Bulking up $\mathrm{Cp}^{\mathrm{BIG}}$: A Penta-Terphenyl Cyclopentadienyl Ligand

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Supporting Information Placeholder

ABSTRACT: The modification of cyclopentadienyl ligands with carefully selected substituents is a widely used strategy to tune their steric and electronic properties. We describe the synthesis of an extremely bulky penta-terphenyl cyclopentadienyl ligand ($\mathrm{Cp}^{\mathrm{T5}}$) by arylation of cyclopentadiene. Deprotonation reactions with various group 1 metals and bases afforded a complete series of alkali metal salts $\mathrm{MCp}^{\mathrm{T5}}$ with M = Li to Cs. The compounds were isolated as solvate-free salts, which were characterized by multinuclear NMR spectroscopy, UV-vis spectroscopy and elemental analysis. Single-crystal X-ray diffraction studies on $\mathrm{LiCp}^{\mathrm{T5}}$, $\mathrm{NaCp}^{\mathrm{T5}}$ (crystallized as a solvate with one THF molecule per formula unit) and $\mathrm{KCp}^{\mathrm{T5}}$ revealed the formation of metallocene-like sandwich structures in the solid state.

INTRODUCTION

Since the discovery of ferrocene in 1951,[1,2] cyclopentadienyl ligands have developed into one of the most fundamental ligand families in organometallic chemistry and have found widespread use in (asymmetric) catalysis,[3,4] small molecule activation,[5] and coordination chemistry (e.g. for the synthesis of single molecule magnets).[6,7] 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 higher steric protection of the coordinated metal centre. As a consequence, metal complexes become more stable compared to their unsubstituted analogues or possess higher catalytic activity.[8]

The permethylated pentamethylcyclopentadienyl C_5Me_5 (Cp*, Figure 1A) was introduced in 1960 and has developed into a ubiquitous ligand due to its higher steric demand and stronger donating properties.[9] These properties led to isolation of metal complexes which were previously unstable with Cp ligands, e.g. decamethyltitanocene (Figure 1B).[10] Moreover, the introduction of even bulkier substituents such as *tert*-butyl or *iso*-propyl groups has led to cyclopentadienyls with still higher steric demand such as $C_5H_2t\mathrm{Bu}_3$ (Cp‴) and $C_5i\mathrm{Pr}_5$.[11–16] The latter ligand has recently received attention through its capability to stabilise a dysprosium metallocene single-molecule magnet $[(\eta^5\text{-}C_5i\mathrm{Pr}_5)(\mathrm{Cp}^*)\mathrm{Dy}][\mathrm{B}(C_6F_5)_4]$ showing magnetic hysteresis up to 80 K and the linear uranocene $[(\eta^5\text{-}C_5i\mathrm{Pr}_5)_2\mathrm{U}]$.[7,17]

Apart from bulky alkyl substituents, the introduction of aryl substituents on the cyclopentadienyl ring has also been a major focus in this research field. The (nowadays commercially available) pentaphenylcyclopentadienyl ligand has afforded fascinating new structures (Figure 1).[18] For instance, the introduction of a pentaphenylcyclopentadienyl ligand caused the formation of a linear stannocene, whose structure is in contrast to those of $\mathrm{Cp}_2\mathrm{Sn}$ and $\mathrm{Cp}^*{}_2\mathrm{Sn}$, which are significantly bent [Cp(centroid)-Sn-Cp(centroid) angles of 33 and 25°, respectively).[19–21]

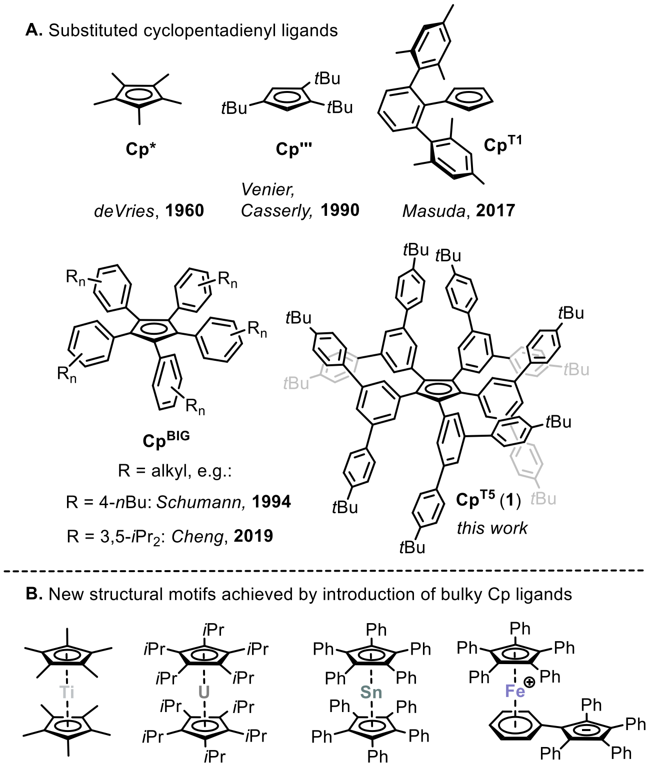


Figure 1. Examples of alkyl- and aryl-substituted cyclopentadienyl ligands (A) and structural motifs stabilised by introduction of bulky cyclopentadienyl ligands (B).[9–12,17,21–25]

