptors. Thus, we believe the reductive coupling of diynes at [RhMe(PMe$_3$)$_4$] or [Rh(C≡CR)(PMe$_3$)$_4$] (**1**) (R = −SiMe$_3$ (**a**), −(*p*-C$_6$H$_4$−NMe$_2$) (**b**), −C≡C−(*p*-C$_6$H$_4$−NPh$_2$) (**c**) or −{*p*-C$_6$H$_4$−C≡C−(*p*-C$_6$H$_4$−N(C$_6$H$_{13}$)$_2$)} (**d**)), giving the 2,5-isomers exclusively, to occur for steric reasons. The larger aryl (vs. arylethynyl) groups avoid the 2,5-positions due to interaction with the σ-donors in the developing plane of the metallacycle. We are currently investigating the reaction mechanism, which will be reported in due course.

Photophysics

Most studies of cyclometallated d^6-rhodium compounds have focused on homoleptic and heteroleptic bipyridine and phenylpyridine complexes of the type [Rh(bpy)$_{3-n}$(ppy)$_n$]$^{(3-n)+}$ (n = 0–3) and derivatives thereof.[28] Few of them exhibit significant luminescence at room temperature in solution; thus, most rhodium complexes have been characterized photophysically in glassy matrices at 77 K or in their crystalline form. Under those conditions, these previously investigated cyclometallated rhodium complexes exclusively show weak phosphorescence with emission lifetimes in the range of τ = 3–500 μs. Their emitting excited states have been assigned to be of ^{3}IL(π–π*) nature, with very little ^{3}MLCT(d-π*) or ^{3}MC(d–d*) admixtures to enable a facile intersystem crossing from S$_1$→T$_1$. These admixtures also enhance the radiative decay rate constant of the spin-forbidden phosphorescence (T$_1$→S$_0$) relative to the free ligands, which usually fluoresce from their S$_1$ states.[3b] Although the phosphorescence of such cyclometallated rhodium(III) complexes is weak in comparison with other heavy transition-metal complexes of ruthenium, iridium, or platinum,[28m] the SOC of rhodium is still large enough to ensure efficient intersystem crossing (Φ_{ISC} = 1) from the singlet to the triplet excited states, occurring with rate constants of the order of 10^{11} s^{-1} as found, for example, in *cis*-[RhX$_2$(bpy)$_2$][X] (X = Cl, Br).[29] It should be noted that fluorescence has been observed in late transition-metal complexes of rhenium, osmium, iridium, and platinum resulting from a pure ^{1}IL state due to electronic isolation of the chromophore from the metal center by a spacer unit, inhibiting the spin-orbit coupling effect of the metal atom.[30–33] Only a few examples of Rh complexes with ^{1}IL fluorescence as well as ^{3}IL phosphorescence have been described on the basis of luminescence spectra, but no further details, such as lifetimes and quantum yields, were given.[34] Thus, it is difficult to judge the kinetics of the photophysical excited-state behavior and the efficiency of the intersystem crossing process in those compounds. However, we have investigated the kinetics of the excited-state conversions in rigid conjugated 2,5-bis(*p*-R-arylethynyl)rhodacyclopentadienes, which have been prepared by reaction of [Rh(C≡CSiMe$_3$)(PMe$_3$)$_4$] or [Rh(κ^2-*S,S′*-S$_2$CNEt$_2$)(PMe$_3$)$_2$] with 1,12-diaryldodeca-1,3,9,11-tetraynes. The rhodacycles thus obtained showed fluorescence quantum yields of up to Φ_f = 0.69 and ISC on the timescale of a few nanoseconds, that is, several orders of magnitude slower than expected.[22]

