

Short Note

Bis(3,4-diphenyl)(2-methylthienyl)cyclopentadienyl Terbium Chloride

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Abstract: A new terbium(III) complex with a (3,4-diphenyl)(2-methylthienyl)cyclopentadienyl ligand was synthesized. Single-crystal X-ray analysis revealed a binuclear biscyclopentadienyl complex with a [TbCl₂K]₂ core. Luminescence properties of the terbium complex were analyzed.

Keywords: synthesis; rare-earth; single crystal X-ray diffraction; luminescence



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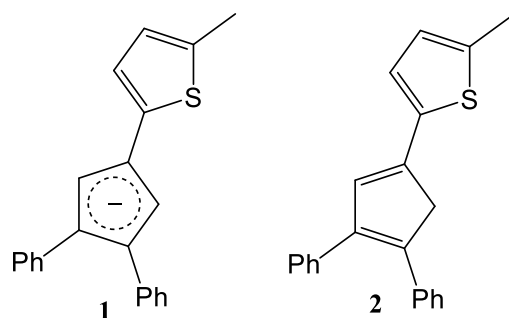
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1. Introduction

Cyclopentadienyl complexes of lanthanides are one of the most common classes of rare earth organometallics. Complexes with substituted cyclopentadienyl ligands have found even wider application in rare-earth chemistry [1–6]. Nevertheless, the range of such Cp derivatives is mainly limited to alkyl-substituted cyclopentadienyl ligands. The aryl-substituted cyclopentadienyl complexes of lanthanides are much less studied [7,8]. It should be noted that polyarylcyclopentadienyl ligands are more promising in the design of organolanthanides, making it possible to implement the basic principles of the stability of such compounds [9,10]. Recently, we described the use of polyphenyl-substituted cyclopentadienyl ligands for the design of various types of cyclopentadienyl complexes, namely mono-, bis, and tris-cyclopentadienyl complexes, having a mononuclear or multinuclear structure. We also suggested this type of ligand system for luminescence sensitization of the Tb³⁺ ion, where an aryl-substituted Cp-ligand plays the role of the so-called antenna-ligand [11,12]. In order to study the effect of various substituents in the arylcyclopentadienyl ligand on the molecular structure and photophysical properties of lanthanide complexes, we previously synthesized (3,4-diphenyl)(9-anthracenyl)cyclopentadienyl complexes of Nd, Tb, and Gd [13]. Herein we report synthesis, structure and photophysical properties of a bis-cyclopentadienyl complex of terbium with a new cyclopentadienyl ligand—(3,4-diphenyl)(2-methylthienyl)cyclopentadienyl-anion (1), derived from the 2-(3,4-diphenylcyclopenta-1,3-dien-1-yl)-5-methylthiophene (2), (Scheme 1).

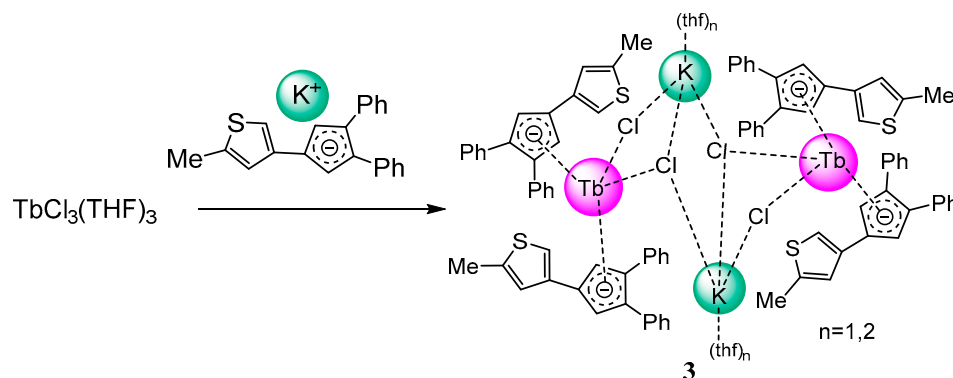


Scheme 1. Structures of the new cyclopentadienyl ligand (3,4-diphenyl)(2-methylthienyl)cyclopentadienyl-anion (**1**) and the corresponding cyclopentadiene 2-(3,4-diphenylcyclopenta-1,3-dien-1-yl)-5-methylthiophene (**2**).

