

# Bulking up Cp<sup>BIG</sup>: A Penta-Terphenyl Cyclopentadienyl Ligand

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Cite This: *Organometallics* 2022, 41, 776–784



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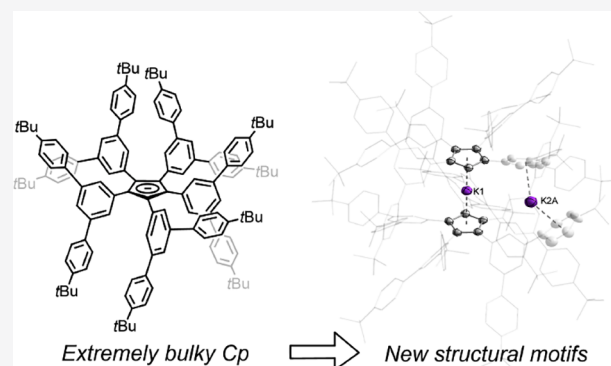


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**ABSTRACT:** The modification of cyclopentadienyl ligands with carefully selected substituents is a widely used strategy for tuning their steric and electronic properties. We describe the synthesis of an extremely bulky penta-terphenyl cyclopentadienyl ligand (Cp<sup>T5</sup>) by arylation of cyclopentadiene. Deprotonation reactions with various group 1 metals and bases afforded a complete series of alkali metal salts MCp<sup>T5</sup> (M = Li–Cs). The compounds were isolated as solvate-free salts, which were characterized by multinuclear nuclear magnetic resonance spectroscopy, ultraviolet–visible spectroscopy, and elemental analysis. Single-crystal X-ray diffraction studies of LiCp<sup>T5</sup>, NaCp<sup>T5</sup> (crystallized as a solvate with one tetrahydrofuran molecule per formula unit), and KCp<sup>T5</sup> revealed the formation of metallocene-like sandwich structures in the solid state.



## INTRODUCTION

Since the discovery of ferrocene in 1951,<sup>1,2</sup> cyclopentadienyl ligands have developed into some of the most fundamental ligand families in organometallic chemistry and have found widespread use in (asymmetric) catalysis,<sup>3,4</sup> small molecule activation,<sup>5</sup> and coordination chemistry (e.g., for the synthesis of single-molecule magnets).<sup>6–9</sup> Cyclopentadienyl ligands are classical “spectator” ligands, and their steric and electronic properties can be readily modified by introducing one or more substituents on the carbon atoms. These substitutions have dramatic effects, including slower rotational dynamics in the five-membered ring as well as stronger steric protection of the coordinated metal center. As a consequence, metal complexes become more stable compared to their unsubstituted analogues or possess higher catalytic activity.<sup>10</sup>

The permethylated pentamethylcyclopentadienyl C<sub>5</sub>Me<sub>5</sub> [Cp\* (Figure 1A)] was introduced in 1960 and has developed into a ubiquitous ligand due to its greater steric demand and stronger donating properties.<sup>11</sup> These properties led to isolation of metal complexes that were previously unstable with Cp ligands, e.g., decamethyltitanocene (Figure 1B).<sup>12</sup> Moreover, the introduction of even bulkier substituents such as *tert*-butyl or *iso*-propyl groups has led to cyclopentadienyls with still stronger steric demand such as C<sub>5</sub>H<sub>2</sub>tBu<sub>3</sub> (Cp<sup>m</sup>) and C<sub>5</sub>iPr<sub>5</sub>.<sup>13–19</sup> The former ligand has recently been used for the synthesis of unusual metallocene anions,<sup>8,9</sup> while the latter ligand has recently received attention through its capability to stabilize a dysprosium metallocene single-molecule magnet [(η<sup>5</sup>-C<sub>5</sub>iPr<sub>5</sub>)(Cp\*)Dy][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] showing magnetic hysteresis up to 80 K and the linear uranocene [(η<sup>5</sup>-C<sub>5</sub>iPr<sub>5</sub>)<sub>2</sub>U].<sup>7,18</sup>

Apart from bulky alkyl substituents, the introduction of aryl substituents on the cyclopentadienyl ring has also been a major

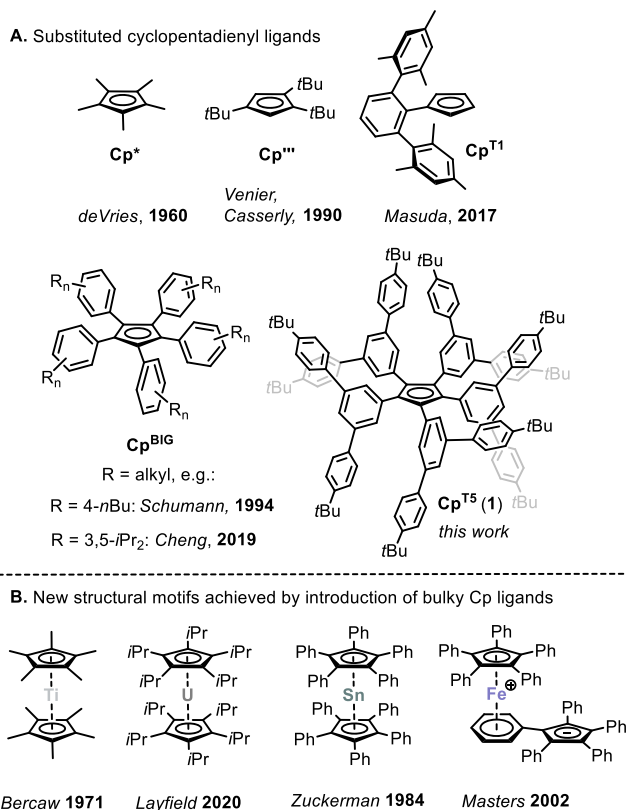
focus in this research field. A recent example is the terphenyl-substituted cyclopentadienyl ligand Cp<sup>T1</sup> reported by Masuda (Figure 1A), which forms remarkable oligomeric structures with Li, K, and Cs.<sup>20</sup> The (today commercially available) pentaphenylcyclopentadienyl ligand has likewise afforded fascinating structures (Figure 1).<sup>21</sup> For instance, the pentaphenylcyclopentadienyl ligand causes its stannocene to be linear. In contrast, Cp<sub>2</sub>Sn and Cp\*<sub>2</sub>Sn are significantly bent with Cp(centroid)–Sn–Cp(centroid) angles of 33° and 25°, respectively.<sup>22–24</sup>

Moreover, the isolation of a linkage isomer of decaphenylferrocene was accomplished.<sup>21,25</sup> Due to the poor solubility of pentaphenylcyclopentadienyl complexes in common organic solvents, recent studies have focused on the introduction of substituted arene rings to increase solubility. For instance, Harder and co-workers employed the so-called Cp<sup>BIG</sup> ligand featuring *p*-*n*-butyl groups on the arene rings.<sup>26</sup> Due to the high solubility even in *n*-hexane, which commonly hinders purification, and the severe disorder in crystallography caused by the *n*-butyl groups, the related *p*-ethyl-substituted ligand has been introduced recently.<sup>27,28</sup> Furthermore, 3,5-substitution on the arene rings (using groups such as Me, *i*Pr, and *t*Bu) has been achieved.<sup>29–31</sup> It is worth noting that the stability of complexes containing pentaarylcyclopentadienyl ligands is provided by steric protection of the metal center and

Received: January 8, 2022

Published: March 15, 2022





**Figure 1.** (A) Examples of alkyl- and aryl-substituted cyclopentadienyl ligands and (B) structural motifs stabilized by the introduction of bulky cyclopentadienyl ligands.<sup>11–14,18,20,24–29</sup>

attractive dispersion interactions between the cyclopentadienyl ligands also play a crucial role.<sup>32</sup>

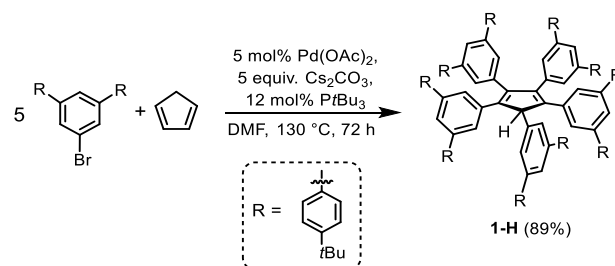
Herein, we describe the development of a penta-terphenyl cyclopentadienyl ligand  $\text{Cp}^{\text{ST}}$  (**1**) with a large three-dimensional profile. For this purpose, a suitable 3,5-terphenyl substituent was chosen to achieve penta-substitution of the cyclopentadiene ring. This ligand is deprotonated by alkali metals or alkali metal bases. The resulting cyclopentadienyl anion forms a remarkable dinuclear structure in combination with potassium.