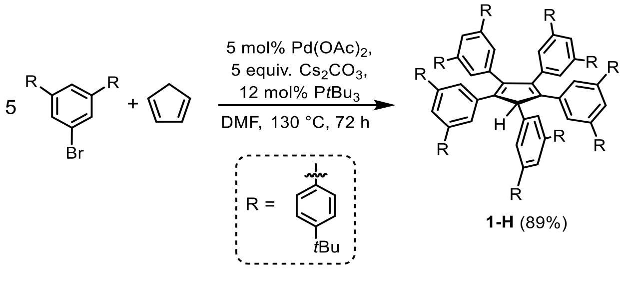
Moreover, the isolation of a linkage isomer of decaphenylferrocene was accomplished.[18,22] Due to poor solubility of pentaphenylcyclopentadienyl complexes in common organic solvents, recent studies have focused on the introduction of substituted arene rings in order to increase solubility. For instance, Harder and co-workers employed the so-called Cp^{BIG} ligand featuring *para*-*n*-butyl groups on the arene rings.[23] Due to high solubility even in *n*-hexane, which commonly hinders purification, and severe disorder in crystallography caused by the *n*-butyl groups, the related *p*-ethyl-substituted ligand has been introduced lately.[26] Furthermore, 3,5-substitution on the arene rings (using groups such as Me, *i*Pr or *t*Bu) has been achieved.[24,27] It is worth noting that the stability of complexes containing pentaarylcyclopentadienyl ligands is provided not only by steric protection of the metal centre, but attractive dispersion interactions between the cyclopentadienyl ligands also play a crucial role.[28]

Herein, we describe the development of a penta-terphenyl cyclopentadienyl ligand with a large three-dimensional profile. For this purpose, a suitable 3,5-terphenyl substituent was chosen in order 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 dimeric structure in combination with potassium.

RESULTS AND DISCUSSION

This study started with the investigation of the palladium-catalysed Heck reaction of suitable 3,5-terphenyl bromides with cyclopentadiene according to the protocol developed by Dyker and Miura.[29] After synthesising three different 3,5-terphenyl bromides 3,5-R_2-C_6H_3Br (R = 4-*t*Bu-C_6H_4, 3,5-*t*Bu_2-C_6H_3 and 2,4,6-Me_3-C_4H_2),[30,31] their behaviour in the Heck reaction was investigated. After work-up, the solids obtained were characterised by ^1H NMR spectroscopy. While the products from the mono- and di-*tert*-butyl substituted terphenyls (R = 4-*t*Bu-C_6H_4 and 3,5-*t*Bu_2-C_6H_3) gave a single set of signals in the alkyl-region, the product from the arylation reaction with the mesityl-substituted terphenyl bromide (R = 2,4,6-Me_3-C_4H_2) contained more than one species, suggesting an unselective reaction which was not pursued further. Analysis of the products from the arylation reactions with 3,5-R_2-C_6H_3Br (R = 4-*t*Bu-C_6H_4 and 3,5-*t*Bu_2-C_6H_3) by LIFDI-MS revealed the formation of the pentaarylated $C_5[3,5\text{-}(4\text{-}t\text{Bu-}C_6H_4)_2C_6H_3]_5H$ (**1-H**, Scheme 1) as evidenced by a molecular ion peak at *m/z* = 1768.262 and the tetraarylated $C_5[3,5\text{-}(3,5\text{-}t\text{Bu}_2\text{-}C_6H_3)_2C_6H_3]_4H_2$ (*m/z* = 1876.448).

Scheme 1. Synthesis of the 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 expected values for C−C single and double bonds [C2−C3: 1.3599(17) and 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 18.0 to 87.8°, which confirms a significant deviation from co-planarity and suggests a sufficient three-dimensional structure for stabilisation of low-coordinate metal complexes. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1-H** show the presence of three signals for the *t*Bu-substituents (δ = 1.33-1.34 ppm). This is in line with the molecular structure determined by X-ray crystallography (*vide supra*) with three inequivalent terphenyl environments. Notably, however, the observation of three signal sets is in contrast to the ^1H NMR spectrum obtained for the 4-Et-Cp^{BIG} ligand, which features only one signal set for the aryl-substituents due to the fast [1,5]-sigmatropic shift of the hydrogen atom bound to the five-membered cyclopentadiene ring. The cyclopentadiene proton of **1-H** was observed at a chemical shift of 5.60 ppm.

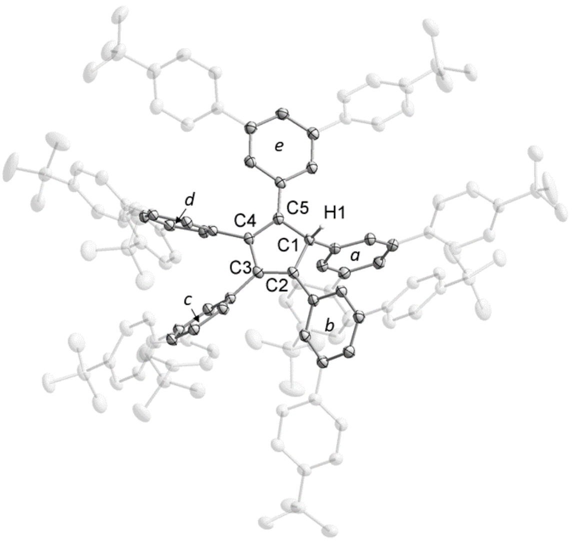


Figure 2. Molecular structure of **1-H** in the solid state. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms (except for H1) and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]:C1−C2 1.5173(17), C2−C3 1.3599(17), C3−C4 1.4741(18), C4−C5 1.3592(17), 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 [°]: a/C1−C5 87.8, b/C1−C5 36.9, c/C1−C5 58.0, d/C1−C5 72.8, e/C1−C5 18.0.