With this in mind, it is remarkable that the rhodacyclopentadienes presented in this work behave more like related organo-main group cyclopentadienes such as boroles,[9] pyroles, siloles,[10] phospholes,[11] and thiophenes,[12] which, in general, show fluorescence in the visible region of the electromagnetic spectrum.[35] The kinetics of the general excited-state processes seem to be largely independent of the substituents at the aryl rings or at the rhodium atom. A comparison with main group 2,5-bis(arylethynyl)cyclopentadienes is of particular interest, and highlights the unexpected photophysical behavior of the rhodacyclopentadienes.[6a] Pagenkopf and co-workers have prepared luminescent 2,5-bis(arylethynyl)siloles by adaption of a synthetic route discovered by Tamao et al.[10c] The compounds exhibit fluorescence with low to moderate quantum yields of $\Phi_f = 0.004–0.09$, depending on the aryl substituents. We have reported similar behavior for a series of 2,5-bis(arylethynyl)thiophenes.[13] Their absorption and emission spectra look very similar to the ones recorded for the compounds in this work, although the thiophene compounds are blueshifted compared to the rhodacyclopentadienes ($\lambda_{abs} = 345–387$ nm, $\lambda_{em} = 382–435$ nm), and the extinction coefficients ($\varepsilon = 33\,000–52\,000$) and fluorescence quantum yields ($\Phi_f = 0.19–0.33$) are both higher. The hypsochromic shift of the S_0–S_1 energy gap might arise from the bent structure of the 2,5-bis(arylethynyl)thiophenes, whereas the larger rhodium atom, in comparison with sulfur, leads to a change in the bond angles of the MC_4 ring, influencing the orbital energies of the carbon π-system. Intriguingly, oxygen sensitization with a quantum yield of about 0.60 for 2,5-bis(phenylethynyl)thiophene and the 210–400 ps emission lifetimes indicate an intersystem crossing process on the timescale of 10^{-9}–10^{-8} s mediated by the spin-orbit coupling of the sulfur ($\xi = 100$ cm^{-1}). It is difficult to rationalize why the rhodium ($\xi = 1200$ cm^{-1}) containing compounds **2**–**14** exhibit an ISC that is about one order of magnitude slower than for the thiophenes, and even several orders of magnitude slower than in other octahedral organo-transition-metal complexes.[2e,3b,c,4a,7b,28m] The singlet oxygen sensitization experiments indicate the formation of the T_1 state, but it is presumably very low in energy, undergoing fast non-radiative decay, as we could not observe any phosphorescence. Large energy differences between the S_1 and T_1 state are normally found in organic systems, whereas organo-transition-metal complexes often exhibit lower energy gaps due to low-lying $^{1/3}$MLCT states. However, the small changes in the photophysical properties upon substitution of the ligands at the rhodium in the plane of the metallacycle indicate a certain influence of the transition-metal center on the excited-state properties, which leads us to assign the excited state as an ^{1}IL state with very little ^{1}MLCT admixture. This assignment would be in agreement with the results of our cyclovoltammetric measurements, indicating that the HOMO is mainly located at the organic π-ligand system, and with the dominant influence of the π-ligand system on the photophysical properties. Spin-orbit coupling, leading to efficient triplet state formation, seems to be largely inhibited. The origin of the unusual excited-state behavior of the rhodacyclopentadienes reported in this paper is currently the subject of extensive theoretical and experimental studies in our group.

Conclusion

We have developed a versatile synthetic route to a series of 2,5-bis(*p*-R-arylethynyl)rhodacyclopentadienes by reductive coupling of two equivalents of 1,4-bis(*p*-R-aryl)-1,3-butadiyne with Rh^I precursors. The reactions occur quantitatively and regiospecifically, forming the 2,5-isomer only. The methyl-substituted rhodacyclopentadienes **2e**, **4e**, **5e**, **7e**, and **8e** were converted into their respective chloro analogues by treatment with HCl etherate. The compounds are generally stable to air and moisture in the solid state, and the acceptor-substituted rhodacyclopentadienes are exceedingly robust, being stable even in aerated solution. Our photophysical investigations show the highly unusual excited-state behavior of our rhodacyclopentadienes with fluorescence originating from the S_1 state in low to moderate quantum yields of $\Phi_f = 0.01–0.22$, but no observable phosphorescence, which normally would have been expected for octahedral late organo-transition metal complexes. Nevertheless, singlet oxygen sensitization experiments indicate relatively slow formation of a T_1 state with quantum yields of $\Phi_\Delta = 0.38–0.65$. The reason for the largely inhibited spin-orbit coupling of the rhodium atom, which should lead to efficient intersystem crossing to the triplet states, remains unclear. The organic π-chromophore ligand apparently neglects the presence of the heavy rhodium atom to a large extent, so that the emitting state can be assigned as a nearly unperturbed ^{1}IL(π–π^*) state. We are currently undertaking detailed theoretical studies to clarify the details of the photophysical processes in the rhodacyclopentadienes, as they raise questions with respect to the traditional picture of optical excited-state behavior of organo-transition-metal complexes, according to which the decay occurs by steps well separated in time and energy. Thus, intersystem crossing is expected to be orders of magnitude faster (10^{-14}–10^{-10} s) than the radiative decay $S_1 \rightarrow S_0$, in contrast to what we observe in our rhodium compounds, which show fluorescence and ISC on the timescale of nanoseconds (10^{-8} s). Our preliminary studies show that this new class of luminescent materials and related organometallic systems deserve further attention. They have been largely neglected with respect to their photophysical properties due to the fact that synthetic access was limited until now, and because of the concentration on bpy- and ppy-based metallacyclopentadienes.