## RESULTS AND DISCUSSION

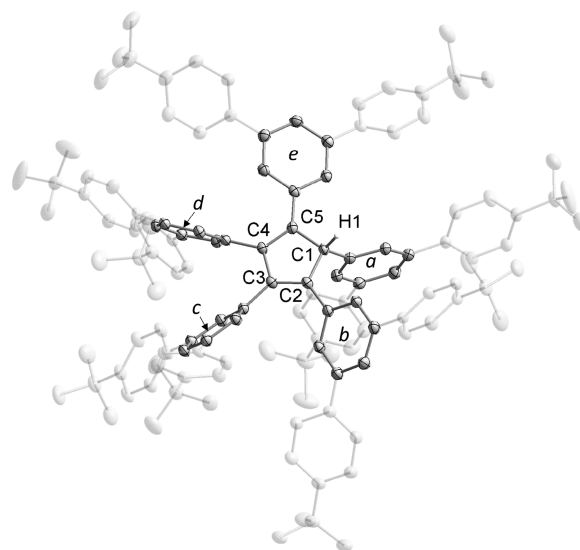
This study started with the investigation of the palladium-catalyzed Heck reaction of suitable 3,5-terphenyl bromides with cyclopentadiene according to the protocol developed by Dyker and Miura.<sup>31</sup> After the synthesis of three different 3,5-terphenyl bromides  $3,5\text{-R}_2\text{-C}_6\text{H}_3\text{Br}$  ( $\text{R} = 4\text{-}t\text{Bu-C}_6\text{H}_4$ ,  $3,5\text{-}t\text{Bu}_2\text{-C}_6\text{H}_3$ , or  $2,4,6\text{-Me}_3\text{-C}_6\text{H}_2$ ),<sup>33,34</sup> their behavior in the Heck reaction was investigated. After workup, the solids obtained were characterized by  $^1\text{H}$  NMR spectroscopy. While the products from the mono- and di-*tert*-butyl-substituted terphenyls ( $\text{R} = 4\text{-}t\text{Bu-C}_6\text{H}_4$  and  $3,5\text{-}t\text{Bu}_2\text{-C}_6\text{H}_3$ , respectively) gave a single set of signals in the alkyl region, the product from the arylation reaction with the mesityl-substituted terphenyl bromide ( $\text{R} = 2,4,6\text{-Me}_3\text{-C}_6\text{H}_2$ ) contained more than one species, suggesting an unselective reaction that was not pursued further. Analysis of the products from the arylation reactions with  $3,5\text{-R}_2\text{-C}_6\text{H}_3\text{Br}$  ( $\text{R} = 4\text{-}t\text{Bu-C}_6\text{H}_4$  and  $3,5\text{-}t\text{Bu}_2\text{-C}_6\text{H}_3$ ) by LIFDI-MS revealed the formation of pentaarylated  $\text{C}_5[3,5\text{-}(4\text{-}t\text{Bu-C}_6\text{H}_4)_2\text{C}_6\text{H}_3]_4\text{H}$  [**1-H** (Scheme 1)], as evidenced by a molecular ion peak at  $m/z$  1768.262 and

tetraarylated  $\text{C}_5[3,5\text{-}(3,5\text{-}t\text{Bu}_2\text{-C}_6\text{H}_3)_2\text{C}_6\text{H}_3]_4\text{H}_2$  ( $m/z$  1876.448).

### Scheme 1. Synthesis of Penta-terphenyl Cyclopentadiene 1-H



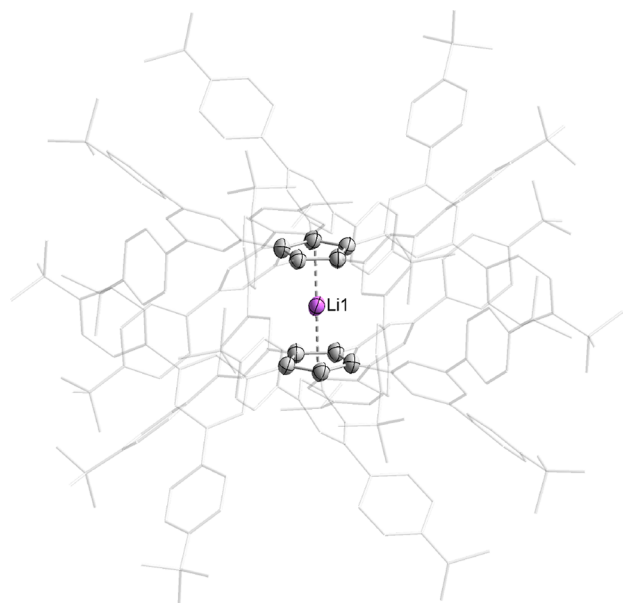
Single crystals grown from *n*-hexane confirm the molecular structure of **1-H** (Figure 2). The bond lengths show the



**Figure 2.** Molecular structure of **1-H** in the solid state. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms (except for H1) and disorder in the *t*Bu groups have been omitted for the sake of clarity. Selected bond lengths (angstroms) and angles (degrees): C1–C2, 1.5173(17); C2–C3, 1.3599(17); C3–C4, 1.4741(18); C4–C5, 1.3592(17); C5–C1, 1.5200(17); C5–C1–C6, 112.08(10); C3–C2–C1, 108.87(11); C2–C3–C4, 109.01(11); C5–C4–C3, 110.21(11); C4–C5–C1, 108.07(11). Plane-to-plane twist angles (degrees): a, C1–C5, 87.78(6); b, C1–C5, 36.89(5); c, C1–C5, 58.96(5); d, C1–C5, 72.84(5); e, C1–C5, 18.01(5).

expected values for C–C and C=C bonds [C2–C3, 1.3599(17) Å; C4–C5, 1.3592(17) Å; C1–C2, 1.5173(17) Å; C3–C4, 1.4741(18) Å; C5–C1, 1.5200(17) Å]. The cyclopentadiene to arene plane-to-plane twist angles range from 18.01(5)° to 87.78(6)°, which confirms a significant deviation from coplanarity and suggests a sufficient three-dimensional structure for stabilization of low-coordinate metal complexes. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **1-H** show the presence of three signals for the *t*Bu substituents ( $\delta = 1.33\text{--}1.34$  ppm). This is in line with the molecular structure determined by X-ray crystallography (*vide supra*) with three inequivalent terphenyl environments. The cyclopentadiene proton of **1-H** was observed at a chemical shift of 5.60 ppm.

