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Photophysics

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

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

Mononuclear metal complexes usually show very rapid conversion from singlet into triplet excited states, which is attributed to the "heavy-atom effect". The heavy-atom effect is the promotion of intersystem crossing (ISC) processes by the spin-orbit coupling (SOC) of the metal atom. These effects can begin to be observed with elements as light as sulphur ($z = 16$).[4] For example, the formation of the ^{3}MLCT (MLCT = metal-to-ligand charge transfer) excited state of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) occurs on a timescale of less than 20 fs.[5] The precise factors governing the singlet-to-triplet excited state interconversion have recently been questioned by observations which have shown that formation of the ^{3}MLCT state of the first-row complex $[Fe(bpy)_3]^{2+}$ occurs in less than 20 fs, whereas the second-row complexes $[Re(X)(CO)_3(bpy)]^+$ (X = Cl, Br, I) show a much slower interconversion (ca. 100 fs).[6] Furthermore, the order was found to be Cl (85 fs) < Br (128 fs) < I (152 fs), which is contrary to that predicted by the simplistic consideration of the effect of the heavy atom. Tetrahedral $[Pt(binap)_2]$ (binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) and $[Cu\{bis(diimine)\}]^+$ complexes have been shown to have unusually long-lived ^{1}MLCT states of $\tau = 3$ ps and $\tau = 15$ ps, respectively, attributed to a distortion towards a square-planar geometry which reduces the mixing of the ^{1,3}MLCT states.[7]

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

The reaction of $[Rh(C{\equiv}CSiMe_3)(PMe_3)_3]$ (**1**) with the bis(diyne)s **2a–d** leads to the formation of the metallacyclic complexes **3a–d** (Scheme 1, top), which have been unambiguously characterized by ^{1}H and ^{31}P NMR and IR spectroscopy, mass spectrometry, elemental analysis, and by single-crystal X-ray diffraction studies on **3a–c** (Figure 1). In situ NMR spectroscopic studies show that the reactions occur quantitatively, and the products have been isolated in 23–82% yield after several recrystallizations, to ensure high purity for photophysical studies. The photophysical data are summarized in Table 1 and Table 2.

Compounds **3a–d** absorb light with extinction coefficients of 15000–44000 $L\,mol^{-1}\,cm^{-1}$ and emit in the visible region (Figure 2). A vibrational progression typical of aromatic stretching modes (ca. 1360 cm^{-1}) is observable in the absorp-

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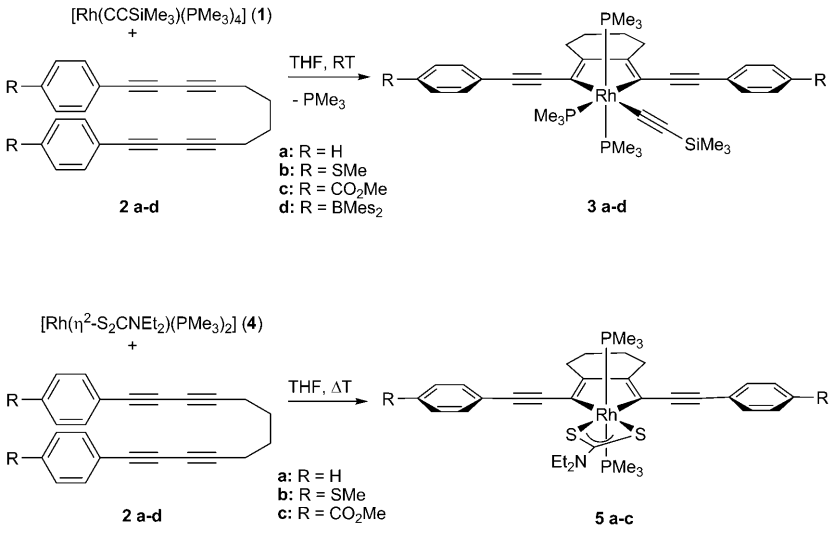

Scheme 1. Synthesis of 2,5-bis(arylethynyl)rhodacyclopentadienes.

