Organometallics **2010,** *29,* 2390–2393
DOI: 10.1021/om1003094

ORGANOMETALLICS
Communication

Photofunctionalization of a Pentamethylcyclopentadienyl Ligand with the *N*-Phenylcarbazolyl Group To Prepare a Highly Luminescent Tb^{3+} Complex Having a Fast Radiation Rate

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Received April 16, 2010

Summary: Lanthanide(III) bent-metallocene complexes with a novel photofunctionalized pentamethylcyclopentadienyl ligand having an N-phenylcarbazolyl group ($Cp^{PhCar} = \eta^5\text{-}C_5Me_4CH_2\text{-}C_{18}H_{12}N$), $[Ln(Cp^{PhCar})_2I(THF)]$ (*Ln* = *Tb* (***1***), *Gd* (***2***)), *were prepared and their molecular structures and luminescence properties were investigated. The f*–*f emission from the terbium metal center of **1** was efficiently sensitized by* Cp^{PhCar} ($\varepsilon = 0.88 \times 10^4\ M^{-1}\ cm^{-1}$ *at 331 nm,* $\Phi = 0.67$ *at 330 nm excitation,* $k_r = 1.68 \times 10^3\ s^{-1}$). *Additionally, the solid-state structure of potassium salts of* C_5*-ring* ($\eta^5\text{-}C_5R_5$, *R* = *Me, H*) *derivatives was uncommonly characterized in* Cp^{PhCar}.

Ligand functionalization is a common approach to form metal complexes that have a desired structure and functionality. To date, various photofunctionalized ligands have been developed and successfully utilized as photosensitizers for transition-metal and lanthanide complexes.[1] Among them, macrocyclic polyamines such as cyclam (1,4,8,11-tetraazacyclotetradecane) and tacn (1,4,7-triazacyclononane), which are popular ligands in inorganic chemistry, are widely employed as useful frameworks to construct adaptable and efficient photofunctionalized ligands.[2,3] Although the anionic pentamethylcyclopentadienyl ligand ($Cp^* = \eta^5\text{-}C_5Me_5$) is one of the most common and important ligands in organometallic chemistry,[4] photofunctionalized Cp* derivatives have been hitherto unknown because of troublesome synthesis and isolation of the ligand.[5] We believe that photofunctionalized Cp* ligands could open a new field of organometallic chemistry, including developments of novel photocatalysts and luminous materials. We have now found that a new class of photofunctionalized ligands, the *N*-phenylcarbazolyl-functionalized Cp* ligand ($Cp^{PhCar} = \eta^5\text{-}C_5Me_4CH_2C_{18}H_{12}N$), serves as an efficient photosensitizer for the terbium(III) ion. Thus, a highly luminescent organolanthanide complex having a fast radiation rate was successfully prepared by proper combination of the metal ion and the photofunctionalized Cp* ligand (vide infra). Herein we report the synthesis, structure, and photophysical properties of a terbium(III) complex with Cp^{PhCar}, $[Tb(Cp^{PhCar})_2I(THF)]$ (**1**). The gadolinium(III) complex $[Gd(Cp^{PhCar})_2I(THF)]$ (**2**) was also synthesized to gain insight into the photosensitization of the *N*-phenylcarbazolyl group. Furthermore, the solid-state polymeric structure of the THF-solvated Cp^{PhCar} potassium salt, which is a key precursor for the preparation of **1** and **2**, is presented. Solid-state structural information for the Cp* or Cp ($\eta^5\text{-}C_5H_5$) derivative alkali-metal salts is comparatively limited, even though their salts are widely used for preparing organometallic complexes.[4a,6]

