Synthesis and Structures of s- and p-Block Metal Complexes Containing Sterically Demanding Pentaarylcyclopentadienyl Substituents.

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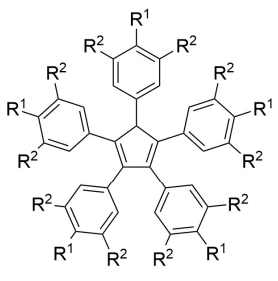
ABSTRACT: The synthesis of alkali metal salts of sterically demanding cyclopentadienyls $Cp^{BIGi\text{-}Pr}M$ ($Cp^{BIGi\text{-}Pr}$ = Cp(4-*i*-Pr-Ph)$_5$; M = Li **1**, Na **2**, K **3**, Rb **4**, Cs **5**), $Cp^{BIGn\text{-}Bu}M$ ($Cp^{BIGn\text{-}Bu}$ = Cp(4-*n*-Bu-Ph)$_5$; M = Li **6**, Na **7**, K **8**, Rb **9**, Cs **10**) and $Cp^{BIGt\text{-}Bu}M$ ($Cp^{BIGt\text{-}Bu}$ = Cp(4-*t*-Bu-Ph)$_5$; M = Li **11**, Na **12**, K **13**, Rb **14**, Cs **15**) and their complete characterization including IR and heteronuclear (^{1}H, ^{13}C, ^{7}Li, ^{23}Na, ^{87}Rb, ^{133}Cs) NMR spectroscopy is reported. In addition, the solid-state structures of **5**, **10**, **11**, and **13** were determined by single crystal X-ray diffraction, revealing the formation of infinite one-dimensional chain structures in the solid state (**5**, **10**) or solvents-separated ion pairs (**11**, **13**). Salt elimination reactions of $Cp^{BIGt\text{-}Bu}K$ **13** with ECl_3 yielded the mono-substituted cyclopentadienyl compounds $Cp^{BIGt\text{-}Bu}ECl_2$ (E = P **16**, As **17**, Sb **18**, Bi **19**), which were characterized by elemental analysis, IR, and heteronuclear (^{1}H, ^{13}C, ^{31}P) NMR spectroscopy and single crystal X-ray diffraction (**17**).

INTRODUCTION

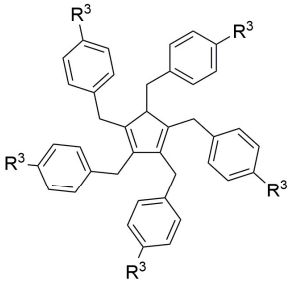
Since the discovery of ferrocene in 1951,[1,2] the monoanionic cyclopentadienyl (Cp = C_5H_5) ligand has become one of the most popular ligands in organometallic synthesis.[3,4] Because of its high stability, the cyclopentadienyl group often acts as a *spectator ligand,* for example in organometallic catalysis.[5] A feature of the cyclopentadienyl group, which is useful in this kind of applications, is its ability to bind to a metal center with varying hapticity.[6] Moreover the steric bulk and electronic influence of the cyclopentadienyl moiety can easily be modified by incorporation of different substituents to the cyclopentadienyl ring, resulting in the formation of mono-, di-, tri-, tetra- and pentasubstituted cyclopentadienyls of the general type $C_5H_{5-x}R_x$ (x = 1 - 5; R = Me, Et, *i*-Pr, *t*-Bu, benzyl).[6] The most prominent example for this strategy is the pentamethylcyclopentadienyl (Cp* = C_5Me_5) ligand, which is sterically more demanding as well as stronger electron donating than the unsubstituted Cp ligand. This ligand has been widely applied in the synthesis of metal complexes of main group and transition metals as well as lanthanides, including complexes in which the metal centers adopt unusual oxidation states such as +I in group 12 ($Cp^*_2Zn_2$)[7] or group 13 complexes of the type $[Cp^*M]_x$ (M = Al, Ga, In),[8-11] respectively.

In addition to alkyl-substituted cyclopentadienyl substituents, the synthesis of several symmetrically substituted pentaarylcyclopentadienes has been reported. Pentaphenylcyclopentadiene $Cp^{Ph}H$ (Cp^{Ph} = C_5Ph_5) was first prepared in 1925.[12] This research was strongly motivated by the search for the pentaphenylcyclopentadienyl radical (Cp^{Ph}·). Since then, several pentaphenylcyclopentadienyl complexes of both transition and main group metals have been synthesized and some of them were used in asymmetric catalysis.[13] This specific ligand is known to greatly enhance selectivity in some cases, most likely caused by its high steric bulk and conformational rigidity.[14,15] Unfortunately, their applicability in organic reactions is sometimes hampered by their low solubility in organic solvents. A promising method to overcome this experimental problem is the use of *para*-alkyl-substituted pentaarylcyclopentadienyl ligands C_5(p-alkyl-Ph)$_5$[16-19] such as pentakis-(4-*n*-butylphenyl)cyclopentadienyl (Cp^{Big} = C_5(p-*n*-Bu-Ph)$_5$)[16] as well as the corresponding pentakis-(4-ethylphenyl)cyclopentadienyl (C_5(p-Et-Ph)$_5$) and pentakis-(4-*i*-propylphenyl)cyclopentadienyl derivatives (C_5(p-*i*-Pr-Ph)$_5$).[20] In addition, the introduction of (bulky) substituents in *para*-position furthermore enhances the steric bulk of the ligand.