2. Results and Discussion

2.1. Synthesis and Structure

The reaction of $\text{TbCl}_3(\text{thf})_3$ with two equivalents of (3,4-diphenyl)(2-methylthienyl)cyclopentadienylpotassium ($\text{Cp}^{\text{Th}}\text{K}$), obtained in situ from 2-(3,4-diphenylcyclopenta-1,3-dien-1-yl)-5-methylthiophene and benzylpotassium, gave the bis(cyclopentadienyl) binuclear terbium complex $[(\text{Cp}^{\text{Th}})_2\text{Tb}_2(\mu_2\text{-Cl})(\mu_3\text{-Cl})\text{K}(\text{thf})_{1.5}]_2$ (**3**), where $\text{Cp}^{\text{Th}} = (2\text{-methylthienyl})\text{-}3,4\text{-Ph}_2\text{C}_5\text{H}_2$. (Scheme 2).



Scheme 2. Synthesis of $[(\text{Cp}^{\text{Th}})_2\text{Tb}_2(\mu_2\text{-Cl})(\mu_3\text{-Cl})\text{K}(\text{thf})_{1.5}]_2$ (**3**).

Compound **3** has been obtained as binuclear ate-complexes with two bent metallocene ($\text{Cp}^{\text{Th}})_2\text{Tb}$ units connected with a nearly planar K_2Cl_4 bridging fragment (Figure 1).

The molecular structure of **3** is essentially similar to the previously reported $[(\text{Cp}^{\text{Ph}_3})_2\text{Tb}_2(\mu_2\text{-Cl})(\mu_3\text{-Cl})\text{K}]_2$ [11], except that complex **3** contains THF molecules coordinated to the potassium cation.

There are two independent molecules in a unit cell $[(\text{Cp}^{\text{Th}})_2\text{Tb}_2(\mu_2\text{-Cl})(\mu_3\text{-Cl})\text{K}(\text{thf})]_2$ (**3a**) and $[(\text{Cp}^{\text{Th}})_2\text{Tb}_2(\mu_2\text{-Cl})(\mu_3\text{-Cl})\text{K}(\text{thf})_2]_2$ (**3b**), both of which are located in the center of symmetry (Figures 1 and 2). The difference between the two molecules which can be more correctly considered as two different complexes is the number of THF molecules coordinated by potassium. In **3a**, the potassium cation is surrounded with 3 chloride ligands and THF ligand and η^6 -coordinated with one of the phenyl groups. In **3b**, the potassium cation is surrounded with 3 chloride ligands and two thf ligands and η^3 -coordinated with one of the phenyl groups. The variation of THF molecules coordinated to potassium lead to pronounced difference in potassium $\text{K} \dots \text{Cp}(\text{centroid})$ distance up to 3.13 Å in comparison to 2.97 Å (Table 1). Furthermore, in **3b** the ring slippage is 0.35 compared to 0.08 Å in **3a**. In contrast to $\text{K} \dots \text{Ph}$ interaction, all other geometric parameters in **3a** and **3b** are rather close to each other. In particular, the $\text{Tb}\text{-Cp}$ centroid distances vary in the range 2.406(6)–2.417(6) Å.