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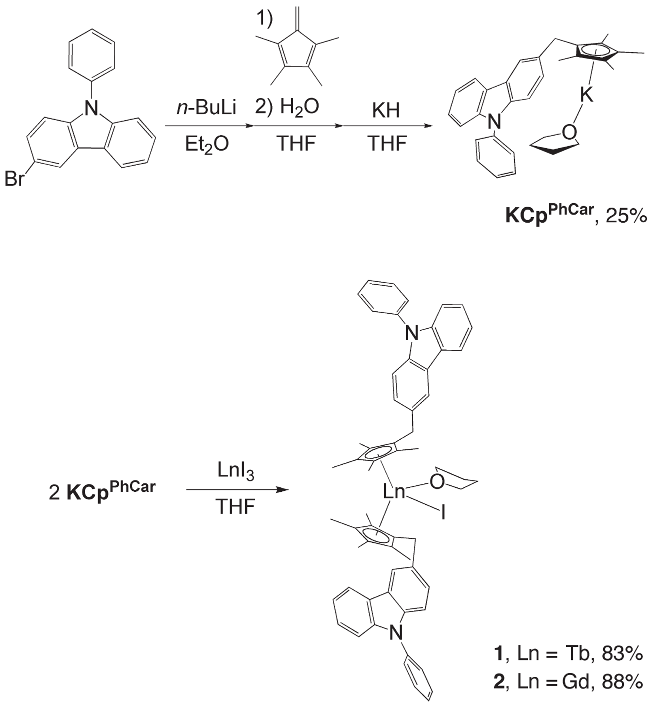
(8) Crystal data for $\mathbf{KCp^{PhCar}}$: $C_{32}H_{34}KNO$, $M = 487.72$, pale yellow block, $T = 123 \pm 1$ K, monoclinic, space group $P2_1/c$, $a = 9.1871(14)$ Å, $b = 28.378(4)$ Å, $c = 10.3886(17)$ Å, $\beta = 100.365(4)°$, $V = 2664.2(7)$ Å^3, $Z = 4$, 27 744 reflections measured, 6041 unique ($R_{int} = 0.055$), R1 = 0.0768 ($I > 2\sigma(I)$), wR2 = 0.2347 (all data), GOF = 1.081. CCDC 772830. Crystal data for $\mathbf{1}\cdot 2Et_2O$: $C_{68}H_{80}IN_2O_3Tb$, $M = 1259.22$, colorless block, $T = 123 \pm 1$ K, triclinic, space group $P\bar{1}$, $a = 8.6876(9)$ Å, $b = 17.4407(14)$ Å, $c = 20.9653(16)$ Å, $\alpha = 66.995(4)°$, $\beta = 88.645(6)°$, $\gamma = 88.545(6)°$, $V = 2922.7(4)$ Å^3, $Z = 2$, 32 800 reflections measured, 13 080 unique ($R_{int} = 0.056$), R1 = 0.0599 ($I > 2\sigma(I)$), wR2 = 0.1551 (all data), GOF = 1.109. CCDC 772828. Crystal data for $\mathbf{2}\cdot 2Et_2O$: $C_{68}H_{80}IN_2O_3Gd$, $M = 1257.55$, colorless block, $T = 123 \pm 1$ K, triclinic, space group $P\bar{1}$, $a = 8.6986(13)$ Å, $b = 17.4586(18)$ Å, $c = 21.033(2)$ Å, $\alpha = 67.005(7)°$, $\beta = 88.451(12)°$, $\gamma = 88.659(12)°$, $V = 2939.0(6)$ Å^3, $Z = 2$, 31 615 reflections measured, 13 050 unique ($R_{int} = 0.076$), R1 = 0.0678 ($I > 2\sigma(I)$), wR2 = 0.1719 (all data), GOF = 1.107. CCDC 772829.

Scheme 1. Preparation of the Potassium Salt $\mathbf{KCp^{PhCar}}$ and Lanthanide(III) Complexes 1 and 2



$\mathbf{KCp^{PhCar}}$, 25%

1, Ln = Tb, 83%
2, Ln = Gd, 88%

The *N*-phenylcarbazolyl-functionalized Cp* ligand $\mathrm{Cp^{PhCar}}$ was synthesized by a method used to synthesize other types of C_5Me_4R ligands, where R = NMe_2, allyl, indenyl, dithianyl,[7] and was isolated as the potassium salt, $[\mathrm{K(Cp^{PhCar})(THF)}]$ ($\mathbf{KCp^{PhCar}}$), in 25% overall yield from 3-bromo-9-phenylcarbazole (Scheme 1). Pale yellow crystals suitable for X-ray diffraction analysis were obtained from a saturated THF solution of $\mathbf{KCp^{PhCar}}$ at room temperature. An X-ray diffraction study shows that the crystal structure of $\mathbf{KCp^{PhCar}}$ consists of polymeric zigzag chains of composition $[\mathrm{K(Cp^{PhCar})(THF)}]_\infty$, in which a weak interaction between the potassium ion and the tethered *N*-phenylcarbazolyl substituent is observed (K···C12(carbazole) distance 3.495(2) Å) (Figure 1).[8] The K−O(THF) distance is 2.663(2) Å. The centroid of the five ring-carbon atoms in the cyclopentadienyl group, $\mathrm{ring^{cen}}$, is 2.746 Å from the potassium ion on one side and 2.760 Å from another potassium ion on the other. The $\mathrm{ring^{cen}}$−K−$\mathrm{ring^{cen}}$ and K−$\mathrm{ring^{cen}}$−K angles are 141.68(4) and 174.01(5)°, respectively. This is a rare example of a crystallographically characterized THF-solvated potassium salt of Cp* or Cp derivatives.[6]