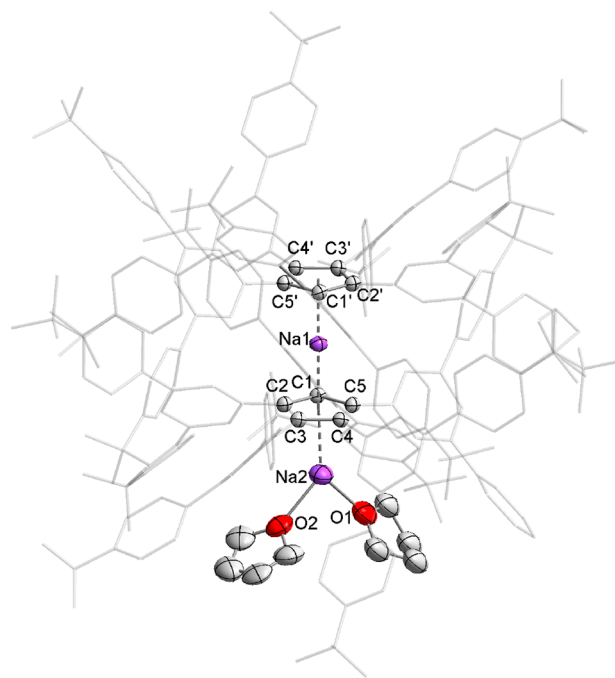
Having substantial amounts of this superbulky ligand precursor in hand, we investigated deprotonation reactions with a variety of alkali metals or alkali metal bases. The reaction of **1-H** with *n*BuLi proceeded extremely slowly even at increased temperatures. After the mixture had been stirred for 4 weeks at ambient temperature, a light green solid was obtained. Analysis by  $^1\text{H}$  NMR spectroscopy showed just a single aryl environment similar to that observed in terphenyl bromide 3,5-(4-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>Br. The observation of a single set of aryl signals can be explained by planarization of the Cp<sup>T5</sup> ligand and equivalence of the terphenyl substituents and thus is consistent with the formation of Cp<sup>T5</sup>Li (**1-Li**). Crystals of **1-Li** were obtained from *n*-hexane solutions at ambient temperature and reveal a [(Cp<sup>T5</sup>)<sub>2</sub>Li]<sup>-</sup>, where the position of the second lithium atom could not be detected due to poor high-angle data. Nevertheless, the sandwich structure of **1-Li** is clearly evident from the experiment (Figure 3).



**Figure 3.** Structural drawing of [(Cp<sup>T5</sup>)<sub>2</sub>Li]<sup>-</sup> as part of the structure of **1-Li** from a single-crystal X-ray diffraction experiment. The position of the second Li<sup>+</sup> cation was not determined due to the poor resolution of the crystallographic data. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms and disorder in the Cp ligand have been omitted for the sake of clarity. Bond lengths and angles are not given due to poor refinement data.

Next, we assessed the deprotonation reaction of **1-H** with sodium and sodium bases. Small chunks of Na metal did not react with **1-H** even at increased temperatures of 80 °C. However, the reaction of sodium hexamethyldisilazide (NaHMDS) with **1-H** in THF produced a light green solid after the mixture had been stirred at 80 °C overnight. Analysis of this solid by  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy revealed the formation of five equivalent terphenyl groups. This is indicative for the formation of Cp<sup>T5</sup>Na (**1-Na**), which was isolated in 21% yield after washing the precipitate formed during the reaction with *n*-hexane.

Upon crystallization by slow diffusion of *n*-hexane into a benzene solution of **1-Na**, crystals of **1-Na·thf** were obtained. Similar to the structure of Cp<sup>T5</sup>Li, the single-crystal X-ray structure analysis revealed the formation of a sandwich structure (Figure 4). One Na<sup>+</sup> cation (Na1) is sandwiched



**Figure 4.** Molecular structure of **1-Na·thf** in the solid state. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms, noncoordinating solvent molecules, and disorder in the Cp ligand have been omitted for the sake of clarity. Selected bond lengths (angstroms) and angles (degrees): C1–C2, 1.428(3); C2–C3, 1.428(3); C3–C4, 1.416(3); C4–C5, 1.431(3); C5–C1, 1.420(3); Na2–O1, 2.357(7); Na2–O2, 2.233(9); Na1–Cp(centroid), 2.359(1); Na2–Cp(centroid), 2.490(3); Na1–Cp(centroid)–Na2, 174.52(9); C5–C1–C2, 108.1(2); C1–C2–C3, 107.9(2); C4–C3–C2, 108.0(2); C3–C4–C5, 108.2(2); C1–C5–C4, 107.9(2).

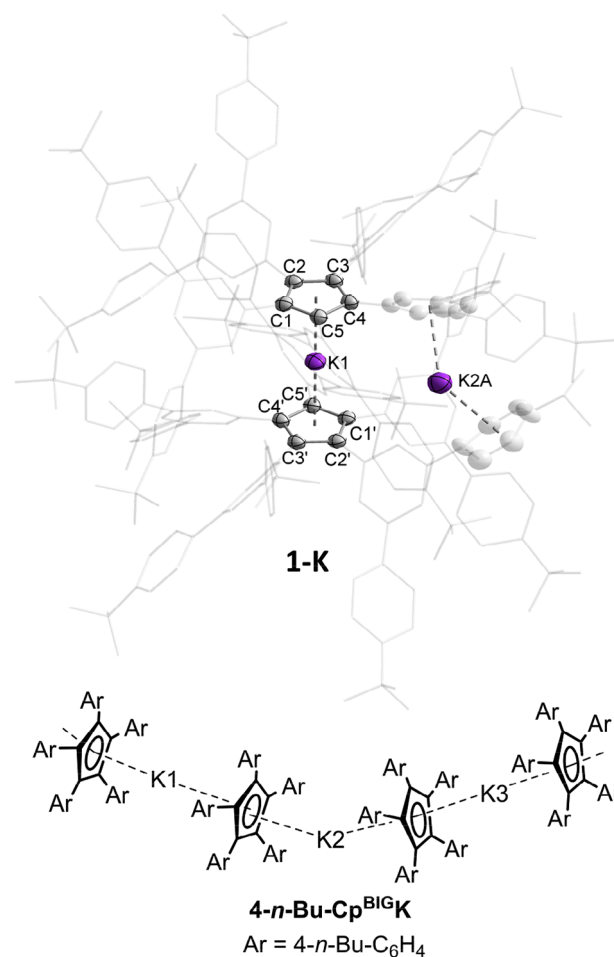
between the cyclopentadienyl rings of two anionic Cp<sup>T5</sup> ligands. The second Na<sup>+</sup> cation (Na2) is coordinated by only one Cp<sup>T5</sup> ligand and, surprisingly, by two additional THF molecules, which presumably stem from the presence of traces of THF during crystallization. Note that no traces of THF were observed in the NMR spectra or elemental analysis of **1-Na** before crystallization. Unfortunately, attempts to grow suitable THF-free crystals of **1-Na** have been unsuccessful so far. In the structure of **1-Na·thf**, the Na–Cp(centroid) distances are 2.359(1) Å [Na1–Cp(centroid)] and 2.490(3) Å [Na2–Cp(centroid)]. The Na1–Cp(centroid) distance compares very well to the Na–Cp(centroid) distance observed in NaCp (2.357 Å).<sup>35</sup> The C–C bond lengths within the cyclopentadienyl ring [1.416(3)–1.431(3) Å] are in the area typically observed for cyclopentadienyl compounds.<sup>35–39</sup> The cyclopentadiene to arene plane-to-plane twist angles in **1-Na·thf** range from 46.86(9)° to 52.10(9)°. The dinuclear structure of **1-Na·thf** is distinct from those of other sodium cyclopentadienides. Solvent-free NaCp itself features a chainlike structure,<sup>35</sup> and addition of donor solvents such as THF or DME (1,2-dimethoxyethane) typically breaks up these chains to afford compounds with a piano-stool structure, e.g., [Cp<sup>R</sup>Na(thf)<sub>3</sub>] (Cp<sup>R</sup> = C<sub>5</sub>Me<sub>4</sub>-C≡C-SiMe<sub>3</sub>).<sup>37–39</sup> **1-Na·thf**, in contrast, features a dinuclear structure with a μ<sup>2</sup>-bridging Cp<sup>T5</sup> ligand.