Having substantial amounts of this super-bulky ligand precursor in hand, deprotonation reactions with a variety of alkali metals or alkali metal bases were investigated. The reaction of **1-H** with *n*BuLi proceeded extremely slow even at elevated temperatures. After stirring for four weeks at ambient temperature, a light green solid was obtained. Analysis by ^1H NMR spectroscopy showed just a single aryl-environment similar to that observed in the terphenyl bromide 3,5-(4-*t*Bu-C_6H_4)$_2$-C_6H_3Br. The observation of a single set of aryl signals can be explained by planarisation of the Cp^{T5} ligand and equivalence of the terphenyl substituents and thus is consistent with the formation of $Cp^{T5}Li$ (**1-Li**). Crystals of **1-Li** were obtained from *n*-hexane solutions at ambient temperature and reveal a $[(Cp^{T5})_2Li]^-$ sandwich. Due to poor low angle date, the position of the second lithium atom could not be detected and further analysis of the molecular structure is not possible. Nevertheless, the sandwich structure of **1-Li** is clearly evident from the experiment (Figure 3).

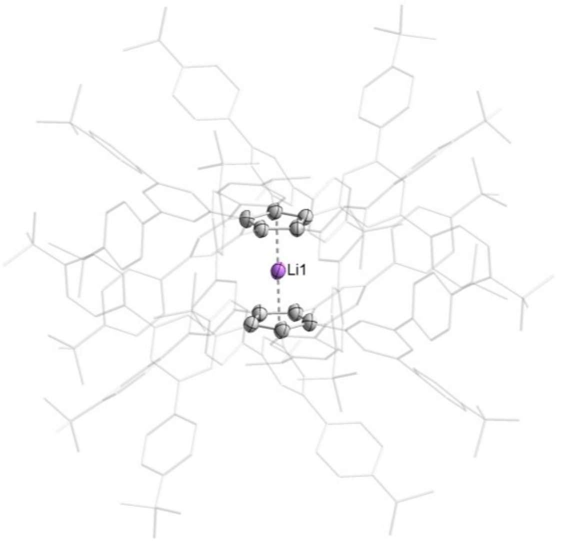


Figure 3. Structural drawing of [(Cp^{T5})Li]$^{-}$ as part of the structure of **1-Li** from a single crystal X-ray diffraction experiment. The position of the second Li^{+} cation was not determined due to strong disorder of this cation. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for 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 elevated temperatures of 80 °C. However, the reaction of sodium hexamethyldisilazide (NaHMDS) with **1-H** in THF produced a light green solid after stirring at 80 °C overnight. Analysis of this solid by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy revealed the formation of five equivalent terphenyl groups. This is indicative for the formation of Cp^{T5}Na (**1-Na**), which was isolated in 21% yield after washing the precipitate formed during the reaction with *n*-hexane.

Upon crystallisation 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^{T5}Li, the single-crystal X-ray structure analysis revealed the formation of a sandwich structure (Figure 4). One Na^{+} cation (Na1) is sandwiched between the cyclopentadienyl rings of two anionic Cp^{T5} ligands. The second Na^{+} cation (Na2) is coordinated by only one Cp^{T5} ligand, and, surprisingly, by two additional THF molecules, which presumably stem from the presenc of traces of THF during crystallisation. Note that no traces of THF were observed in the NMR spectra or elemental analysis of **1-Na** before crystallisation. 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) [Na1–Cp(centroid)] and 2.488(1) Å [Na2–Cp(centroid)]. The Na1–Cp(centroid) distance compares very well to the Na–Cp(centroid) distance observed in NaCp (2.357 Å).[32] The C–C bond lengths within the cyclopentadienyl ring (1.416(3) to 1.430(3) Å) are in the area typically observed for cyclopentadienyl compounds.[32–36] The dimeric structure of **1-Na·thf** is distinct from other sodium cyclopentadienides. Solvent-free NaCp itself features a chain-like structure,[32] and addition of donor-solvents such as THF or DME (1,2-dimethoxyethane) typically break up these chains to afford compounds with a piano-stool structure, e.g. [Cp^{R}Na(thf)$_3$] (Cp^{R} = C$_5$Me$_4$-C≡C-SiMe$_3$).[34–36] **1-Na·thf**, in contrast, features a dimeric structure with a μ^{2}-bridging Cp^{T5} ligand.