The reaction of two equivalent $\mathbf{KCp^{PhCar}}$ groups with TbI_3 in THF at room temperature led to the formation of the terbium(III) complex **1** in good yield (83%) as a white powder (Scheme 1). The isolated complex is stable indefinitely under a dry nitrogen atmosphere. Crystals of **1** suitable for X-ray diffraction analysis were grown from a saturated Et_2O solution at −22 °C. The solid-state molecular structure of **1** is depicted in Figure 2.[8] The structure is typical of a bent metallocene species that contains two additional ligands. The ligand arrangements around the formally eight-coordinate Tb atom are pseudotetrahedral, with the two C_5 rings of $\mathrm{Cp^{PhCar}}$, an oxygen atom of THF, and an iodide ligand. The $\mathrm{ring^{cen}}$−Tb−$\mathrm{ring^{cen}}$ and iodide−Tb−oxygen angles are 134.03(9) and 88.30(9)°, respectively. These values are in the range of typical bis(pentamethylcyclopentadienyl)lanthanide complexes with two other ligands (133(1)−137.22(11)° for the angle of $\mathrm{ring^{cen}}$−metal−$\mathrm{ring^{cen}}$, 87.17(12)−91.6(5)° for the angle of halide−metal−oxygen).[9]

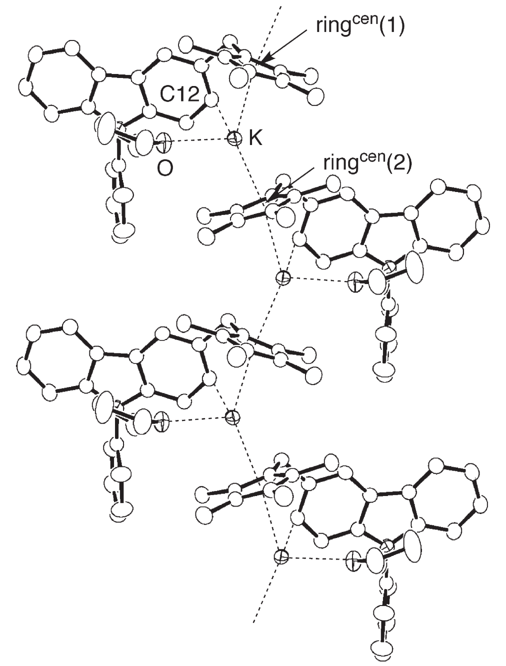


Figure 1. ORTEP drawing of a zigzag $[\mathrm{K(Cp^{PhCar})(THF)}]_\infty$ chain. Hydrogen atoms are omitted for clarity, thermal ellipsoids are at 50% probability. Selected bond distances (Å) and angles (deg): K−$\mathrm{ring^{cen}}$(1) = 2.746, K−$\mathrm{ring^{cen}}$(2) = 2.760, K−O = 2.663(2), K···C12 = 3.495(2); $\mathrm{ring^{cen}}$(1)−K−$\mathrm{ring^{cen}}$(2) = 141.68(4), K−$\mathrm{ring^{cen}}$(1)−K = 174.01(5). "$\mathrm{ring^{cen}}$" indicates the centroid of the five ring-carbon atoms.