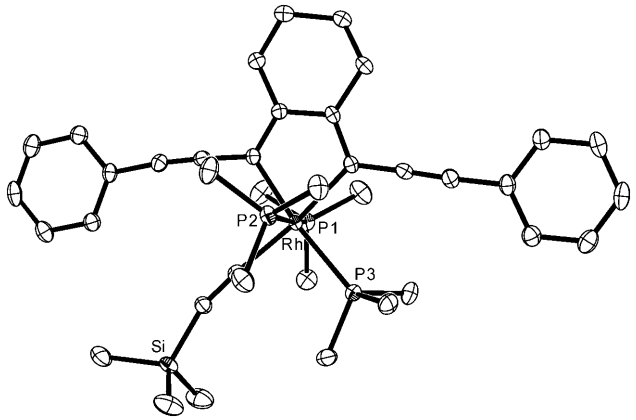

Figure 1. Molecular structure of **3a**. Hydrogen atoms omitted for clarity, thermal ellipsoids drawn at 50% probability.[17]

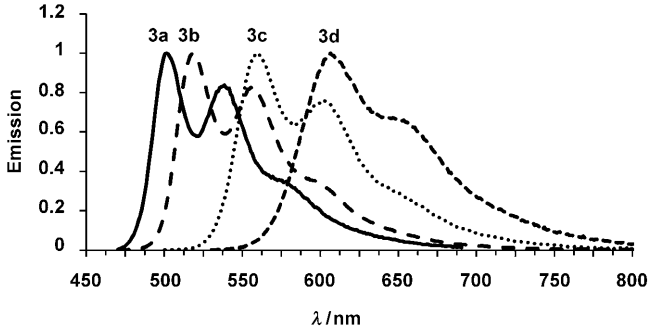

Figure 2. Photoluminescence spectra of 2,5-bis(*p*-*R*-arylethynyl)rhodacyclopentadienes [R = H (**3a**), SMe (**3b**), CO_2Me (**3c**), $BMes_2$ (**3d**)] recorded in degassed toluene at 298 K upon excitation at the respective λ_{max} values.

tion and emission spectra. Both donor and acceptor substituents at the *para* position of the phenyl rings of the ligand lead to a bathochromic shift, the influence of the acceptor substituents exceeding that of the donors. The effect of donors and acceptors can be rationalized by the fact that acceptors have a greater influence on the lowest unoccupied molecular orbital (LUMO) than on the highest unoccupied molecular orbital (HOMO), and donors show an opposite effect, therefore both decrease the HOMO–LUMO gap as previously reported for related 2,5-bis(arylethynyl)thiophenes.[11] A solvatochromic effect has been found for **3c** and **3d**. Comparison of the emission data from *n*-hexane to MeCN for **3d** shows an 85 nm shift of the emission maximum and a 1600 cm^{-1} increase in the Stokes shift (Table 1), indicating charge-transfer character in the emissive excited state.

The results from luminescence measurements suggest that the emission occurs from the excited singlet state S_1, since small

Table 1: Emission and absorption properties of **3a–d** and **5a–c**.

	Solvent	λ_{max} (abs) [nm]	ε [$mol^{-1}\,cm^{-1}\,dm^3$]	λ_{max} (em) [nm]	Stokes shift [cm^{-1}]
3a	toluene	456	22000	501	2000
3b	toluene	467	41000	518	2100
3c	*n*-hexane	487		538	1900
3c	toluene	497	44000	560	2300
3c	THF	497	39000	580	2900
3c	MeCN	497	43000	588	3100
3d	*n*-hexane	518		581	2100
3d	toluene	529		606	2400
3d	THF	534		631	2900
3d	MeCN	535		666	3700
5a	toluene	476	24000	526	2000
5b	toluene	487	21000	541	2000
5c	*n*-hexane	508		566	2000
5c	toluene	518	15000	586	2200
5c	THF	519		599	2600
5c	MeCN	518		611	2900

Stokes shifts (ca. 2000 cm^{-1}, Figure 3) are observed, which is unexpected for coordination and organometallic compounds. The rhodacyclopentadienes **3a–d** exhibit anomalously long fluorescence lifetimes and unprecedented high fluorescence quantum yields ($\tau_f = 1.2$–3.0 ns, $\Phi_f = 0.33$–0.69), leading us to conclude that the rates of radiative decay and ISC are on the order of $10^8\,s^{-1}$. Neither the photoluminescence quantum yield nor the emission lifetimes are influenced by the presence of molecular oxygen.