Experimental Section

General considerations

Unless otherwise stated, all manipulations were performed using standard Schlenk or glovebox (Innovative Technology Inc.) techniques under an atmosphere of dry nitrogen (BOC). Reagent grade solvents (Fisher Scientific and J.T. Baker) were nitrogen-saturated and were dried and deoxygenated using an Innovative Technology Inc. Pure-Solv 400 Solvent Purification System, and further deoxygenated by using the freeze-pump-thaw method. C_6D_6 and $CDCl_3$ were purchased from Cambridge Isotope Laboratories and were dried over sodium/benzophenone or CaH_2, respectively, deoxygenated using the freeze-pump-thaw method and vacuum transferred into sealed vessels. The precursor 1,4-bis(*p*-R-phenylethynyl)-1,3-butadiynes[36] and $[RhMe(PMe_3)_4]$[37] were prepared according to literature procedures. All other reagents were purchased from Alfa-

Aesar, Acros, Aldrich or Lancaster, and were checked for purity by GCMS and/or ^{1}H NMR spectroscopy and used as received.

Flash chromatography was carried out in air using silica gel (Silicagel LC60A 40–63 μm) obtained from Fluorochem or basic alumina (aluminum oxide, activated, basic, 58 Å) from Alfa-Aesar. Commercially available, precoated TLC plates (Polygram Sil G/UV254) were purchased from Machery-Nagel. The removal of solvent was performed on a rotary evaporator in vacuo at a maximum temperature of 40 °C.

All NMR spectra were recorded at ambient temperature using 200 MHz Varian Mercury (^{1}H: 200 MHz), 400 MHz Varian Mercury (^{1}H: 400 MHz, ^{13}C{^{1}H}: 100 MHz, ^{19}F: 376 MHz, ^{31}P{^{1}H}: 162 MHz), 400 MHz Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C{^{1}H}: 100 MHz), Varian Inova 500 (^{1}H: 500 MHz, ^{31}P{^{1}H}: 202 MHz) or 700 MHz Varian VNMRS-700 spectrometers (^{1}H: 700 MHz, ^{31}P{^{1}H}: 284 MHz). ^{1}H NMR chemical shifts are reported relative to TMS and were referenced through residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: $\delta = 7.24$, C_6D_6: 7.16 ppm) whereas ^{13}C NMR spectra are reported relative to TMS using the carbon signals of the deuterated solvent ($CDCl_3$: $\delta = 77.23$, C_6D_6: 128.39 ppm). ^{19}F NMR chemical shifts are reported relative to external $CFCl_3$ and ^{31}P NMR spectra were referenced to 85% H_3PO_4. Elemental analyses were obtained using an Exeter Analytical Inc. CE-440 elemental analyzer. Unit mass spectrometric determinations were obtained either by EI using a Finnigan MAT 95 XP spectrometer at the EPSRC National Mass Spectrometry Service Centre in Swansea, by ES using a Thermo-Finnigan LTQ FT spectrometer operating in positive ion mode or by using a MALDI-TOF Applied Biosystems Voyager-DE STR mass spectrometer.

Cyclic voltammograms were recorded ($v = 100\ \mathrm{mV\,s^{-1}}$) from 0.1 M n-Bu_4PF_6/MeCN solutions about 1×10^{-4} M in analyte by using a three-electrode cell equipped with a glassy carbon working electrode, a Pt-wire counter electrode, and a Pt-wire pseudo reference electrode. All redox potentials are reported with reference to an internal standard of the decamethylferrocene/decamethylferrocenium couple ($[FeCp^*_2]/[FeCp^*_2]^+ = 0.00$ V).