Figure 3 (black) displays the UV−vis absorption spectrum of **1** in THF at room temperature. The absorption bands at 296, 331, and 345 nm ($\varepsilon = 4.56 \times 10^4$, 0.88×10^4, and 0.84×10^4 M^{-1} cm^{-1}, respectively) are assigned to the intramolecular $\pi \rightarrow \pi^*$ transition of the *N*-phenylcarbazolyl moieties.[10] Under the excitation of **1** at 330 nm, the luminescence spectrum characteristic of terbium ions was observed (Figure 3, red). The seven bands in the spectrum are assigned to the following transitions: $^5D_4 \rightarrow {}^7F_6$ (497 nm), $^5D_4 \rightarrow {}^7F_5$ (547 nm), $^5D_4 \rightarrow {}^7F_4$ (590 nm), $^5D_4 \rightarrow {}^7F_3$ (620 nm), $^5D_4 \rightarrow {}^7F_2$ (648 nm), $^5D_4 \rightarrow {}^7F_1$ (662 nm), and $^5D_4 \rightarrow {}^7F_0$ (679 nm).[1b,c] The absence of broad luminescence arising from the ligand-centered transitions indicates that the ligand-centered excited state in the $\mathrm{Cp^{PhCar}}$ ligand was almost completely quenched by the terbium ion (Figure S1, Supporting Information). Furthermore, the excitation spectrum monitored at 547 nm ($^5D_4 \rightarrow {}^7F_5$ transition) was almost identical to the absorption spectrum of **1** (Figure S2). These findings univocally indicate that an efficient intramolecular energy transfer occurs from the *N*-phenylcarbazolyl moieties to the terbium ion.

In the luminescent lanthanide complexes, the energy level of the lowest triplet ligand-centered excited state is one of the crucial factors determining the luminescence quantum yields.[1b,c] To estimate the energy level of the lowest triplet state in **1**, the gadolinium(III) complex **2** having the same

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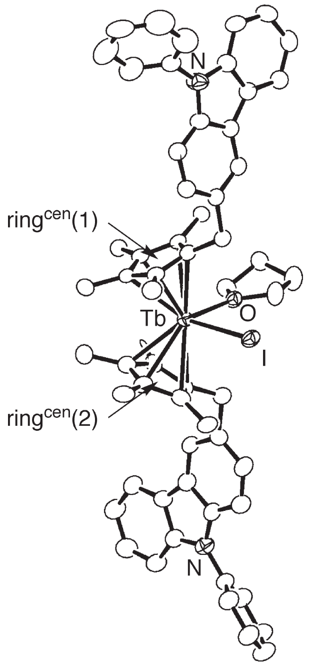

Figure 2. ORTEP drawing of terbium(III) complex **1**. Hydrogen atoms and cocrystallized solvent molecules are omitted for clarity; thermal ellipsoids are at the 50% probability level. Selected bond distances (Å) and angles (deg): Tb−ring^{cen}(1) = 2.391, Tb−ring^{cen}(2) = 2.404, Tb−I = 3.0308(4), Tb−O = 2.414(3); ring^{cen}(1)−Tb−ring^{cen}(2) = 134.03(9), I−Tb−O = 88.30(9), ring^{cen}(1)−Tb−O = 104.98(12), ring^{cen}(2)−Tb−O = 106.63(13), ring^{cen}(1)−Tb−I = 105.44(7), ring^{cen}(2)−Tb−I = 108.01(7). "ring^{cen}" indicates the centroid of the five ring-carbon atoms.

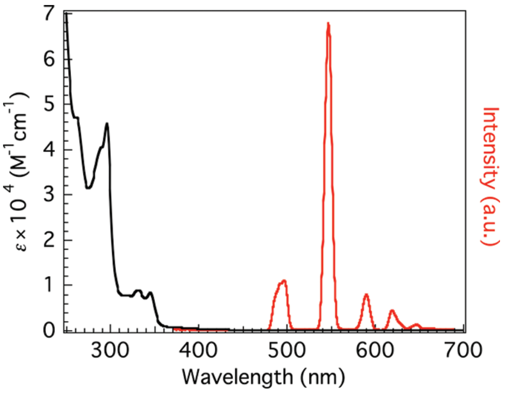

Figure 3. UV−vis absorption (black) and corrected luminescence (red) spectra of **1** in THF at room temperature (λ_{ex} = 330 nm).