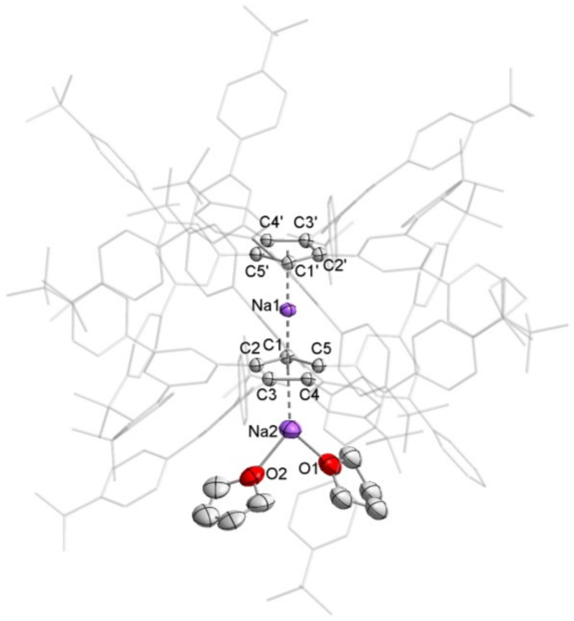
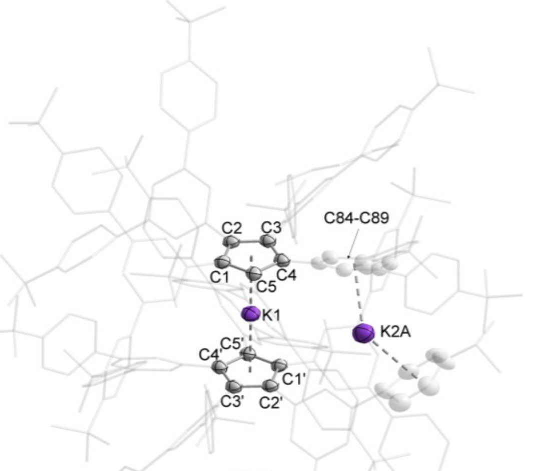


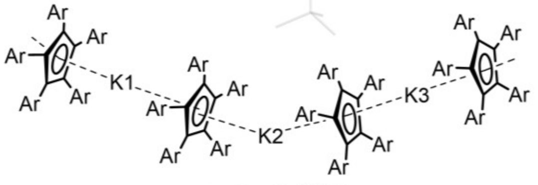
Figure 4. Molecular structure of **1-Na·thf** in the solid state. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms and non-coordinating solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–C2 1.426(3), C2–C3 1.426(3), C3–C4 1.416(3), C4–C5 1.430(3), C5–C1 1.420(3), Na2–O1 2.363(8), Na2–O2 2.236(9), Na1–Cp(centroid) 2.359(3), Na2–Cp(centroid) 2.488(3), Na1–Cp(centroid)–Na2 174.51(3), C5–C1–C2 108.2(2), C1–C2–C3 107.8(2), C4–C3–C2 108.1(2), C3–C4–C5 108.2(2), C1–C5–C4 107.7(2).

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^{BIG}K, 4-*n*-Bu-Cp^{BIG}K) are far more commonly employed. The corresponding potassium salt was therefore also synthesised by deprotonation with KH in THF.[37] Full consumption of **1-H** was observed after stirring the reaction for 18 hours at 60 °C. Analysis of the yellow powder obtained after work-up by ^{1}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.[38] Despite the lack of a definite structural proof by XRD for this compound, **1-K·(thf)$_x$** (with *x* = 2-4 THF molecules) 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 ^{1}H NMR (as an example, see Figure S10**Fehler! Verweisquelle konnte nicht gefunden werden.**). The ^{1}H and ^{13}C{^{1}H} NMR data in C$_6$D$_6$ are similar to **1-Li** and **1-Na** and the elemental analysis on a sample with three coordinating THF molecules supports the THF content determined by ^{1}H NMR spectroscopy.

Next, we sought to deprotonate **1-H** with a potassium base in a non-coordinating solvent. As such, the reaction of **1-H** with potassium metal in *n*-hexane produced a light green powder, which possesses a similar ^{1}H NMR spectrum in C$_6$D$_6$ to **1-K·(thf)$_3$**, 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 dimeric arrangement of two Cp^{T5}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). As a consequence, the C−C bond lengths in these arene rings are slightly elongated (C−C bond lenghts in arene ring C84-C89: 1.403(2)-1.388(3) Å, see Figure 5). The dimeric structure of **1-K** is particularly fascinating considering the distinct (bent) chain-like arrangement of solvent-free 4-*n*-Bu-Cp^{BIG}K in the solid state (Figure 5, bottom).[37] 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^{BIG}K, **1-K** features a slightly longer K1−Cp(centroid) distance (**1-K**: 2.708(3) Å, 4-*n*-Bu-Cp^{BIG}K: K1−Cp(centroid): 2.6464(17) Å; K3−Cp(centroid) 2.6601(16) Å), K2−Cp(centroid) 2.6738(19) Å).[37]



2-K



4-*n*-Bu-Cp^{BIG}K

Ar = 4-*n*-Bu-C_6H_4

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^{BIG}K in the solid state.[37] Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms and non-coordinating solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1−C2 1.425(2), C2−C3 1.418(3), C3−C4 1.416(3), C4−C5 1.421(2), C5−C1 1.417(3), C84−C85 1.403(2), C85−C86 1.391(3), C86−C87 1.388(3), C87−C88 1.400(3), C89−C88 1.397(3), C89−C84 1.394(3), K1−Cp(centroid) 2.708(3), K2A−C38−C42(centroid) 2.867(2), K2A−C85−C89(centroid) 2.826(3), C5−C1−C2 107.77(15), C3−C2−C1 108.15(16), C4−C3−C2 107.84(14), C3−C4−C5 108.27(16), C1−C5−C4 107.98(15).

Metallocenes of s-block elements are rare.[39,40] Paquette and coworkers reported that lithium cyclopentadienyl compounds are speciated in the dimeric form [Li(thf)$_4$][Cp′$_2$Li] (Cp′ = *iso*-dicyclopentadienide) at low temperature by means of variable-temperature NMR studies.[41] Such species can be isolated by introduction of a sterically demanding 4-*t*Bu-Cp^{BIG} ligand, as recently demonstrated by the group of Schulz.[40] Moreover, Harder and co-workers showed that substitution of 0.5 equivalents of the lithium cations with the non-coordinating cation PPh_4^+ results in discrete lithocene anions [Cp$_2$Li]$^-$ in the solid state.[42] However, the formation of dimeric 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.