Despite many reports on the use of sodium cyclopentadienides for salt metathesis reactions to produce transition metal complexes, the potassium salts of bulky cyclopentadienides (e.g., 4-Et-Cp<sup>BIG</sup>K and 4-*n*-Bu-Cp<sup>BIG</sup>K) are

far more commonly employed. The corresponding potassium salt was therefore also synthesized by deprotonation with KH in THF.<sup>40</sup> Full consumption of **1-H** was observed after the reaction mixture had been stirred for 18 h at 60 °C. Analysis of the yellow powder obtained after workup by <sup>1</sup>H NMR spectroscopy again revealed the formation of one distinct terphenyl environment. THF could not be removed completely from the product *in vacuo* and presumably coordinates to the potassium ion to form either a solvent-separated ion pair or a piano-stool complex.<sup>41</sup> Despite the lack of definite structural proof by XRD for this compound, **1-K**·(thf)<sub>x</sub> (with *x* = 2–4) was isolated in a high yield (95%) on a gram scale. The THF content varies for every batch and was individually determined by integration in <sup>1</sup>H NMR (as an example, see Figure S10). The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR data in C<sub>6</sub>D<sub>6</sub> are similar to those of **1-Li** and **1-Na**, and the elemental analysis on a sample with three coordinating THF molecules supports the THF content determined by <sup>1</sup>H NMR spectroscopy.

Next, we sought to deprotonate **1-H** with a potassium base in a noncoordinating solvent. As such, the reaction of **1-H** with potassium metal in *n*-hexane produced a light green powder, which possesses a <sup>1</sup>H NMR spectrum in C<sub>6</sub>D<sub>6</sub> similar to that of **1-K**·(thf)<sub>3</sub>, with the only difference being the absence of THF. Single-crystal X-ray diffraction on a crystal grown from benzene/*n*-hexane revealed that the solvate-free structure of **1-K** shows a dinuclear arrangement of two Cp<sup>TS</sup>K units. One potassium ion (K1) is sandwiched between two symmetry-related cyclopentadienyl moieties in a staggered conformation with a K1–Cp(centroid) distance of 2.708(3) Å. A second potassium ion (K2) is sandwiched between the aryl rings of several terphenyl substituents and disordered over three positions (K2A–K2C). The dinuclear structure of **1-K** is particularly fascinating considering the distinct (bent) chain-like arrangement of solvent-free **4-*n*-Bu-Cp<sup>BIG</sup>K** in the solid state (Figure 5, bottom).<sup>40</sup> The higher degree of aggregation is presumably prevented by the high steric bulk of **1**. In comparison to the structure of **4-*n*-Bu-Cp<sup>BIG</sup>K**, **1-K** features a slightly longer K1–Cp(centroid) distance [**1-K**: 2.707(1) Å; **4-*n*-Bu-Cp<sup>BIG</sup>K**: K1–Cp(centroid), 2.6464(17) Å; K3–Cp(centroid), 2.6601(16) Å; K2–Cp(centroid), 2.6738(19) Å].<sup>40</sup> The cyclopentadiene to arene plane-to-plane twist angles in **1-K** range from 44.38(6)° to 50.79(6)°, which is significantly lower than in the case of **1-Na**·thf and in agreement with the increased ionic radius of K compared to Na.

Metallocenes of s-block elements are rare.<sup>42–45</sup> Paquette and co-workers reported that lithium cyclopentadienyl compounds are speciated in the dinuclear form [Li(thf)<sub>4</sub>][Cp'<sub>2</sub>Li] (Cp' = isodicyclopentadienide) at low temperature by means of variable-temperature NMR studies.<sup>46</sup> Such species can be isolated by introduction of a sterically demanding 4-*t*Bu-Cp<sup>BIG</sup> ligand, as recently demonstrated by the group of Schulz.<sup>45</sup> Moreover, Harder and co-workers showed that substitution of 0.5 equiv of the lithium cations with the noncoordinating cation PPh<sub>4</sub><sup>+</sup> results in discrete lithocene anions [Cp<sub>2</sub>Li]<sup>−</sup> in the solid state.<sup>47</sup> However, the formation of dinuclear units in the solid state similar to those in **K-1** has not been observed previously for binary alkali cyclopentadienyl salts. This observation can be attributed to the exceptional bulk of **1** and its ability to coordinate additional metal ions with the terphenyl substituents.



**Figure 5.** Molecular structure of **1-K** in the solid state (top) and schematic drawing of the structure of the related compound **4-*n*-Bu-Cp<sup>BIG</sup>K** in the solid state.<sup>40</sup> Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms, noncoordinating solvent molecules, and disorder in the Cp-ligand and in K2 have been omitted for the sake of clarity. Selected bond lengths (angstroms) and angles (degrees): C1–C2, 1.426(2); C2–C3, 1.419(3); C3–C4, 1.417(3); C4–C5, 1.422(2); C5–C1, 1.416(3); K1–Cp(centroid), 2.707(1); K2A–C38–C42(centroid), 2.877(5); K2A–C85–C89(centroid), 2.829(3); C5–C1–C2, 107.80(15); C3–C2–C1, 108.08(16); C4–C3–C2, 107.88(14); C3–C4–C5, 108.22(16); C1–C5–C4, 108.01(15).

DOSY NMR measurements suggest that the dinuclear structure of **1-K** is not preserved in solution. Using the experimentally observed diffusion coefficient ( $4.00 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ), the hydrodynamic radius of cyclopentadiene **1-H** in C<sub>6</sub>D<sub>6</sub> was determined to be 9.93 Å using the Stokes–Einstein equation.<sup>48</sup> This is quite in line with the molecular structure in the solid state, featuring Cp(centroid)–C(*t*Bu) distances of 8.92–10.38 Å. The hydrodynamic radii of **1-K**·(thf)<sub>2,3</sub> and **1-K** dissolved in C<sub>6</sub>D<sub>6</sub> were then determined to be 10.30 and 10.37 Å, respectively (see the Supporting Information). These data compare well with the radius determined for **1-H** and thus strongly indicate the formation of monomers in solution.

Considering the intriguing structure of compound **1-K**, the corresponding rubidium and cesium compounds were also prepared by reacting **1-H** with the elemental alkali metals. The desired salts **1-Rb** and **1-Cs** could be isolated in excellent yields (94% for M = Rb and 89% for M = Cs) as analytically pure powders according to NMR spectroscopy and elemental

analysis. Unfortunately, crystals of these compounds have not been obtained so far.

The entire series of alkali metal salts was also characterized by ultraviolet–visible (UV–vis) absorption spectroscopy. All compounds feature absorption bands in the range from 350 to 370 nm, which account for their yellow colors in solution (see Figures S16–S21).