The compounds act as potent sensitizers of singlet oxygen (Table 2), and the $^1O_2$ phosphorescence observed at $\lambda = 1270$ nm showed a decay time characteristic of the solvent in which the measurement was conducted. Partial degassing of the solution led to a reduction in signal intensity, but the temporal profile remained unchanged. Resaturation with O_2 regenerated the original signal decay profile and intensity. These observations imply that the lifetime of the sensitizing state, which we assign as the T_1 state, is on the order of the risetime of the detection system, that is, $\tau \leq 400$ ns. However,

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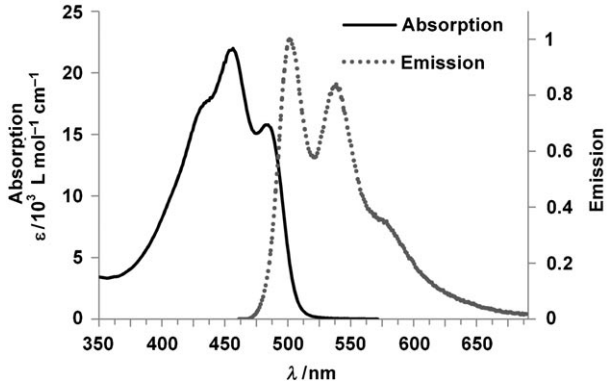

Figure 3. Absorption and photoluminescence spectra of **3a** recorded in degassed toluene at 298 K.

Table 2: Photophysical data for **3a–d** and **5a–c** in degassed toluene at 298 K.

	Φ_{PL}	τ_f [ns]	τ_0 [ns]	Φ_Δ[a]	k_f [10^8 s^{-1}]	k_Δ [10^8 s^{-1}]
3a	0.33	1.2 (1.9[b])	3.6	0.65	2.75	5.42
3b	0.34	1.8	5.3	0.40	1.89	2.22
3c	0.69	3.0	4.3	0.26	2.30	0.87
3d	0.69	2.6	3.8			
5a	0.07	1.0 (13%)		0.32	0.09	
		0.4 (87%)			1.52	
5b	0.16	1.1 (72%)		0.19	1.05	
		0.7 (28%)			0.64	
5c	0.46	2.5	5.4	0.20	1.84	0.80

[a] Quantum yield for O_2 ($^1\Delta_g$) formation in O_2 saturated solutions. [b] Measured in degassed dichloromethane.

no phosphorescence (between 400–1000 nm) could be observed at room temperature or in an *iso*-pentane/Et_2O/EtOH glass at 77 K.

To examine the effect of modulating the metal participation in the frontier orbitals, we changed the $^-C{\equiv}CSiMe_3$ ligand to *N*,*N*-diethyldithiocarbamate, as a strong σ and π donor should destabilize the filled d orbitals of Rh. The quantitative reactions occurred as shown in Scheme 1 (bottom), representing an organometallic analogue of the atom-economical click chemistry, which is well-established in the organic synthesis of heterocyclic rings.[12] The dithiocarbamate rhodacyclopentadienes have been fully characterized and a single crystal X-ray diffraction study was carried out for **5a**. In general, compounds **5a–c** show a similar behavior to those of **3a–d** upon optical excitation (Table 2).

However, the emission is significantly red-shifted, but a decrease in the fluorescence and $^1O_2$ formation quantum yields is observed, indicating that changing the ligand sphere alters the photophysical properties of the compounds, therefore the rhodium center must be involved in the transitions. Despite the presence of the rhodium atom, no phosphorescence is observed for **5a–c**, even at 77 K.

It is informative to compare the rhodacyclopentadienes **3a–d** and **5a–c** with their "thiacyclopentadiene" analogues, that is, 2,5-bis(arylethynyl)-substituted thiophenes ($\Phi_f = 0.2$–0.3, $\tau_f = 0.2$–0.3 ns).[12] Counterintuitively, despite the much higher spin-orbit coupling constant of rhodium (1200 cm^{-1}) than sulphur (380 cm^{-1}), the rhodacycles exhibit higher fluorescence quantum yields and longer fluorescence lifetimes than the thiophenes. The emission solvatochromism for **3c**, **d** and **5c** (Table 1) indicates significant charge transfer in the excited state, which we propose is a mixed ^{1}ML/ILCT state (ILCT = intraligand charge transfer).