UV–visible absorption and emission spectra, lifetime and quantum yield measurements were all recorded in degassed toluene. UV–visible absorption spectra and extinction coefficients were obtained on a Hewlett–Packard 8453 diode array spectrophotometer using standard 1 cm path length quartz cells. Fluorescence spectra and quantum yield measurements of dilute solutions with absorbance maxima of less than 0.2 were recorded on a Horiba Jobin–Yvon Fluoromax-3 spectrophotometer using conventional 90° geometry. The emission spectra were fully corrected using the manufacturer's correction curves for the spectral response of the emission optical components. The quantum yield of each compound was measured either by comparison with standards of known quantum yield, or by use of an integrating sphere with a HORIBA Jobin–Yvon Fluorolog 3–22 Tau-3, following a method described in the literature.[38] The absorbance of the samples was kept below 0.12 to avoid inner filter effects and all measurements were carried out at room temperature. The fluorescence quantum yields of compounds **2a**–**4a** and **2b**–**4b** were measured using 9,10-bis(phenylethynyl)anthracene (BPEA) in $CHCl_3$ ($\Phi_f = 0.95$)[16c] and fluorescein in 0.1 M NaOH ($\Phi_f = 0.79$),[39] whereas those of **5a**, **7a**–**9a**, and **11** were measured using acridine orange in EtOH ($\Phi_f = 0.46$)[40] and fluorescein in 0.1 M NaOH ($\Phi_f = 0.79$),[39] that of **10a** was measured using cresyl violet in methanol ($\Phi_f = 0.54$)[41] and rhodamine 101 in ethanol ($\Phi_f = 1.00$)[42] and that of compounds **15**–**17** were measured using quinine sulphate in 0.1 M H_2SO_4 ($\Phi_f = 0.54$)[43] and anthracene in EtOH ($\Phi_f = 0.27$)[43b] as reference compounds. Quantum yields were corrected for refractive index differences of the solvents.

The quantum yields of singlet-oxygen formation were determined relative to perinaphthanone in toluene ($\Phi_\Delta = 1.0$) using a method described by Nonell.[44] The samples and the reference compounds were analyzed in the same solvent because of strong dependence of the radiative and non-radiative rate constants for deactivation of the triplet states on the solvent. The singlet-oxygen emission was detected at 1269 nm from solutions in a 1 cm path length quartz cuvette after being excited at 355 nm by a frequency-tripled Q-switched Nd:YAG laser (Spectra Physics, Quanta Ray GCR-150–10) with a 10 Hz repetition rate. The emission was collected at 90° to the excitation beam by a liquid nitrogen cooled germanium photodiode (North Coast E0–817P) after passing through an interference filter centered at 1270 nm. The photodiode output was amplified and AC coupled to a digital oscilloscope, which digitized and averaged the transients. The averaged data were then analyzed using the Microsoft Excel package.

The fluorescence lifetimes were measured by using time correlated single-photon counting (TCSPC), using either a 396 nm pulsed laser diode or the 3rd harmonic of a cavity-dumped, mode-locked Ti-sapphire laser (Coherent MIRA) at 300 nm. The fluorescence emission was collected at right angles to the excitation source with the emission wavelength selected by using a monochromator and detected by a single-photon avalanche diode (SPAD). The instrument response function (IRF) was measured using a dilute LUDOX suspension as the scattering sample, setting the monochromator at the emission wavelength of the laser, giving an IRF of 200 or 100 ps at 396 or 300 nm, respectively. The resulting intensity decay is a convolution of the fluorescence decay with the IRF and iterative reconvolution of the IRF with a decay function and non-linear least-squares analysis was used to analyze the convoluted data.

Raman spectra were recorded on solid samples using a LabRamHR Raman microscope with a He:Ne laser (633 nm). IR spectra were recorded as KBr discs using either a PerkinElmer 1600 series or Spectrum 100 series FT-IR spectrometer.

X-ray diffraction experiments were carried out on Bruker 3-circle diffractometers with CCD area detectors SMART 1000 (for **2a**, **3e**, **5f**, **8e**), ProteumM APEX (for **7a**) or SMART 6000, using Mo_K ($\bar{\lambda} = 0.71073$ Å) radiation from a sealed X-ray tube with graphite monochromator or (for **7a**) a 60 W microfocus Bede Microsource with glass polycapillary optics. The crystals were maintained at $T = 120$ K using Cryostream open-flow N_2 gas cryostats. All structures were solved by direct methods and refined by full-matrix least-squares against F^2 of all data, using SHELXTL[45] and OLEX2[46] software.