## CONCLUSION

The extremely bulky cyclopentadienyl ligand Cp<sup>5T</sup> (**1**) featuring five 3,5-terphenyl substituents can be synthesized in high yield by arylation of cyclopentadiene with the corresponding terphenyl bromide. Cyclopentadiene **1-H** can be deprotonated by alkali metals or alkali metal bases to afford compounds **1-M** (M = Li–Cs). However, in some cases (M = Li or Na), these deprotonation reactions require long reaction times and heating. The need for such harsh conditions can presumably be attributed to the steric protection and inaccessibility of the cyclopentadiene proton. X-ray structure determination on the lithium, sodium, and potassium salts reveals dimers of Cp<sup>T5</sup>M units in the solid state that result in a metallocene sandwich. The second alkali metal could not be located in the case of **1-Li**. In **1-Na**, the second sodium cation was coordinated to one cyclopentadienyl ring and two additional THF molecules. Potassium salt **1-K** features a sandwich structure where one potassium cation is coordinated by cyclopentadienyl rings and the other potassium cation is sandwiched by arene rings of terphenyl substituents from opposite Cp<sup>T5</sup> ligands. To the best of our knowledge, this structure is the first example of a potassocene. Our results demonstrate that the high steric demand of Cp<sup>T5</sup> in combination with its ability to additionally coordinate metal ions gave access to new structural motifs. In future studies, this stabilizing effect could be exploited for the synthesis of low-coordinate metal complexes.<sup>9</sup>

## EXPERIMENTAL SECTION

**General Procedures.** All reactions and product manipulations were carried out in flame-dried glassware under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques (maintained at <0.1 ppm H<sub>2</sub>O and <0.1 ppm O<sub>2</sub>). 3,5-R<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>Br (R = 4-*t*Bu-C<sub>6</sub>H<sub>4</sub>,<sup>33</sup> 3,5-*t*Bu<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>,<sup>33</sup> or 2,4,6-Me<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>)<sup>34</sup> and PtBu<sub>3</sub><sup>49</sup> were prepared according to procedures previously reported in the chemical literature. Cyclopentadiene was obtained from dicyclopentadiene according to a previously reported procedure.<sup>50</sup> It was stored at –30 °C and redistilled before use. Elemental rubidium and cesium were kindly provided by the group of N. Korber (Universität Regensburg). All other chemicals were purchased from commercial suppliers and used without further purification.

Solvents were dried and degassed with a MBraun SPS800 solvent purification system. All dry solvents except *n*-hexane were stored under argon over activated 3 Å molecular sieves in gastight ampules. *n*-Hexane was instead stored over a potassium mirror.

**General Analytical Techniques.** NMR spectra were recorded on Bruker Avance 300 or 400 spectrometers at 300 K unless otherwise noted. <sup>1</sup>H NMR spectra were internally referenced to residual solvent resonances, and <sup>13</sup>C{<sup>1</sup>H} NMR spectra to the corresponding deuterated solvent signals (<sup>1</sup>H NMR: C<sub>6</sub>D<sub>6</sub>, 7.16 ppm; CDCl<sub>3</sub>, 7.26 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR: C<sub>6</sub>D<sub>6</sub>, 128.06 ppm; CDCl<sub>3</sub>, 77.16 ppm). <sup>7</sup>Li NMR spectra were externally referenced to LiCl in D<sub>2</sub>O. Chemical shifts (δ) are given in parts per million referring to external standards of tetramethylsilane (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}). <sup>1</sup>H and <sup>13</sup>C NMR signals were assigned on the basis of two-dimensional (2D) NMR spectra (<sup>1</sup>H–<sup>1</sup>H COSY, <sup>1</sup>H–<sup>13</sup>C HSQC, and <sup>1</sup>H–<sup>13</sup>C HMQC).

DOSY (diffusion-ordered spectroscopy) spectra were recorded on an Avance III 600 (600.25 MHz) spectrometer equipped with a z-gradient (53.5 G/cm), a 5 mm TXI cryoprobe, and a BVT 3000 unit at 298 K. The NMR spectra were processed with the Bruker program TopSpin 3.2, and the diffusion coefficients were calculated by applying the Bruker software T1/T2 relaxation module. For the calibration of the diffusion coefficients using temperature and viscosity corrections, TMS (tetramethylsilane) was added as a standard. The <sup>1</sup>H diffusion measurement was performed with the convection suppressing DSTE (double stimulated echo) pulse sequence, developed by Müller and Jerschow<sup>51</sup> in a pseudo-2D mode. One hundred twenty dummy scans and 16 scans were used with a relaxation delay of 2 s. Sinusoidal shapes were used for the gradient, and a linear gradient ramp with 20 increments between 5% and 95% of the maximum gradient strength was applied. With regard to the homospoil gradient strengths, values of –13.17, 20, and –17.13 G cm<sup>–1</sup> were used. The length of gradient pulse δ was adjusted for every species in the sample, giving δ values of 2.4 ms for TMS and 5.0 ms [**1-H** and **1-K**·(thf)<sub>2,3</sub>] and 5.4 ms (**1-K**) for the complexes. A diffusion time Δ of 50 ms was applied. From DOSY experiments, the translational self-diffusion coefficients *D* of molecules in solution can be calculated according to the Stejskal–Tanner equation.<sup>52–54</sup> The obtained values were 4.00 × 10<sup>–10</sup> m<sup>2</sup> s<sup>–1</sup> (**1-H**), 3.94 × 10<sup>–10</sup> m<sup>2</sup> s<sup>–1</sup> (**1-K**), and 3.97 × 10<sup>–10</sup> m<sup>2</sup> s<sup>–1</sup> [**1-K**·(thf)<sub>2,3</sub>]. With the diffusion coefficients *D* of the analyte and TMS (standard for viscosity referencing), hydrodynamic radius *r*<sub>H</sub> of the analyte can be estimated following the Stokes–Einstein equation.<sup>48</sup> Correction factor *c* of the Stokes–Einstein equation was calculated according to the semi-empirical modification according to Chen.<sup>55</sup> For this work, *r*<sub>H</sub> = 9.93 Å for Cp<sup>T5</sup>H, *r*<sub>H</sub> = 10.30 Å for **1-K**, and *r*<sub>H</sub> = 10.37 Å for **1-K**·(thf)<sub>2,3</sub>. This is in very good agreement with the crystal-derived radii of 8.92–10.38 Å [for Cp(centroid)–C*t*Bu in **1-H**] in the solid state. Therefore, these results clearly indicate the presence of monomeric structures in solution.

UV–vis absorption spectra were recorded on an Ocean Optics Flame Spectrometer. Mass spectra were recorded by the Central Analytics Department at Universität Regensburg using a Jeol AccuTOF GCX. Elemental analysis was performed by the Central Analytics Department of Universität Regensburg using a Vario micro cube.

Single-crystal X-ray diffraction data were recorded on Rigaku Oxford Diffraction SuperNova Atlas, Rigaku GV 1000, and XtaLAB Synergy R (DW system, Hypix-Arc 150) devices with Cu Kα radiation (λ = 1.54184 Å). Crystals were selected under mineral oil, mounted on micromount loops, and quench-cooled using an Oxford Cryosystems open flow N<sub>2</sub> cooling device. Either semiempirical multiscan absorption corrections<sup>56,57</sup> or analytical ones<sup>58</sup> were applied to the data. The structures were determined with the SHELXT<sup>59</sup> solution program using dual methods and by using Olex2 as the graphical interface.<sup>60</sup> The models were refined with ShelXL<sup>61</sup> using full matrix least-squares minimization on *F*<sup>2</sup>.<sup>62</sup> The hydrogen atoms were located in idealized positions and refined isotropically with a riding model.

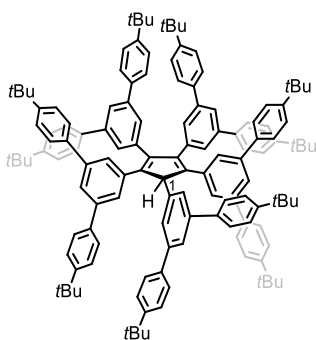
Crystals of compounds containing **1** typically also contain larger amounts of disordered solvent molecules in the lattice, which could not be successfully modeled. Therefore, the solvent mask of Olex2 was used to refine the molecular structures of **1-H**, **1-Li**, **1-Na**·thf, and **1-K**, and the presence of *n*-hexane was confirmed.