DOSY NMR measurements suggest that the dimeric structure of **1-K** is not preserved in solution. Using the experimentally observed diffusion coefficient ($4.00 \cdot 10^{-10}$ m^2·s^{-1}), the hydrodynamic radius of the cyclopentadiene **1-H** in C_6D_6 was determined as 9.93 Å using the Stokes-Einstein equation.[43] This is well in line with the molecular structure in the solid state, featuring Cp(centroid)-C(*t*Bu) distances of 8.92 to 10.38 Å. The hydrodynamic radii of **1-K·(thf)$_{2.3}$** and **1-K** dissolved in C_6D_6 were then determined as 10.30 and 10.37 Å, respectively (see the Supporting Information). These data compare well to 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 caesium 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 (M = Rb: 94% and M = Cs: 89%) as analytically pure powders according to NMR spectroscopy and elemental analysis. Unfortunately, crystals of neither of these compounds have been obtained so far.

The entire series of alkali metal salts was also characterised by UV/Vis absorption spectroscopy. All compounds feature absorption bands in the range from 350-370 nm, which account for their yellow colours in solution (see Figures S16 to S21 in the Supporting Information).

CONCLUSION

The extremely bulky cyclopentadienyl ligand Cp^{5T} (**1**) featuring five 3,5-terphenyl substituents can be synthesised in high yield by arylation of cyclopentadiene with the corresponding terphenyl bromide. The 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, 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 the potassium salt reveal dimers of Cp^{T5}M units in the solid state which result in a metallocene sandwich. The second alkali metal could not be located in case of **1-Li**. In **1-Na**, the second sodium cation was coordinated to one cyclopentadienyl ring and two additional THF molecule. The potassium salt **1-K** features a sandwich structure where one potassium cation is coordinated by cyclopentadienyl rings and the other potassium cation is sandwich by arene rings of terphenyl substituents from opposite Cp^{T5} ligands. To our knowledge, this structure is the first example of a potassocene. Our results demonstrate that the high steric demand of Cp^{T5} in combination with its ability to additionally coordinate metal ions gave access to new structural motifs. In future studies, this stabilising effect could be exploited for the synthesis of low coordinate metal complexes.

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_2O and <0.1 ppm O_2). 3,5-R_2-C_6H_3Br (R = 4-*t*Bu-C_6H_4,[30] 3,5-*t*Bu_2-C_6H_3[30] and 2,4,6-Me_3-C_4H_2[31]) and P*t*Bu_3,[44] were prepared according to procedures previously reported in the chemical literature. Cyclopentadiene was obtained from dicyclopentadiene according to a previously reported procedure.[45] It was stored at −30 °C and re-distilled before use. Elemental rubidium and caesium were kindly provided by the group of Prof. Dr. Nikolaus 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 gas-tight 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 and were internally referenced to residual solvent resonances (^1H NMR: C_6D_6: 7.16 ppm $CDCl_3$ 7.26 ppm; $^{13}C\{^1H\}$ NMR: C_6D_6: 128.06 ppm, $CDCl_3$ 77.16 ppm). ^7Li NMR spectra were externally referenced to LiCl in D_2O. Chemical shifts, δ, are given in ppm referring to external standards of tetramethylsilane (^1H, $^{13}C\{^1H\}$). ^1H and ^{13}C NMR signals were assigned based on 2D NMR spectra (^1H,^1H-COSY, ^1H,^{13}C-HSQC, ^1H,^{13}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 Gauss/cm), 5 mm TXI cryo probe and BVT 3000 unit at 298 K. The NMR spectra were processed with the Bruker program TopSpin® 3.2 and the diffusion coefficients were calculated 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 standard. The ^1H-diffusion measurement was performed with the convection suppressing DSTE (double stimulated echo) pulse sequence, developed by Mueller and Jerschow[46] in a pseudo 2D mode. 120 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. Regarding the homospoil gradient strengths, −13.17, 20 and −17.13 G cm^{-1} were used. The length of the gradient pulse δ was adjusted for every species in the sample, giving δ values of 2.4 ms for TMS, 5.0 ms (**1-H**, **1-K·(thf)$_{2.3}$**,) 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.[47–49] The obtained values were: $4.00 \cdot 10^{-10}$ $m^2 \cdot s^{-1}$ (**1-H**), $3.94 \cdot 10^{-10}$ $m^2 \cdot s^{-1}$ (**1-K**) and $3.97 \cdot 10^{-10}$ $m^2 \cdot s^{-1}$ (**1-K·(thf)$_{2.3}$**). With the diffusion coefficients D of the analyte and TMS (standard for viscosity referencing), the hydrodynamic radius r_H of the analyte can be estimated following the Stokes-Einstein equation.[43] The correction factor c of the Stokes-Einstein equation was calculated according to the semi-empirical modification according to Chen.[50] For the present work r_H= 9.93 Å for $Cp^{T5}H$, r_H= 10.30 Å for **1-K** and r_H= 10.37 Å **1-K·(thf)$_{2.3}$** were obtained. This in very good agreement with the crystal derived radii of 8.92 to 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 the University of Regensburg using a Jeol AccuTOF GCX. Elemental analysis were performed by the Central Analytics Department of the University of Regensburg using a Vario micro cube.