General procedure for the synthesis of rhodacyclopentadienes with alkynyl ligands (2a–d–10a–d and 11–13)

The respective terminal alkyne HCCR (0.047 mmol) was dissolved in THF (1 mL) and added drop-wise to a stirred solution of $[RhMe(PMe_3)_4]$ (20 mg, 0.047 mmol) in THF (1 mL) at room temperature. Then, 1,4-bis(p-R′-arylethynyl)-1,3-butadiyne (0.094 mmol) in THF (1 mL) was added and the solution was stirred for an additional minute before the volatiles were removed in vacuo. The residue was re-dissolved in THF (2 mL) and the solution was stirred for 5 min. Again, the volatiles were removed in vacuo. This process was repeated once more. In the case of donor-substituted 1,4-bis(p-R′-arylethynyl)-1,3-butadiynes, the residue had to be dissolved in toluene (5 mL) and heated at 80 °C, overnight, to achieve full conversion. The product was recrystallized from THF and hexane to give an orange/red solid.

***mer,cis*-[Tris(trimethylphosphine)trimethylsilylethynyl-2,5-bis-(phenylethynyl)-3,4-bis(phenyl)rhodacyclopenta-2,4-diene] (2a)**: Orange solid; yield 33 mg (85%); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.72$ (d, ^3J(H,H) = 8 Hz, 2H; CH_{arom}), 7.40 (d, ^3J(H,H) = 7 Hz, 2H; CH_{arom}), 7.31 (d, ^3J(H,H) = 8 Hz, 2H; CH_{arom}), 7.23 (d, ^3J(H,H) = 8 Hz, 2H; CH_{arom}), 7.06 (m, 12H; CH_{arom}), 1.38 (d, ^2J(H,P) = 8 Hz, 9H; PMe_3), 1.35 (vt, $J = 3$ Hz, 18H; PMe_3), 0.37 ppm (s, 9H; $SiMe_3$); ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): $\delta = -9.32$ (dd, ^1J(P,Rh) = 98 Hz, ^2J(P,P) = 31 Hz, 2P; PMe_3), −23.10 ppm (dt, ^1J(P,Rh) = 82 Hz, ^2J(P,P) = 31 Hz, 1P; PMe_3); IR (KBr): $\tilde{\nu} = 2024$, 2126, 2156 cm^{-1} (all C≡C); Raman (solid): $\tilde{\nu} =$ 1418, 1444, 1594 (all aryl), 2141 cm^{-1} (C≡C); elemental analysis calcd (%) for $C_{46}H_{56}RhP_3Si$: C 66.34, H 6.78, N 0.00; found: C 66.36, H 6.94, N 0.00.

General procedure for the synthesis of rhodacyclopentadienes with a methyl ligand (2e–8e)

[$RhMe(PMe_3)_4$] (50 mg, 0.118 mmol) and the respective 1,4-bis(*p*-R′-phenyl)-1,3-butadiyne (0.237 mmol) were added to THF (5 mL) and the resulting solution was stirred for 5 min. The volatiles were removed in vacuo and then THF (2 mL) was added and the reaction mixture was stirred for an additional 5 min before the volatiles were again removed in vacuo. After further addition of THF (2 mL), the solution was heated to 80 °C for 3 h. The solvent was removed in vacuo to give the crude products as brown solids, which were recrystallized from THF/hexane.