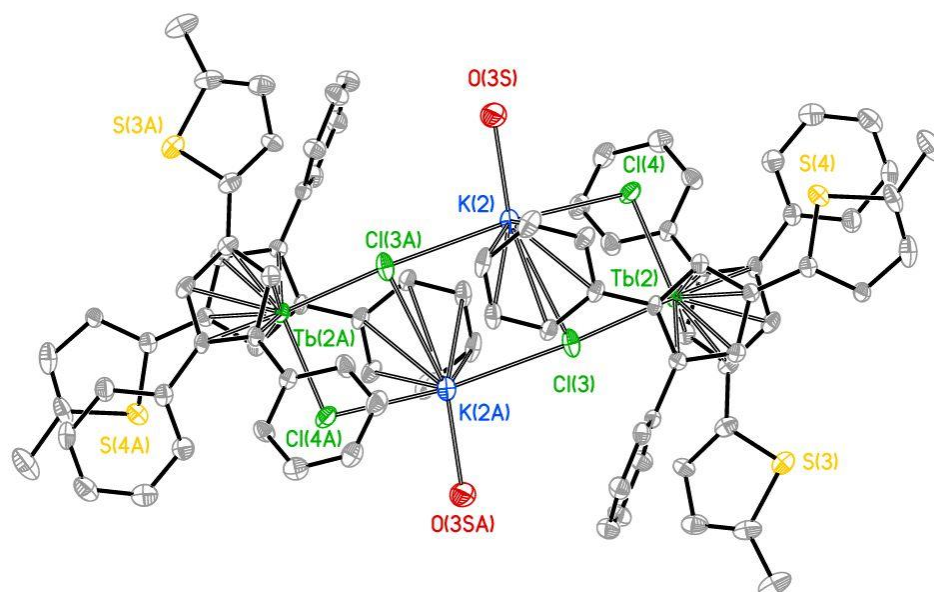


Figure 1. The general view of **3a** in representation of atoms by thermal ellipsoids ($p = 50\%$). The carbon atoms of THF are omitted for clarity.

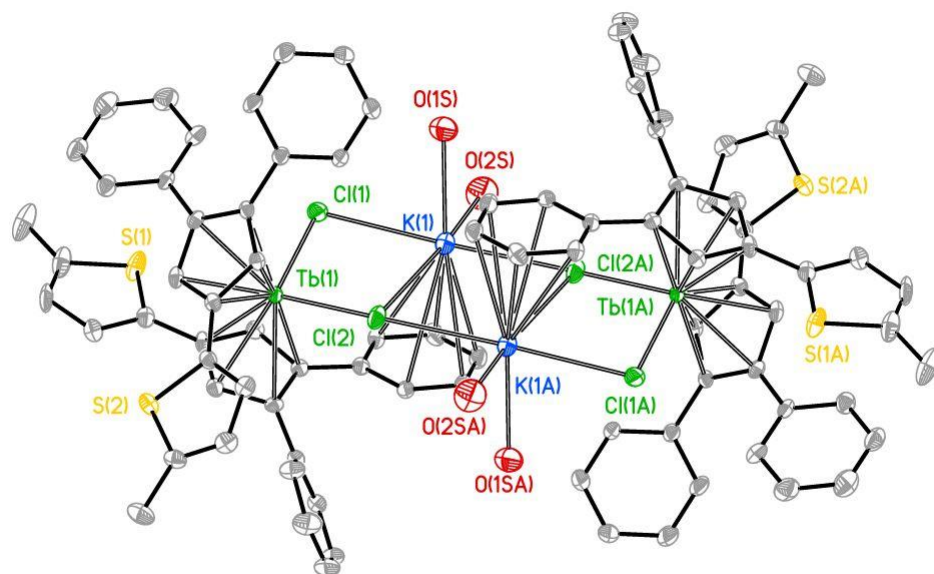


Figure 2. The general view of **3b** in representation of atoms by thermal ellipsoids ($p = 50\%$). The carbon atoms of THF are omitted for clarity.

Table 1. Selected structural parameters of complexes **3a** and **3b**.

Title 1	3a	3b
Tb-Cp _{cent} (Å)	2.406(6), 2.417(6)	2.407(6), 2.415(6)
Tb-Cl (Å)	2.5895(11), 2.6322(11)	2.6022(12), 2.6232(11)
K-Cl (Å)	3.0229(16), 3.1403(15)	3.0092(16), 3.0481(15)
	3.4307(17)	3.4301(17)
K-O (Å)	2.662(5), 2.759(4)	2.638(4)

As expected, the thienyl ring is almost coplanar with the Cp ring (the corresponding torsion angles vary in the range of 0.5–5.8°). The angles of rotation for phenyl rings are considerably larger and differ for Ph coordinated by potassium (ca 17°) and the rest one (ca 57°). Clearly, the different conjugation of aromatic rings and their nonequivalence can lead to intramolecular charge transfer.