Single-crystal X-ray diffraction data were recorded on Rigaku Oxford Diffraction SuperNova Atlas, Rigaku GV 1000 or XtaLAB Synergy R (DW system, Hypix-Arc 150) devices with Cu-K_α 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_2 cooling device. Either semi-empirical multi-scan absorption corrections[51,52] or analytical ones[53] were applied to the data. The structures were solved with SHELXT[54] solution program using dual methods and by using Olex2 as the graphical interface.[55] The models were refined with ShelXL[56] using full matrix least squares minimisation on F^2.[57] 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-Na·thf** and **1-K** and the presence of *n*-hexane was confirmed.

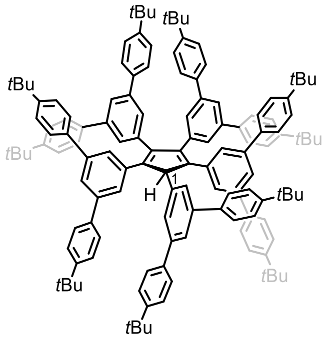
Further details on the single crystal X-ray diffraction studies are given in the Supporting Information.

Synthesis of $Cp^{T5}H$ (1-H).

This compound was prepared according to an adapted literature procedure from Dyker and Miura.[29] Only four equivalents of 3,5-(4-*t*Bu-C_6H_4)$_2C_6H_3Br$ referring to cyclopentadiene were used; the use of five equivalents resulted in unconsumed starting material, which proved to be difficult to separate from the product.

Solid 3,5-(4-*t*Bu-C_6H_4)$_2C_6H_3Br$ (**1**, 10.0 g, 23.7 mmol, 5.0 equiv.), $Pd(OAc)_2$ (67.0 mg, 5.9 mmol, 0.05 equiv.) and Cs_2CO_3 (9.7 g, 29.7 mmol, 6.3 equiv.) were combined. Subsequently, freshly distilled cyclopentadiene (0.5 mL, 5.9 mmol, 1.2 equiv.), P*t*Bu_3 (144.0 mg, 0.7 mmol, 0.15 equiv.) and DMF (35 mL) were added. The reaction mixture was heated for 72 hours to 130 °C, affording a deep green suspension. After cooling to ambient temperature, DCM (300 mL) and *para*-toluenesulfonic acid monohydrate (9.0 g, 47.4 mmol, 10.0 equiv.) were added. The red-brown suspension was filtered over silica (5 cm x 20 cm) using DCM as eluent. DCM was removed under reduced pressure. The DMF-containing brown oil was added dropwise to water (500 mL), affording a light brown solid which was isolated by filtration and dried at 80 °C *in vacuo*.

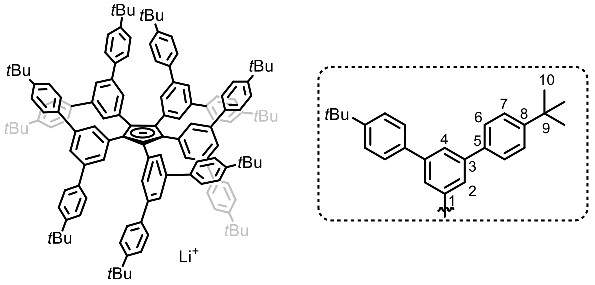
Crystals suitable for single crystal X-ray diffraction were obtained from a saturated solution of **1-H** in *n*-hexane.



$C_{135}H_{146}$, MW = 1768.65 g/mol. Yield: 7.5 g (89%, referenced to terphenyl bromide). ^1H NMR (400 MHz, 300 K, $CDCl_3$) δ = 1.33 (s, 36H, *t*Bu), 1.33 (s, 36H, *t*Bu), 1.34 (s, 18H, *t*Bu), 5.60 (s, 1H, C^1H), 7.26-7-66 (s, 33H, $C^{Ar}H$), 7.75 (t, J_{HH} = 1.60 Hz, 2H, $C^{Ar}H$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 300 K, $CDCl_3$) δ = 31.5 (s, C-CH_3), 34.6 (s, *C*-CH_3), 34.7 (s, *C*-CH_3), 62.4 (s, C^1), 123.9 (s, CH^{Ar}), 124.7 (s, CH^{Ar}), 125.7 (s, CH^{Ar}), 125.9 (s, CH^{Ar}), 126.7 (s, CH^{Ar}), 126.9 (s, CH^{Ar}), 127.0 (s, CH^{Ar}), 127.15 (s, CH^{Ar}), 127.21 (s, CH^{Ar}), 128.4 (s, CH^{Ar}), 136.1 (s, $C^{Ar/Cp}$), 137.7 (s, $C^{Ar/Cp}$), 138.4 (s, $C^{Ar/Cp}$), 138.5 (s, $C^{Ar/Cp}$), 138.5 (s, $C^{Ar/Cp}$), 139.8 (s, $C^{Ar/Cp}$), 141.0 (s, $C^{Ar/Cp}$), 141.9 (s, $C^{Ar/Cp}$), 142.0 (s, $C^{Ar/Cp}$), 145.3 (s, $C^{Ar/Cp}$), 146.5 (s, $C^{Ar/Cp}$), 150.1 (s, $C^{Ar/Cp}$), 150.28 (s, $C^{Ar/Cp}$), 150.37 (s, $C^{Ar/Cp}$) ppm. 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 (8 signals each) and from overlapping cyclopentadiene signals expected for C_{2v} 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 **Fehler! Verweisquelle konnte nicht gefunden**