***mer,cis*-[Tris(trimethylphosphine)methyl-2,5-bis(phenylethynyl)-3,4-bis(phenyl)rhodacyclopenta-2,4-diene] (2e)**: Pale-brown solid; yield 71 mg (81%); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 7.61$ (d, ^3J(H,H) = 8 Hz, 2H; CH_{arom}), 7.48 (d, ^3J(H,H) = 8 Hz, 2H; CH_{arom}), 7.41 (d, ^3J(H,H) = 8 Hz, 2H; CH_{arom}), 7.31 (d, ^3J(H,H) = 8 Hz, 2H; CH_{arom}), 7.21 (m, 4H; CH_{arom}), 7.08 (t, ^3J(H,H) = 8 Hz, 2H; CH_{arom}), 7.03 (t, ^3J(H,H) = 8 Hz, 4H; CH_{arom}), 6.93 (m, 2H; CH_{arom}), 1.32 (d, ^2J(H,P) = 7 Hz, 9H; PMe_3), 1.16 (vt, $J = 4$ Hz, 18H; PMe_3), 0.09 ppm (quint, $J = 7$ Hz, 3H; RhMe); ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): $\delta = -6.35$ (dd, ^1J(P,Rh) = 105 Hz, ^2J(P,P) = 34 Hz, 2P; PMe_3), −18.47 ppm (dt, ^1J(P,Rh) = 89 Hz, ^2J(P,P) = 34 Hz, 1P; PMe_3); IR (KBr): $\tilde{\nu} = 2125$ cm^{-1} (C≡C); elemental analysis calcd (%) for $C_{42}H_{50}RhP_3$: C 67.20, H 6.71, N 0.00; found: C 67.58, H 6.95, N 0.00.

General procedure for the synthesis of rhodacyclopentadienes with a chloro ligand (2f, 4f, 5f, 7f, 8f)

The respective rhodacyclopentadiene with a methyl ligand at the rhodium (compounds **2e**, **4e**, **5e**, **7e**, **8f**; 0.125 mmol) was dissolved in THF (4 mL) and a solution of HCl etherate (1 M, 0.13 mL, 0.13 mmol) was added drop-wise while stirring at room temperature. After a further 5 min of stirring, the volatiles were removed in vacuo. The crude products were recrystallized either from CH_2Cl_2/hexane or from CH_2Cl_2/toluene.

***mer,cis*-[Tris(trimethylphosphine)chloro-2,5-bis(phenylethynyl)-3,4-bis(phenyl)rhodacyclopenta-2,4-diene] (2f)**: Dark-red solid, yield: 86 mg (89%); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.43$ (d, ^3J(H,H) = 8 Hz, 2H; CH_{arom}), 7.05–7.22 (m, 18H; CH_{arom}), 1.73 (d, ^2J(H,P) = 7 Hz, 9H; PMe_3), 1.52 ppm (vt, $J = 3$ Hz, 18H; PMe_3); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): $\delta = -8.95$ (dd, ^1J(P,Rh) = 102 Hz, ^2J(P,P) = 32 Hz, 2P; PMe_3), −23.38 ppm (dt, ^1J(P,Rh) = 86 Hz, ^2J(P,P) = 32 Hz, 1P; PMe_3); elemental analysis calcd (%) for $C_{41}H_{47}RhClP_3$: C 63.86, H 6.14, N 0.00; found: C 64.03, H 6.39, N 0.00.

Synthesis of cyclotrimers (15–17)

1,2,4-Tris(phenylethynyl)-3,5,6-triphenylbenzene (15): Compound **2a** (20 mg, 0.027 mmol) was dissolved in toluene (2 mL) and added to a solution of 1,4-diphenylbuta-1,3-diyne (114 mg, 0.559 mmol) in toluene (2 mL). The reaction mixture was heated at reflux under N_2 for 3 weeks. The volatiles were removed in vacuo. The residual solid was applied to the top of a silica gel column, which was first eluted with hexanes to remove unreacted diyne starting material and then with 50:50 CH_2Cl_2/hexane as eluent. The solvent was removed in vacuo and the product was obtained as a light brown solid which was further purified by sublimation under high vacuum. Slow evaporation of a CH_2Cl_2/hexane solution of **15** gave white crystals that were suitable for X-ray diffraction analysis. Yield 37 mg (33%); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.72$ (m, 4H; CH_{arom}), 7.54 (m, 8H; CH_{arom}), 7.20 (m, 14H; CH_{arom}), 6.74 ppm (m, 4H; CH_{arom}); IR (KBr): $\tilde{\nu} = 1442$, 1491, 1596 (all aryl), 2210 cm^{-1} (C≡C); MALDI: *m/z*: 606 [M^+]; elemental analysis calcd (%) for $C_{48}H_{30}$: C 95.02, H, 4.98, N 0.00; found: C 94.12, H 4.85, N 0.00

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Keywords: fluorescence · metallacycles · rhodium · spin-orbit coupling · transition metals

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