2.2. Photophysical Properties

The bis-triphenylcyclopentadienyl terbium complex $[(\text{Cp}^{\text{Ph}_3})_2\text{Tb}(\mu_2\text{-Cl})(\mu_3\text{-Cl})\text{K}]_2$ exhibits relatively strong luminescence (quantum yield of photoluminescence is 25% [11]). However, the introduction of a thienyl substituent instead of one phenyl ring changes dramatically the efficiency of luminescence sensitization of the Tb^{3+} ion (Figure 3). In the excitation spectrum two intense bands centered at 270 and 410 nm are observed and tentatively assigned to the Cp ring and to the intraligand charge transfer (ILCT) state, respectively [11,12]. It should be noted that this charge transfer state can be caused by both the presence of the thienyl ring and $\text{K}^+-\pi$ interaction with the phenyl ring. Replacement of the phenyl ring by the thienyl ring usually leads to decreasing the energy of the triplet state of the ligand [14]. Taking into account that the energy of the triplet state in the bis-cyclopentadienyl complex with triphenyl-substituted Cp was found to be 435 nm, it is logical to expect a back energy transfer (BET) process leading to luminescence quenching in complex 3. As a result, the luminescence spectrum exhibits only one weak line assigned to $^5\text{D}_4\text{-}^7\text{F}_5$ transition of the Tb^{3+} ion as well as a broad band of the ligand.

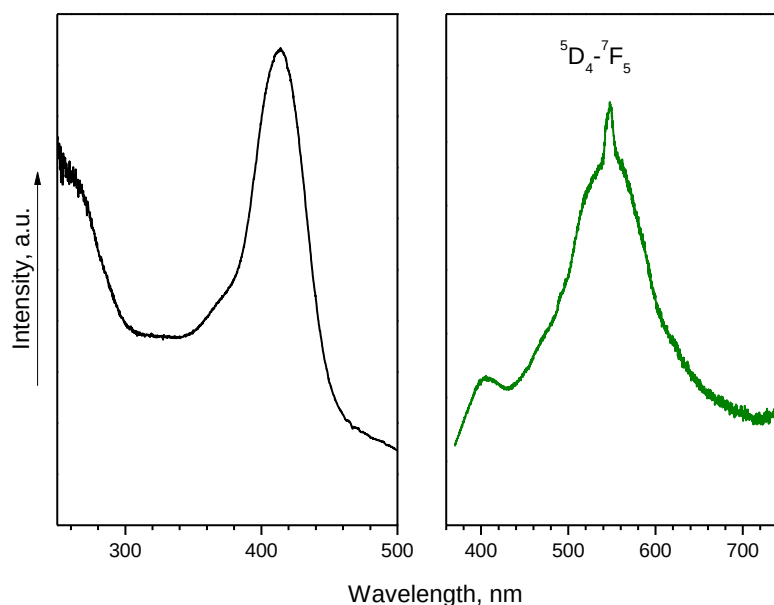


Figure 3. Luminescence excitation (left) and luminescence (right) spectra of complex 3 in solid state at 300 K, $\lambda_{\text{reg}} = 545$ nm, and $\lambda_{\text{exc}} = 270$ nm.

3. Materials and Methods

3.1. General Considerations

All synthetic manipulations with organolanthanides were carried out under an argon atmosphere in a glovebox with rigorous exclusion of air and water (Specs, <1ppm of O_2 , <1 ppm of H_2O). Tetrahydrofuran and ether were predried over NaOH and distilled from potassium/benzophenone ketyl. Hexane was distilled from Na/K alloy/benzophenone ketyl. $\text{TbCl}_3(\text{THF})_3$ was prepared according to literature [15]. Benzyl potassium was prepared according to a slightly modified literature procedure [16], and THF solutions of potassium arylcyclopentadienides were prepared as described in [11].

3.2. Synthesis

3.2.1. 2-(3,4-diphenylcyclopenta-1,3-dien-1-yl)-5-methylthiophene (2)

To the solution of 1.57 g (13 mmol) of 2-methylthiophene in 50 mL of dry ether, cooled to -50°C , 6.4 mL of 2.5 M BuLi solution in hexanes was added under rigorous stirring. The reaction mixture was allowed to warm up to the room temperature and stirred for another 40 min. Then the flask was cooled to -20° , a THF solution of 3 g (12.6 mmol) of 3,4-diphenylcyclopenten-2-one was added, and the reaction mixture stirred for 40 min.