Crystallization attempts for **1-Li** repeatedly gave poorly diffracting crystals, which gave weak data only at high 2θ angles. One of these data sets was used for structure determination. Although the sandwich structure of **1-Li** was clearly evident, a satisfactory refinement of the structure was not possible due to the poor quality of the data.

Crystallographic data for the structures in this paper have been deposited in the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, U.K. Copies of the data can be obtained free of charge on quoting the depository numbers 2132166 (for **1-H**), 2133268 (for **1-Li**), 2132167 (for **1-Na**·thf), and 2132165 (for **1-K**). Further details about the single-crystal X-ray diffraction studies are given in the Supporting Information.

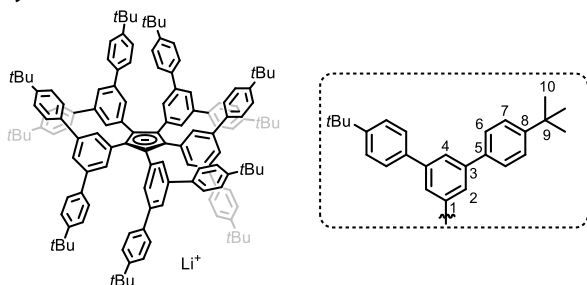
**Synthesis of Cp<sup>T5</sup>H (1-H).** This compound was prepared according to an adapted literature procedure from Dyker and Miura.<sup>31</sup> Only 4 equiv of 3,5-(4-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Br referring to cyclopentadiene was used; the use of 5 equiv resulted in unconsumed starting material, which proved to be difficult to separate from the product.

Solid 3,5-(4-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Br (**1**, 10.0 g, 23.7 mmol, 5.0 equiv), Pd(OAc)<sub>2</sub> (67 mg, 0.29 mmol, 0.05 equiv), and Cs<sub>2</sub>CO<sub>3</sub> (9.7 g, 29.7 mmol, 6.3 equiv) were combined. Subsequently, freshly distilled cyclopentadiene (0.5 mL, 5.9 mmol, 1.2 equiv), PtBu<sub>3</sub> (144.0 mg, 0.7 mmol, 0.15 equiv), and DMF (35 mL) were added. The reaction mixture was heated for 72 h to 130 °C, affording a deep green suspension. After the mixture had cooled to ambient temperature, DCM (300 mL) and *p*-toluene sulfonic acid monohydrate (9.0 g, 47.4 mmol, 10.0 equiv) were added. The red-brown suspension was filtered over silica (5 cm × 20 cm) using DCM as the eluent. DCM was removed under reduced pressure. The DMF-containing brown oil was added dropwise to water (500 mL), affording a light brown solid that was isolated by filtration and dried at 80 °C *in vacuo*.



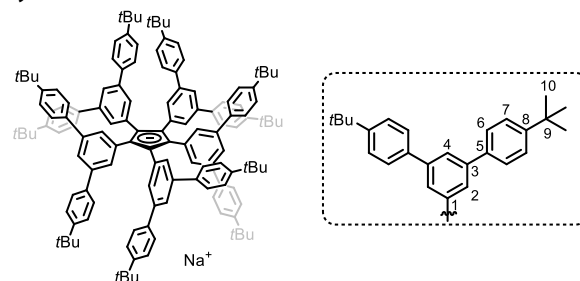
Crystals suitable for single-crystal X-ray diffraction were obtained from a saturated solution of **1-H** in *n*-hexane: C<sub>135</sub>H<sub>146</sub>; MW = 1768.65 g/mol; yield 7.5 g (89%, referenced to terphenyl bromide); <sup>1</sup>H NMR (400 MHz, 300 K, CDCl<sub>3</sub>) δ 1.33 (s, 36H, *t*Bu), 1.33 (s, 36H, *t*Bu), 1.34 (s, 18H, *t*Bu), 5.60 (s, 1H, C<sup>1</sup>H), 7.26–7.66 (s, 33H, C<sup>Ar</sup>H), 7.75 (t, *J*<sub>HH</sub> = 1.60 Hz, 2H, C<sup>Ar</sup>H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 300 K, CDCl<sub>3</sub>) δ 31.5 (s, C-CH<sub>3</sub>), 34.6 (s, C-CH<sub>3</sub>), 34.7 (s, C-CH<sub>3</sub>), 62.4 (s, C<sup>1</sup>), 123.9 (s, CH<sup>Ar</sup>), 124.7 (s, CH<sup>Ar</sup>), 125.7 (s, CH<sup>Ar</sup>), 125.9 (s, CH<sup>Ar</sup>), 126.7 (s, CH<sup>Ar</sup>), 126.9 (s, CH<sup>Ar</sup>), 127.0 (s, CH<sup>Ar</sup>), 127.15 (s, CH<sup>Ar</sup>), 127.21 (s, CH<sup>Ar</sup>), 128.4 (s, CH<sup>Ar</sup>), 136.1 (s, C<sup>Ar/Cp</sup>), 137.7 (s, C<sup>Ar/Cp</sup>), 138.4 (s, C<sup>Ar/Cp</sup>), 138.5 (s, C<sup>Ar/Cp</sup>), 138.5 (s, C<sup>Ar/Cp</sup>), 139.8 (s, C<sup>Ar/Cp</sup>), 141.0 (s, C<sup>Ar/Cp</sup>), 141.9 (s, C<sup>Ar/Cp</sup>), 142.0 (s, C<sup>Ar/Cp</sup>), 145.3 (s, C<sup>Ar/Cp</sup>), 146.5 (s, C<sup>Ar/Cp</sup>), 150.1 (s, C<sup>Ar/Cp</sup>), 150.28 (s, C<sup>Ar/Cp</sup>), 150.37 (s, C<sup>Ar/Cp</sup>). In the region from 123 to 151 ppm, 24 signals were detected (26 expected). Unfortunately, these signals could not be assigned by 2D NMR spectra due to partial overlap. However, we expect these signals to arise from three chemically different terphenyl substituents (eight signals each) and from overlapping cyclopentadiene signals expected for C<sub>2v</sub> symmetrical **1-H**. In particular, the signals of the aromatic C–H carbon atoms (assigned by DEPT-135) overlap partially, and therefore, two resonances of these carbon atoms were likely not detected (see Figure S2). Elemental analysis calcd: C, 91.68; H, 8.32. Found: C, 91.70; H, 8.31. LIFDI-MS *m/z* = 1768.262.