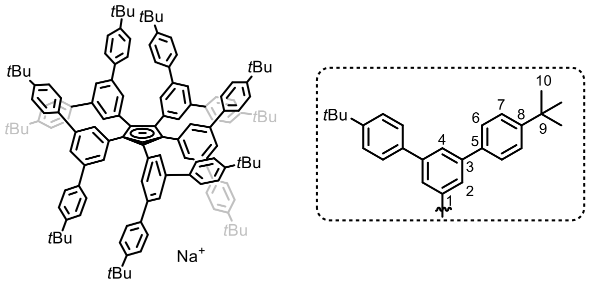
werden., SI). Elemental Analysis calcd. C 91.68, H 8.32; found C 91.70, H 8.31. LIFDI-MS *m/z* = 1768.262.

Synthesis of 1-Li: To a solution of Cp^{T5}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**.



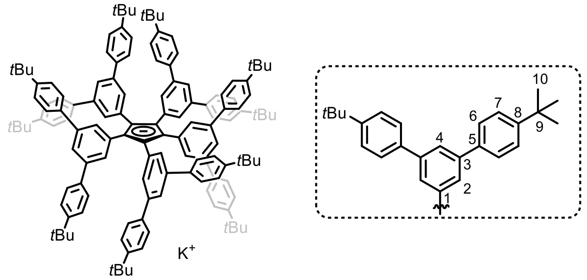
$C_{135}H_{145}Li$, MW = 1774.59 g/mol. Yield: 164 mg (81%). ^1H NMR (400 MHz, 300 K, C_6D_6) δ = 1.16 (s, 90H, $C^{10}H$), 7.33 (m, 20H, C^7H), 7.63 (m, 20H, C^6H), 7.77 (d, $^3J_{HH}$ = 1.60 Hz, 10H, C^2H), 8.04 (t, $^3J_{HH}$ = 1.60 Hz, C^4H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 300 K, C_6D_6) δ = 31.4 (s, C^{10}), 34.4 (s, C^9), 120.2 (s, C^1), 122.6 (s, C^4), 126.2 (s, C^7), 127.4 (s, C^6), 130.3 (s, C^2), 139.7 (s, C^5), 139.8 (s, C^{Cp}), 141.9 (s, C^3), 150.0 (s, C^8) ppm. ^7Li NMR (155 MHz, 300 K, C_6D_6) 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_{max} (nm, ε_{max} /L·mol^{-1}·cm^{-1}) 220 (200 000), 255 (290 000), 350sh (27 000).

Synthesis of 1-Na: To a mixture of Cp^{T5}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 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 x 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_6H_6. Despite several crystallisation attempts, the presence of minor amounts of THF (presumably contamination from the atmosphere of the glove box) caused crystallisation of **1-Na·thf**. Attempts to crystallise **1-Na** from freshly distilled benzene and *n*-hexane did not afford crystals suitable for single-crystal X-ray diffraction.



$C_{135}H_{145}Na$, MW = 1790.63 g/mol. Yield: 76 mg (21%). ^1H NMR (400 MHz, 300 K, C_6D_6) δ = 1.16 (s, 90H, $C^{10}H$), 7.32 (m, 20H, C^7H), 7.64 (m, 20H, C^6H), 7.85 (d, $^3J_{HH}$ = 1.50 Hz, 10H, C^2H), 8.01 (t, $^3J_{HH}$ = 1.50 Hz, C^4H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 300 K, C_6D_6) δ = 31.4 (s, C^{10}), 34.4 (s, C^9), 121.2 (s, C^4), 121.9 (s, C^1), 126.1 (s, C^7), 127.5 (s, C^6), 130.5 (s, C^2), 139.9 (s, C^5), 141.5 (s, C^3), 142.0 (s, C^{Cp}), 149.9 (s, C^8) ppm. Elemental Analysis calcd. C 90.55, H 8.16; found C 89.55, H 8.04. UV/Vis (*n*-hexane): λ_{max} (nm, ε_{max} /L·mol^{-1}·cm^{-1}) 220 (140 000), 255 (220 000), 350sh (24 000).

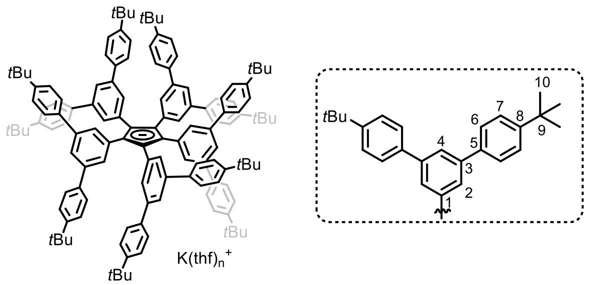
Synthesis of 1-K: To a mixture of Cp^{T5}H (461.4 mg, 0.26 mmol, 1.0 equiv.) and potassium (10.2 mg, 0.26 mmol, 1.0 equiv.) was added *n*-hexane (2 mL). After stirring at ambient temperature overnight, only a small amount of precipitate formed. The reaction was then heated to 50 °C for 6 hours and formation of more green precipitate was observed. The solid was isolated by filtration, washed with cold (−20 °C) *n*-hexane (3 x 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) δ = 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) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 300 K, $CDCl_3$) δ = 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) ppm. Elemental Analysis calcd. C 89.75, H 8.09; found C 87.40, H 8.17. UV/Vis (*n*-hexane): λ_{max} (nm, ε_{max} /L·mol^{-1}·cm^{-1}) 220 (160 000), 250 (250 000), 360 (31 000).