To probe the kinetics of the photophysical processes in our compounds additionally, we measured time-resolved infrared (TRIR) vibrational absorption spectra of **3a** in CH_2Cl_2 (Figure 4). The TRIR spectrum, obtained 11 ps after excitation, clearly shows that the parent band ($\nu_{C\equiv C}$ = 2128 cm^{-1}) is bleached and a new absorption is produced at 2008 cm^{-1}.

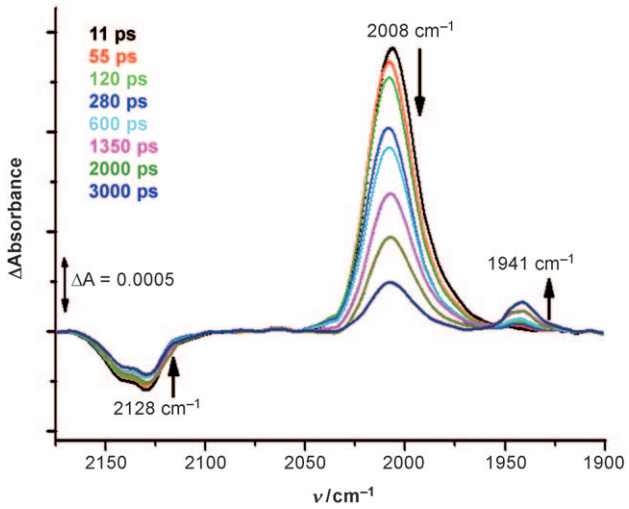

Figure 4. Selected picosecond TRIR spectra of **3a** in CH_2Cl_2 under argon at various time intervals after laser excitation at 400 nm.

This band is assigned to the S_1 excited state which decays at the same rate [$\tau = 1.6 \pm 0.6$ ns] as a new species is formed with an IR band at 1941 cm^{-1}. The parent is also partially reformed (ca. 35%) at a similar rate as the singlet band decays. The partial recovery from the TRIR kinetics is consistent with the 65% ISC $S_1 \rightarrow T_1$ of the $^1O_2$ sensitization experiment. The lifetime of the S_1 state obtained from the TRIR measurements (Figure 5) is consistent with the results from the luminescence measurements of **3a** (Table 2). The state associated with the band at 1941 cm^{-1} decays to the ground state with $\tau = 55$ ns in degassed solution and we attribute this to be the T_1 state. Of particular interest is the exceptionally slow ISC rate of approximately $k_{ISC} = 5 \times 10^8$ s^{-1}.

The unexpected long-lived ^{1}ML/ILCT state, the absence of phosphorescence, and the unusually slow ISC of our 2,5-bis(arylethynyl)rhodacyclopentadienes **3a–d** and **5a–c** having rate constants in the range of 10^7–10^8 s^{-1} are difficult to explain given the fact that they contain a second row transition-metal atom covalently bound to the organic chromophore. Most organometallic Rh^{III} complexes exhibit no fluorescence, but phosphoresce in a glass at 77 K from predominantly ligand-centered $^3\pi \rightarrow \pi^*$ states with only small ^{3}MLCT contributions; the lifetimes are generally between $\tau =$

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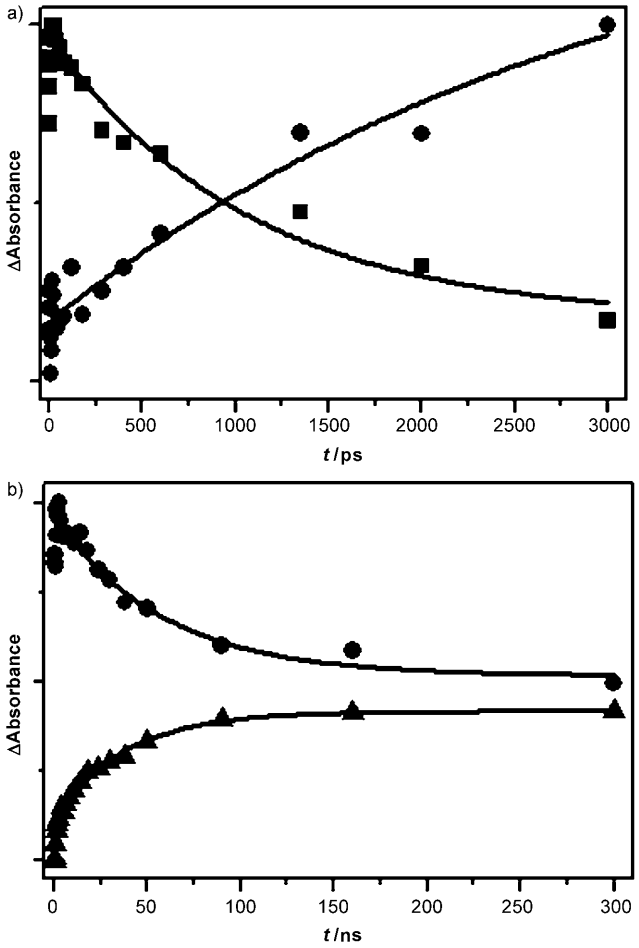