#### Synthesis of 1-Li.



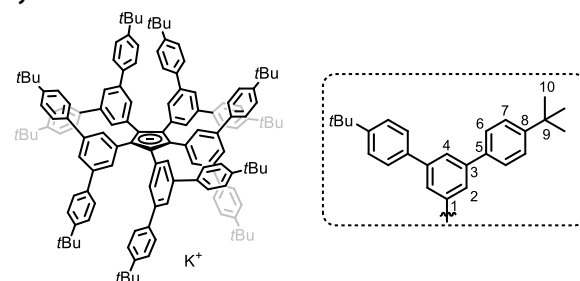
To a solution of **1-H** (200 mg, 0.114 mmol, 1.0 equiv) in *n*-hexane (3 mL) was added *n*BuLi (2.5 M in hexanes, 0.05 mL, 0.13 mmol, 1.1 equiv) at ambient temperature. The solution was stirred for 4 weeks, and a yellow-green solid precipitated. The solid was isolated by filtration and dried *in vacuo* to afford analytically pure **1-Li**: C<sub>135</sub>H<sub>145</sub>Li; MW = 1774.59 g/mol; yield 164 mg (81%); <sup>1</sup>H NMR (400 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) δ 1.16 (s, 90H, C<sup>10</sup>H), 7.33 (m, 20H, C<sup>7</sup>H), 7.63 (m, 20H, C<sup>6</sup>H), 7.77 (d, <sup>3</sup>*J*<sub>HH</sub> = 1.60 Hz, 10H, C<sup>2</sup>H), 8.04 (t, <sup>3</sup>*J*<sub>HH</sub> = 1.60 Hz, C<sup>4</sup>H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) δ 31.4 (s, C<sup>10</sup>), 34.4 (s, C<sup>9</sup>), 120.2 (s, C<sup>1</sup>), 122.6 (s, C<sup>4</sup>), 126.2 (s, C<sup>7</sup>), 127.4 (s, C<sup>6</sup>), 130.3 (s, C<sup>2</sup>), 139.7 (s, C<sup>5</sup>), 139.8 (s, C<sup>Cp</sup>), 141.9 (s, C<sup>3</sup>), 150.0 (s, C<sup>8</sup>); <sup>7</sup>Li NMR (155 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) δ –5.3 ppm. Elemental analysis calcd: C, 91.37; H, 8.24. Found: C, 90.68; H, 8.22. UV–vis (*n*-hexane): λ<sub>max</sub> [nm, ε<sub>max</sub> (L mol<sup>–1</sup> cm<sup>–1</sup>)] 220 (200000), 255 (290000), 350sh (27000).

#### Synthesis of 1-Na.



To a mixture of **1-H** (366 mg, 0.207 mmol, 1.0 equiv) and NaHMDS (38.0 mg, 0.21 mmol, 1.0 equiv) was added *n*-hexane (3 mL). The reaction mixture was heated to 75 °C overnight to afford a light green precipitate. The solid was isolated by filtration, washed with cold (–20 °C) *n*-hexane (2 × 3 mL), and dried *in vacuo* to afford analytically pure **1-Na**. Single crystals suitable for X-ray diffraction were grown by slow diffusion of *n*-hexane into a saturated solution of **1-Na** in C<sub>6</sub>H<sub>6</sub>. Despite several crystallization attempts, the presence of minor amounts of THF (presumably contamination from the atmosphere of the glovebox) caused crystallization of **1-Na**·thf. Attempts to crystallize **1-Na** from freshly distilled benzene and *n*-hexane did not afford crystals suitable for single-crystal X-ray diffraction: C<sub>135</sub>H<sub>145</sub>Na; MW = 1790.63 g/mol; yield 76 mg (21%); <sup>1</sup>H NMR (400 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) δ 1.16 (s, 90H, C<sup>10</sup>H), 7.32 (m, 20H, C<sup>7</sup>H), 7.64 (m, 20H, C<sup>6</sup>H), 7.85 (d, <sup>3</sup>*J*<sub>HH</sub> = 1.50 Hz, 10H, C<sup>2</sup>H), 8.01 (t, <sup>3</sup>*J*<sub>HH</sub> = 1.50 Hz, C<sup>4</sup>H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) δ 31.4 (s, C<sup>10</sup>), 34.4 (s, C<sup>9</sup>), 121.2 (s, C<sup>4</sup>), 121.9 (s, C<sup>1</sup>), 126.1 (s, C<sup>7</sup>), 127.5 (s, C<sup>6</sup>), 130.5 (s, C<sup>2</sup>), 139.9 (s, C<sup>5</sup>), 141.5 (s, C<sup>3</sup>), 142.0 (s, C<sup>Cp</sup>), 149.9 (s, C<sup>8</sup>). Elemental analysis calcd: C, 90.55; H, 8.16. Found: C, 89.55; H, 8.04. Low carbon values were found repeatedly in three independent samples. UV–vis (*n*-hexane): λ<sub>max</sub> [nm, ε<sub>max</sub> (L mol<sup>–1</sup> cm<sup>–1</sup>)] 220 (140000), 255 (220000), 350sh (24000).

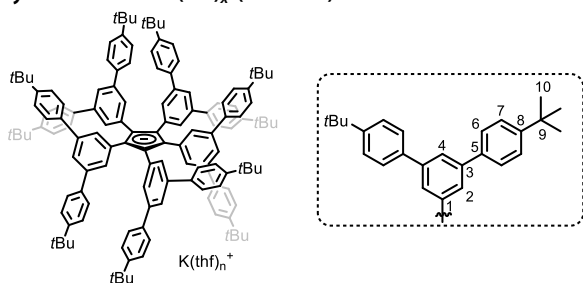
#### Synthesis of 1-K.



To a mixture of **1-H** (461.4 mg, 0.26 mmol, 1.0 equiv) and potassium (10.2 mg, 0.26 mmol, 1.0 equiv) was added *n*-hexane (2 mL). After the mixture had been stirred at ambient temperature overnight, only a small amount of precipitate formed. The reaction mixture was then heated to 50 °C for 6 h, and the formation of more green precipitate was observed. The solid was isolated by filtration, washed with cold (–20 °C) *n*-hexane (3 × 1.5 mL), and dried *in vacuo* to afford analytically pure **1-K**. Single crystals suitable for X-ray diffraction were

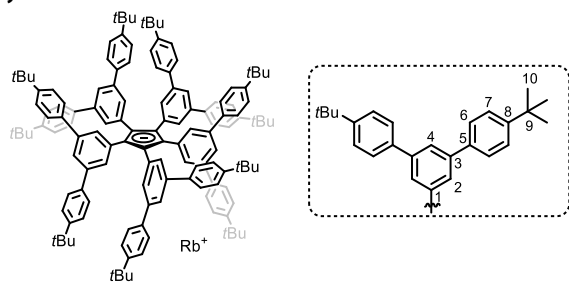
grown by slow diffusion of *n*-hexane into a saturated solution of **1-K** in  $C_6H_6$ :  $C_{135}H_{145}K$ ; MW = 1806.74 g/mol; yield 65 mg (14%);  $^1H$  NMR (400 MHz, 300 K,  $C_6D_6$ )  $\delta$  1.16 (s, 90H,  $C^{10}H$ ), 7.31 (m, 20H,  $C^7H$ ), 7.66 (m, 20H,  $C^6H$ ), 7.88 (d,  $^4J_{HH} = 1.63$  Hz, 10H,  $C^2H$ ), 8.00 (t,  $^4J_{HH} = 1.60$  Hz, 5H,  $C^4H$ );  $^{13}C\{^1H\}$  NMR (100 MHz, 300 K,  $CDCl_3$ )  $\delta$  31.4 (s,  $C^{10}$ ), 34.4 (s,  $C^9$ ), 121.6 (s,  $C^4$ ), 122.4 (s,  $C^1$ ), 126.0 (s,  $C^7$ ), 127.5 (s,  $C^6$ ), 130.5 (s,  $C^2$ ), 140.0 (s,  $C^5$ ), 142.0 (s,  $C^3$ ), 142.2 (s,  $C^{CP}$ ), 149.9 (s,  $C^8$ ). Elemental analysis calcd: C, 89.75; H, 8.09. Found: C, 87.40; H, 8.17. Low carbon values were found repeatedly in three independent samples. UV-vis (*n*-hexane):  $\lambda_{max}$  [nm,  $\epsilon_{max}$  (L mol $^{-1}$  cm $^{-1}$ )] 220 (160000), 250 (250000), 360 (31000).