The reaction was allowed to reach room temperature and 10 mL of water was added. The mixture was extracted with 3×50 mL of ether. The combined organic layers were washed with water and brine, and dried over MgSO_4 . Ten mL of 0.05 g TsOH ether solution was added and the mixture was heated to the boiling point and cooled, washed with saturated solution of NaHCO_3 , water, and brine, dried over MgSO_4 , and rotavaporated; the obtained oil was dried in a dynamic vacuum. The product was purified by column chromatography (benzene:petroleum ether 1:1.2). After drying in vacuum, 2.2 g (56%) of **1** was obtained.

^1H NMR (400 MHz, CDCl_3), δ : 2.50 (3H, s, Me-thienyl), 3.91 (2H, s, $\text{CH}_2\text{-Cp}$), 6.67 (1H, m, CH-thienyl), 6.760 (1H, s, CH-Cp), 6.91 (1H, m, CH-thienyl), 7.1–7.4 (10H, br.m, Ph), (Figure S1).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3), δ : 15.0 (Me_thienyl), 45.1 ($\text{CH}_2\text{-Cp}$), 122.4, 125.5, 126.0, 126.8, 127.3, 127.8, 128.0, 128.1, 130.1, 136.3, 136.6, 137.1, 137.9, 138.1, 139.1, 141.6. Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{S}$: C, 84.03; H, 5.77. Found: C, 84.42; H, 6.05.

3.2.2. Bis-(3,4-diphenyl)(2-methylthienyl)cyclopentadienyl-terbium-dichloro-potassium-tetrahydrofuranate (**3**)

A solution of benzylpotassium (0.217 g, 1.67 mmol) in 10 mL of THF was added slowly to the 10 mL THF solution of 2-(3,4-diphenylcyclopenta-1,3-dien-1-yl)-5-methylthiophene (0.516 g, 1.64 mmol). The reaction mixture was stirred for 15 min. The obtained solution of potassium salt was slowly added in small portions to a stirred suspension of $\text{TbCl}_3(\text{thf})_3$ (0.385 g, 0.8 mmol) in THF (10 mL). The reaction mixture was stirred for 12 h. Then, the reaction mixture was centrifuged (5000 rpm, 15 min) and the obtained precipitate was removed. The solution was concentrated in a vacuum to a volume of ca. 10 mL and layered with 30 mL of hexane to initiate crystallization. Crystals were obtained after several days. The crystals obtained were separated from the mother liquor and dried in dynamic vacuum during 3 h, yielding 0.350 g (43%) of **3**. Anal. Calcd for $\text{C}_{48}\text{H}_{42}\text{S}_2\text{Cl}_2\text{KOTb}$: C, 59.57; H, 4.34. Found: C, 58.95; H, 4.31.

3.3. X-ray Diffraction Studies

Crystals of **3** ($\text{C}_{200}\text{H}_{184}\text{Cl}_8\text{K}_4\text{O}_6\text{S}_8\text{Tb}_4$, $M = 4015.62$) are triclinic, space group P-1, at 120(2) K: $a = 13.4128(4)$, $b = 14.1405(5)$, $c = 24.1077(8)$ Å, $\alpha = 81.6204(7)$, $\beta = 89.3422(7)$, $\gamma = 79.5943(7)^\circ$, $V = 4448.6(3)$ Å³, $Z = 1$ ($Z' = 2/2$), $d_{\text{calc}} = 1.499$ g·cm^{−3}, $\mu(\text{MoK}\alpha) = 19.35$ mm^{−1}, and $F(000) = 2032$. Intensities of 37,943 reflections were collected at 120(2) K on a Bruker APEX II CCD diffractometer (shutterless ϕ - and ω -scan technique), using Mo $\text{K}\alpha$ -radiation. A total of 23,642 independent reflections [$R_{\text{int}} = 0.0837$] were used in further refinement. Considering the highly anisotropic shape of the crystals, the absorption correction was performed using a multiscan routine as implemented in SADABS (Version 2016/2) [17]. The studied crystal of **3** was a twin with the ratio for two major components being of 0.438(1):0.562(1). The structure was solved by direct methods using SHELXT [18,19]. Positions of all atoms were found from the electron density-difference map. Atoms were refined with individual anisotropic (non-hydrogen atoms) or isotropic (hydrogen atoms) displacement parameters. The refinement converged to $wR2 = 0.0980$ and $\text{GOF} = 1.037$ for all independent reflections ($R1 = 0.0499$ was calculated against F for 20,741 observed reflections with $I > 2\sigma(I)$). The SHELXTL program suite was used for molecular graphics. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Center with deposition number CCDC 2216679.