Figure 5. Kinetic traces showing: (a) the decay of the singlet excited state at 2008 cm^{-1} (■) and the growth of the triplet excited state at 1941 cm^{-1} (●); (b) the decay of triplet excited state at 1941 cm^{-1} (●) and the recovery of the parent bleach at 2128 cm^{-1} (▲). Note that the data have been normalized.

0.04–48 ms.[13] Photoluminescence with microseccond lifetimes from metal-centered ligand field states (^{3}LF) has been reported in $[Rh(NH_3)_5L]^{3+}$ (L = NH_3, py, MeCN, H_2O) and $[Rh(trpy)_2]^{3+}$ (trpy = terpyridine).[14] Fluorescence is rarely observed in organometallic and coordination compounds with 4d/5d transition-metal centers, as the ^{1}MLCT states are too short-lived due to strong SOC of the d electrons of the metal facilitating ISC to ^{3}MLCT states. However, it has been reported that d^8–d^8 dinuclear complexes of the type $[M_2L_4]^{2+}$ (M = Rh, Ir; L = 1,3-diisocyanopropane, 2,5-dimethyl-2,5-diisocyanohexane) undergo excitation to a $^1A_{2u}$ ($d\sigma^*$–$p\sigma$) state.[15] The $^{1,3}A_{2u}$ states are only weakly coupled and emission with nanosecond lifetimes even at room temperature is observed with $\Phi_f = 0.08$, as well as the expected phosphorescence ($\Phi_p = 0.3$, $\Phi_{ISC} > 0.8$). As mentioned above, a short-lived ^{1}MLCT state (several femtoseconds) accounts for the prompt fluorescence observed in octahedral $[M(bpy)_3]^{2+}$ (M = Fe, Ru) and $[Re(X)(CO)_3(bpy)]^+$ (X = Cl, Br, I) complexes with extremely low quantum yields ($< 10^{-6}$).[5,6] Prompt fluorescence has also been reported from longer-lived ^{1}MLCT states (several picoseconds) of tetrahedral Pt^0 and Cu^I compounds with quantum yields between 10^{-5}-10^{-4},[3] as well as from Pt^{II}/terpyridine complexes ($\tau = 1$ ns, $\Phi_f = 0.001$).[7,16]

An ^{1}ML/ILCT excited-state structural distortion such as that found to result in weak SOC in the tetrahedral complexes $[Pt(binap)_2]$ and $[Cu(diimine)_2]^+$,[7] vide supra, is unlikely to be responsible for the observed properties of octahedral complexes **3a–d** and **5a–c**. Also, the emission spectrum at 77 K and the TRIR data prove that no delayed fluorescence occurs from our rhodacycles.

We have reported for the first time intense fluorescence from an octahedral organometallic compound, originating from a long-lived S_1 state. Deactivation of this state by intersystem crossing is relatively inefficient. The rhodacyclopentadienes exhibit unexpected slow ISC rates on the nanosecond timescale ($k_{ISC} = 10^7$–10^8 s^{-1}) despite a M–C bound ligand and a SOC of Rh (1200 cm^{-1}) similar to that of Ru (1259 cm^{-1}) in $[Ru(bpy)_3]^{2+}$, for which ultrafast ISC of less than 20 fs has been measured. These results raise questions and contradict the traditional picture of the "cascade" behavior of optical excited states of organotransition-metal compounds, decaying by steps well-separated in time and energy, and according to which ISC should be orders of magnitude faster than the radiative decay $S_1 \rightarrow S_0$.

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[17] CCDC 749476 to 749480 contains the supplementary crystallographic data for **2c**, **3a**, **3b**, **3c**, and **5a**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif..

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