ligands as **1** was synthesized (Scheme 1) and characterized. Because the energy levels of the lowest triplet states for *N*-phenylcarbazole derivatives (ca. 24 000 cm^{-1})[11] are considerably lower than that of the metal-centered state for the gadolinium(III) ion (32 000 cm^{-1}), the ligand-centered luminescence would not be quenched in the gadolinium(III) complex **2**. The solid-state molecular structure of **2** is depicted in Figure S3.[8] The unit cell constants show that the lanthanide complexes **1** and **2** are isomorphous. The ring^{cen}−metal−ring^{cen} and iodide−metal−oxygen angles of **2** (133.85(10) and 88.58(10)°, respectively) are consistent with those of **1** (134.03(9) and 88.30(9)°, respectively). The UV−vis absorption spectrum of **2** in THF at room temperature is also consistent with that of **1** (Figure S4): λ_{max} = 296, 331, and 345 nm ($\varepsilon = 4.38 \times 10^4$, 0.83×10^4, and 0.81×10^4 M^{-1} cm^{-1}, respectively). From the phosphorescence spectra of the gadolinium(III) complex **2** in Me-THF at 77 K (Figure S5), the energy level of the lowest excited state in the *N*-phenylcarbazolyl moieties was estimated as approximately 24 200 cm^{-1}. Thus, the energy gap (ΔE) between the lowest ligand-centered (24 200 cm^{-1}) and metal-centered (20 100 cm^{-1}) levels in **1** is calculated to be 4100 cm^{-1}, much higher than that normally placed as an upper limit (ΔE = 1850 cm^{-1})[12] for back energy transfer from the terbium ion at room temperature: the energy gap in **1** is large enough to cause no back energy transfer to the ligand center. This result supports the efficient and straightforward intramolecular energy transfer from the Cp^{PhCar} ligand to the terbium ion in **1**.

The luminescence quantum yield (Φ) of **1** was determined to be 0.67 in THF using 9,10-diphenylanthracene in cyclohexane as a reference (Φ = 0.97).[13] The quantum yield is comparable to those for recently reported highly luminescent terbium complexes, which used macrocyclic polyamines (0.43−0.78),[3] pyridine derivatives (0.31−0.95),[14] 2-hydroxyisophthalamide derivatives (0.40−0.63),[15] and others (0.40−0.85)[16] as ligands. The lifetime (τ) of **1** in THF at room temperatue (400 μs) is considerably shorter than those found in the highly luminescent terbium complexes discussed above (~3.16 ms)[3,14−16] and is slightly longer than that found in the organometallic terbium complex [Tb(η^5-$C_5H_4CH_3)_2$-Cl(THF)] (300 μs).[17] Thus, the radiative rate constant ($k_r = \Phi/\tau$) of **1** is calculated to be $k_r = 1.68 \times 10^3$ s^{-1}, which is the highest in the terbium complexes discussed above (~1.59×10^3 s^{-1}: mostly less than 0.90×10^3 s^{-1}). Since it is known that asymmetric environments of lanthanide(III) ions promote f−f radiative transition and thereby provide higher quantum yields,[18] the asymmetric structure around the terbium ion of

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1 (vide ante, Figure 2) would contribute to the photophysical properties of **1**.

In conclusion, we have demonstrated the potentiality of the photofunctionalized Cp* ligand $\mathrm{Cp}^{\mathrm{PhCar}}$ to form a highly luminescent lanthanide complex. The newly prepared ligand was isolated as the potassium salt, and its solid-state structure was unequivocally characterized. The terbium complex **1** supported by the $\mathrm{Cp}^{\mathrm{PhCar}}$ ligands shows the efficient photosensitization of f−f luminescence via energy transfer from the photosensitized *N*-phenylcarbazolyl group and the fairly fast radiation rate. Thus, a new class of photofunctionalized ligands, $\mathrm{Cp}^{\mathrm{PhCar}}$ and related Cp* derivative ligands, could provide a new strategy to construct novel photofunctional organometallic compounds and open a new field of organometallic photochemistry. Further work is currently in progress on the basis of this approach.

Acknowledgment. This work was financially supported by a Grants-in-Aid for Scientific Research (KAKENHI) in Priority Areas and "Photochromism (No. 471)" and by the Grant-in-Aid "21750059" from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan, and a "Sasakawa Scientific Research Grant" from the Japan Science Society. We thank Prof. N. Kitamura (Hokkaido University) for useful discussions and Prof. I. Sato and Dr. K. Shirasaki (Laboratory for α-ray emitters, Institute for Materials Research, Tohoku University) for their cooperation in elemental analyses.

Supporting Information Available: Text, table, and figures containing experimental and characterization details of $\mathbf{KCp}^{\mathbf{PhCar}}$, **1**, and **2** and a CIF file giving crystallographic details of $\mathbf{KCp}^{\mathbf{PhCar}}$, **1**, and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.