3.4. Optical Measurements

Luminescent measurements in the visible and NIR regions were performed with a Horiba-Jobin-Yvon-Spex Fluorolog FL 3-22 spectrometer, which has a 450 W xenon arc lamp as the excitation source for steady-state measurements and a 150 W xenon pulse lamp for kinetic experiments. The technique involved the use of specially designed, cylindrical sealed quartz cuvettes for manipulation with air-sensitive compounds. All complexes studied were powdered.

4. Conclusions

2-(3,4-diphenylcyclopenta-1,3-dien-1-yl)-5-methylthiophene was synthesized. A complex of bis(3,4-diphenyl)(2-methylthienyl)cyclopentadienyl terbium has been obtained and structurally characterized. The luminescence intensity of the complex studied is weak owing to the participation of both charge transfer states and back energy transfer in the luminescence sensitization of the Tb^{3+} ion.

Supplementary Materials: The following supporting information can be downloaded. Scheme S1: Synthesis of **2**, Figure S1: 1H NMR spectrum of **2** in $CDCl_3$ residual dichloromethane signal at 5.35 ppm, Figure S2: ^{13}C NMR spectrum of **2** in $CDCl_3$, Figure S3: Expanded fragment ^{13}C NMR spectrum of **2** in $CDCl_3$ (121–145 ppm), Figure S4: DEPT- ^{13}C NMR spectrum of **2** in $CDCl_3$.

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Conflicts of Interest: The authors declare no conflict of interest.