### Synthesis of **1-K**(thf) $_x$ ( $x = 2-4$ ).



To a mixture of **1-H** (6.0 g, 3.4 mmol, 1.0 equiv) and KH (0.54 g, 13.5 mmol, 4.0 equiv) was added THF (120 mL). The green suspension was stirred at 60 °C for 18 h. Subsequently, the suspension was filtered (P4 frit), and the solvent was removed *in vacuo*. The remaining solid was dried under reduced pressure. The product was isolated as a yellow powder with variable THF content ( $x = 2-4$ ):  $C_{135}H_{145}K(C_4H_8O)_n$ ; MW = 2023.06 g/mol ( $n = 3$ ); yield 6.52 g (95%). For full characterization of this compound, a sample with a THF content of  $n = 3$  was chosen [determined by integration of the  $^1H$  NMR signals (see Figure S10)]:  $^1H$  NMR (400 MHz, 300 K,  $C_6D_6$ )  $\delta$  1.16 (s, 90H,  $C^{10}H$ ), 1.26 (m, 12H, THF), 3.32 (m, 12H, THF), 7.30 (m, 20H,  $C^7H$ ), 7.64 (m, 20H,  $C^6H$ ), 7.90 (d,  $^4J_{HH} = 1.50$  Hz, 10H,  $C^2H$ ), 7.98 (t,  $^4J_{HH} = 1.50$  Hz, 5H,  $C^4H$ );  $^{13}C\{^1H\}$  NMR (100 MHz, 300 K,  $CDCl_3$ )  $\delta$  25.6 (s, THF), 31.4 (s,  $C^{10}$ ), 34.4 (s,  $C^9$ ), 67.8 (s, THF), 121.2 (s,  $C^4$ ), 122.3 (s,  $C^1$ ), 126.0 (s,  $C^7$ ), 127.5 (s,  $C^6$ ), 130.6 (s,  $C^2$ ), 140.2 (s,  $C^5$ ), 141.8 (s,  $C^3$ ), 142.5 (s,  $C^{CP}$ ), 149.7 (s,  $C^8$ ). Elemental analysis calcd (for  $n = 3$ ): C, 87.27; H, 8.42. Found: C, 87.40; H, 8.17. UV-vis (*n*-hexane):  $\lambda_{max}$  [nm,  $\epsilon_{max}$  (L mol $^{-1}$  cm $^{-1}$ )] 220 (190000), 255 (280000), 355 (45000).

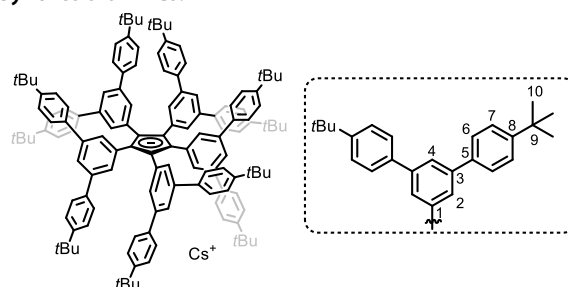
### Synthesis of **1-Rb**.



To a mixture of **1-H** (378.0 mg, 0.214 mmol, 1.0 equiv) and rubidium (20.1 mg, 0.24 mmol, 1.1 equiv) was added *n*-hexane. The mixture was sonicated at 50 °C for 1.5 h to afford a suspension of a green precipitate. Subsequently, the solvent was removed *in vacuo* and the remaining green solid was extracted with toluene (~5 mL). The solvent was again removed *in vacuo*, and the green powder was dried under reduced pressure to afford analytically pure **1-Rb**:  $C_{135}H_{145}Rb$ ; MW = 1853.11 g/mol; yield 372 mg (94%);  $^1H$  NMR (400 MHz, 300 K,  $C_6D_6$ )  $\delta$  1.15 (s, 90H,  $C^{10}H$ ), 7.32 (m, 20H,  $C^7H$ ), 7.66 (m, 20H,  $C^6H$ ), 7.86 (br s, 10H,  $C^2H$ ), 8.01 (br s,  $C^4H$ );  $^{13}C\{^1H\}$  NMR (100 MHz, 300 K,  $C_6D_6$ )  $\delta$  31.4 (s,  $C^{10}$ ), 34.4 (s,  $C^9$ ), 121.4 (s,  $C^4$ ), 122.6 (s,  $C^1$ ), 126.0 (s,  $C^7$ ), 127.6 (s,  $C^6$ ), 130.5 (s,  $C^2$ ), 140.1 (s,  $C^5$ ), 141.9 (s,  $C^3$ ), 142.4 (s,  $C^{CP}$ ), 149.9 (s,  $C^8$ ). Elemental analysis calcd: C, 87.50; H, 7.89. Found: C, 87.81; H, 7.84. UV-vis ( $C_6H_6$ ):  $\lambda_{max}$

[nm,  $\epsilon_{max}$  (L mol $^{-1}$  cm $^{-1}$ )] 280 (180000), 340 (49000), 370sh (44000).

### Synthesis of **1-Cs**.



To a mixture of **1-H** (411.3 mg, 0.233 mmol, 1.0 equiv) and cesium (34 mg, 0.26 mmol, 1.1 equiv) was added *n*-hexane. The mixture was sonicated at 50 °C for 1.5 h to afford a suspension of a green precipitate. Subsequently, the solvent was removed *in vacuo* and the remaining green solid was extracted with toluene (~5 mL). The solvent was again removed *in vacuo*, and the green powder was dried under reduced pressure to afford analytically pure **1-Cs**:  $C_{135}H_{145}Cs$ ; MW = 1900.55 g/mol; yield 394 mg (89%);  $^1H$  NMR (400 MHz, 300 K,  $C_6D_6$ )  $\delta$  1.15 (s, 90H,  $C^{10}H$ ), 7.32 (m, 20H,  $C^7H$ ), 7.67 (m, 20H,  $C^6H$ ), 7.81 (br s,  $^3J_{HH}$  not resolved, 10H,  $C^2H$ ), 8.02 (br s, 5H,  $C^4H$ );  $^{13}C\{^1H\}$  NMR (100 MHz, 300 K,  $CDCl_3$ )  $\delta$  31.4 (s,  $C^{10}$ ), 34.4 (s,  $C^9$ ), 121.4 (s,  $C^4$ ), 123.0 (s,  $C^1$ ), 126.0 (s,  $C^7$ ), 127.6 (s,  $C^6$ ), 130.5 (s,  $C^2$ ), 140.1 (s,  $C^5$ ), 141.9 (s,  $C^3$ ), 142.4 (s,  $C^{CP}$ ), 149.9 (s,  $C^8$ ). Elemental analysis calcd: C, 85.32; H, 7.69. Found: C, 85.28; H, 7.91. UV-vis ( $C_6H_6$ ):  $\lambda_{max}$  [nm,  $\epsilon_{max}$  (L mol $^{-1}$  cm $^{-1}$ )] 280 (150000), 340 (45000), 370sh (41000).

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.2c00009>.

NMR spectroscopic data of all compounds and crystallographic data for **1-H**, **1-Na·thf**, and **1-K** (PDF)

### Accession Codes

CCDC 2132165–2132167 and 2133268 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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<https://pubs.acs.org/doi/10.1021/acs.organomet.2c00009>

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This paper is dedicated to Prof. Philip P. Power, a pioneer in main group inorganic chemistry. The authors thank Nele Berg and Florian Hastreiter (Universität Regensburg) for the acquisition and analysis of DOSY NMR spectra and Nikolaus Korber (Universität Regensburg) for the generous donation of elemental rubidium and cesium. Michael Bodensteiner (Universität Regensburg) and Hendrik Zipse (LMU München, Munich, Germany) are thanked for valuable discussions and advice. Financial support by the Fonds der Chemischen Industrie (Kekulé fellowship for G.H.), the Deutsche Forschungsgemeinschaft (RTG IonPairs in Reaction, Project 426795949), and the European Research Council (ERC CoG 772299) is gratefully acknowledged.

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