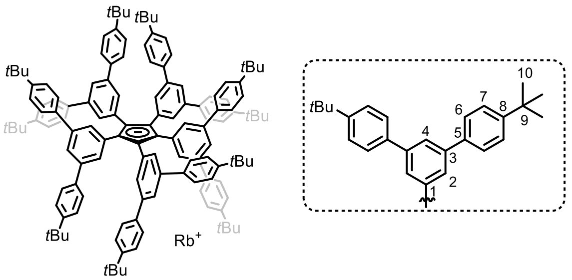
Synthesis of 1-K·(thf)$_x$ (x = 2-4):

To a mixture of Cp^{T5}H (6.0 g, 3.4 mmol, 1.0 equiv.) and KH (0.54 g, 6.8 mmol, 4.0 equiv.) was added THF (120 mL). The green suspension was stirred at 60 °C for 18 hours. 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).



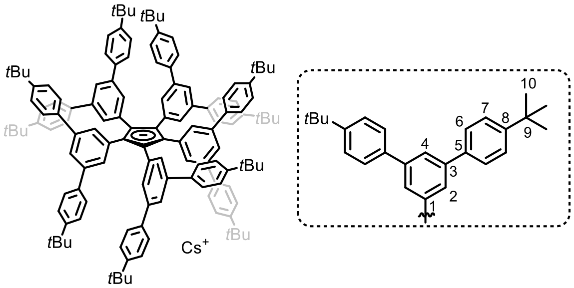
$C_{135}H_{145}K(C_4H_8)_n$, *n* = 3-4, MW = 2023.06 g/mol (n = 3). Yield: 6.52 g (95%). For full characterisation of this compound, a sample with THF-content of *n* = 3 was chosen (determined by integration of the ^1H NMR signals, see **Fehler! Verweisquelle konnte nicht gefunden werden.**). ^1H NMR (400 MHz, 300 K, C_6D_6) δ = 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) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 300 K, $CDCl_3$) δ = 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) ppm. Elemental Analysis calcd. C 87.27, H 8.42; found C 87.40, H 8.17. UV/Vis (*n*-hexane): λ_{max} (nm, ε_{max} /L·mol^{-1}·cm^{-1}) 220 (190 000), 255 (280 000), 355 (45 000).

Synthesis of 1-Rb: To a mixture of Cp^{T5}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 hours to afford a suspension of a green precipitate. Subsequently, the solvent was removed *in vacuo* and the remaining green solid was extracted with toluene (ca. 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) δ = 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) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 300 K, C_6D_6) δ = 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) ppm. Elemental Analysis calcd. C 87.50, H 7.89; found C 87.81, H 7.84. UV/Vis (C_6H_6): λ_{max} (nm, ε_{max} /L·mol^{-1}·cm^{-1}) 280 (180 000), 340 (49 000), 370sh (44 000).

Synthesis of 1-Cs: To a mixture of $Cp^{T5}H$ (411.3 mg, 0.233 mmol, 1.0 equiv.) and caesium (34 mg, 0.26 mmol, 1.1 equiv.) was added *n*-hexane. The mixture was sonicated at 50 °C for 1.5 hours to afford a suspension of a green precipitate. Subsequently, the solvent was removed *in vacuo* and the remaining green solid was extracted with toluene (ca. 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) δ = 1.15 (s, 90H, $C^{10}H$), 7.32 (m, 20H, C^7H), 7.67 (m, 20H, C^7H), 7.81 (br s, $^3J_{HH}$ not resolved, 10H, C^2H), 8.02 (br s, 5H, C^4H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 300 K, $CDCl_3$) δ = 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) ppm. Elemental Analysis calcd. C 85.32, H 7.69; found C 85.28, H 7.91. UV/Vis (C_6H_6): λ_{max} (nm, ε_{max} /L·mol^{-1}·cm^{-1}) 280 (150 000), 340 (45 000), 370sh (41 000).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information (SI) is available free of charge on the ACS Publications website.

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

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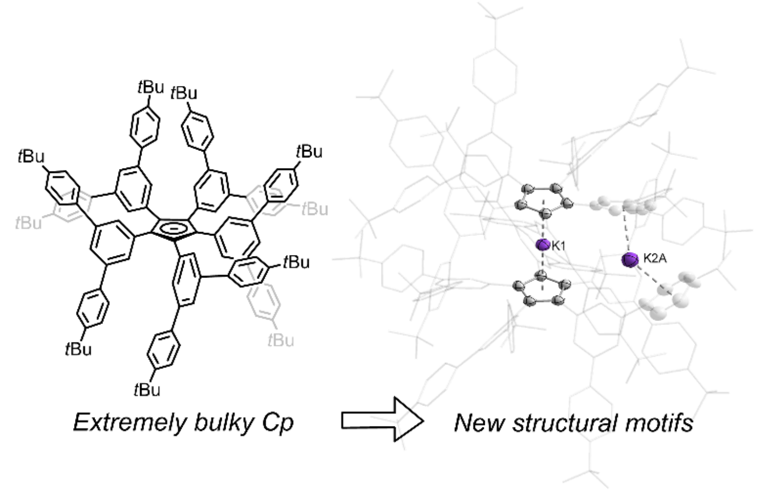
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