References

- Hou, Z.; Wakatsuki, Y. Recent Developments in Organolanthanide Polymerization Catalysts. *Coord. Chem. Rev.* **2002**, *231*, 1–22. [\[CrossRef\]](#)
- Birmingham, J.M.; Wilkinson, G. The Cyclopentadienides of Scandium, Yttrium and Some Rare Earth Elements. *J. Am. Chem. Soc.* **1956**, *78*, 42–44. [\[CrossRef\]](#)
- Manastyrskyj, S.; Maginn, R.E.; Dubeck, M. The Preparation of Cyclopentadienyllanthanide Dichlorides. *Inorg. Chem.* **1963**, *2*, 904–905. [\[CrossRef\]](#)
- Maginn, R.E.; Manastyrskyj, S.; Dubeck, M. The Dicyclopentadienyllanthanide Chlorides. *J. Am. Chem. Soc.* **1963**, *85*, 672–676. [\[CrossRef\]](#)
- Wedal, J.C.; Evans, W.J. A Rare-Earth Metal Retrospective to Stimulate All Fields. *J. Am. Chem. Soc.* **2021**, *143*, 18354–18367. [\[CrossRef\]](#) [\[PubMed\]](#)
- Cooper, O.J.; Mills, D.P.; Lewis, W.; Blake, A.J.; Liddle, S.T. Reactivity of the Uranium(IV) Carbene Complex $[U(BIPM^{TMS})(Cl)(\mu-Cl)_2Li(THF)_2](BIPM^{TMS} = \{C(PPh_2NSiMe_3)_2\})$ towards Carbonyl and Heteroallene Substrates. *Dalt. Trans.* **2014**, *43*, 14275–14283. [\[CrossRef\]](#) [\[PubMed\]](#)
- Harder, S.; Naglav, D.; Ruspig, C.; Wickleder, C.; Adlung, M.; Hermes, W.; Eul, M.; Pöttgen, R.; Rego, D.B.; Poineau, F.; et al. Physical Properties of Superbulky Lanthanide Metallocenes: Synthesis and Extraordinary Luminescence of $[Eu II (CpBIG)_2] (CpBIG = (4-n Bu-C_6H_4)_5-Cyclopentadienyl)$. *Chem.-A Eur. J.* **2013**, *19*, 12272–12280. [\[CrossRef\]](#) [\[PubMed\]](#)
- Kelly, R.P.; Bell, T.D.M.; Cox, R.P.; Daniels, D.P.; Deacon, G.B.; Jaroschik, F.; Junk, P.C.; Le Goff, X.F.; Lemercier, G.; Martinez, A.; et al. Divalent Tetra- and Penta-Phenylcyclopentadienyl Europium and Samarium Sandwich and Half-Sandwich Complexes: Synthesis, Characterization, and Remarkable Luminescence Properties. *Organometallics* **2015**, *34*, 5624–5636. [\[CrossRef\]](#)
- Evans, W.J. Tutorial on the Role of Cyclopentadienyl Ligands in the Discovery of Molecular Complexes of the Rare-Earth and Actinide Metals in New Oxidation States. *Organometallics* **2016**, *35*, 3088–3100. [\[CrossRef\]](#)
- Evans, W.J. The Organometallic Chemistry of the Lanthanide Elements in Low Oxidation States. *Polyhedron* **1987**, *6*, 803–835. [\[CrossRef\]](#)
- Roitershtein, D.M.; Puntus, L.N.; Vinogradov, A.A.; Lyssenko, K.A.; Minyaev, M.E.; Dobrokhodov, M.D.; Taidakov, I.V.; Varaksina, E.A.; Churakov, A.V.; Nifant'ev, I.E. Polyphenylcyclopentadienyl Ligands as an Effective Light-Harvesting μ -Bonded Antenna for Lanthanide +3 Ions. *Inorg. Chem.* **2018**, *57*, 10199–10213. [\[CrossRef\]](#) [\[PubMed\]](#)
- Minyaev, M.E.; Komarov, P.D.; Roitershtein, D.M.; Lyssenko, K.A.; Nifant'ev, I.E.; Puntus, L.N.; Varaksina, E.A.; Borisov, R.S.; Dyadchenko, V.P.; Ivchenko, P.V. Aryloxy Alkyl Magnesium versus Dialkyl Magnesium in the Lanthanidocene-Catalyzed Coordinative Chain Transfer Polymerization of Ethylene. *Organometallics* **2019**, *38*, 2892–2901. [\[CrossRef\]](#)
- Vinogradov, A.A.; Komarov, P.D.; Puntus, L.N.; Taydakov, I.V.; Lyssenko, K.A.; Nifant'ev, I.E.; Varaksina, E.A.; Roitershtein, D.M. Luminescence Sensitization of the Nd^{3+} Ion in Diphenyl(9-Antraceny)Cyclopentadienyl Complexes Containing Antenna-Ligand with Extended π -System. *Inorg. Chim. Acta* **2022**, *533*, 120777. [\[CrossRef\]](#)

14. Varaksina, E.A.; Kiskin, M.A.; Lyssenko, K.A.; Puntus, L.N.; Korshunov, V.M.; Silva, G.S.; Freire, R.O.; Taydakov, I.V. Tuning the Luminescence Efficiency by Perfluorination of Side Chains in Eu³⁺-complexes with β -Diketones of the Thiophene Series. *Phys. Chem. Chem. Phys.* **2021**, *23*, 25748–25760. [[CrossRef](#)] [[PubMed](#)]
15. Edelmann, F.T.; Poremba, P. *Synthetic Methods of Organometallic and Inorganic Chemistry (Herrman/Brauer)*; Edelmann, F.T., Herrmann, W.A., Eds.; Verlag: Stuttgart, Germany, 1997; pp. 34–35.
16. Lochmann, L.; Trekoval, J. Lithium-Potassium Exchange in Alkylolithium/Potassium t-Pentoxide Systems. *J. Organomet. Chem.* **1987**, *326*, 1–7. [[CrossRef](#)]
17. Krause, L.; Herbst-Irmer, R.; Sheldrick, G.M.; Stalke, D. Comparison of Silver and Molybdenum Microfocus X-Ray Sources for Single-Crystal Structure Determination. *J. Appl. Crystallogr.* **2015**, *48*, 3–10. [[CrossRef](#)] [[PubMed](#)]
18. Sheldrick, G.M. SHELXT—Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr. Sect. A Found. Adv.* **2015**, *71*, 3–8. [[CrossRef](#)] [[PubMed](#)]
19. Sheldrick, G.M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8. [[CrossRef](#)] [[PubMed](#)]