Scheme 1: Symmetrically alkyl-substituted pentaaryl- and pentabenzylcyclopentadienes.[13,20-25]



R^1 = H, R^2 = Me, *t*-Bu
R^2 = H, R^1 = Me, Et, Pr, *i*-Pr, Bu, Pentyl, Heptyl



R^3 = H, Me, *i*-Pr

These sterically demanding cyclopentadienyl ligands were successfully applied in the synthesis of decaarylmetallocenes $M[C_5(p\text{-}R\text{-}Ph)_5]_2$, which were found to form relatively strong "merry-go-round" hydrogen bond networks between the neighboring pentaarylcyclopentadienyl ligands, thus favoring the homoleptic and linear coordination of a metal center by two cyclopentadienyl ligands. Quantum chemical calculations at the DFT+D- level of theory showed a combined interaction energy of −87.2 kJ mol^{-1} for all ten hydrogen bonds.[17] Such intramolecular interactions also favor the formation of linear metallocenes even for main group metals such as Ge, Sn, Pb and alkaline-earth metals,[26-30] which typically form bent-type metallocenes with less bulky cyclopentadienyl ligands.[31-35] Moreover, the formation of the hydrogen bond network was assumed to play a major role in the spontaneous reduction of Ln(III) precursors to $Ln(Cp^{Big})_2$ complexes (Ln = Yb, Sm).[36]

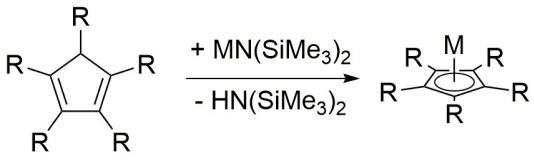
Our long-term interest in the synthesis and reactivity of low-valent organometallic reagents such as Cp*Al, Cp*Ga and $Cp^*_2Zn_2$, which has only recently resulted in the stabilization of unusual bonding situations such as stable metal-centered radicals or π-bonded complexes,[37-41] prompted our attention towards the synthesis of sterically more demanding pentaarylcyclopentadienyl ligands (Cp^{Big}), which are expected to kinetically-stabilize the corresponding (low-valent) metal complexes. Moreover, they may also be applied in the synthesis of metal-centered radicals, which are accessible after homolytic metal-Cp bond breakage, as well as of cluster-type metal complexes, which may be formed by oligomerization of metal-centered radicals. The homolytic cleavage of the metal-carbon bond is expected to be favored with increasing steric demand of the cyclopentadienyl substituents as well as with increasing stability of as-formed cyclopentadienyl radical. In contrast, sterically less demanding Cp substituents such as the widely applied pentamethylcyclopentadienyl ligand (Cp*) often undergo heterolytic metal-Cp bond cleavage reactions, including β-hydride abstraction reactions.[42,43]

We herein report on the synthesis of 15 alkali metal complexes containing three bulky pentaarylcyclopentadienyl ligands - $Cp^{BIGi\text{-}Pr}$, $Cp^{BIGn\text{-}Bu}$ and $Cp^{BIGt\text{-}Bu}$ - by amine elimination reaction of the cyclopentadienes with the corresponding metal amide $MN(SiMe_3)_2$ (M = Li - Cs). The effect of three different alkyl substituents with different steric demand in *para*-position (*n*-Bu, *i*-Pr, *t*-Bu) of the aryl groups on both their solubility in organic solvents, which is a pre-requisite for their use in salt elimination reactions, as well as on their solid-state structures was studied in detail. Our studies revealed that the $Cp^{BIGt\text{-}Bu}$-substituted complexes exhibit the best crystallizing abilities. Moreover, the potassium complexes are well suited for salt metathesis reactions as was demonstrated in reactions of $Cp^{BIGt\text{-}Bu}K$ **13** with pnictogen chlorides ECl_3 (E = P, As, Sb, Bi), yielding the corresponding heteroleptic complexes $Cp^{BIGt\text{-}Bu}ECl_2$.

RESULTS AND DISCUSSION

Cyclopentadienes $Cp^{BIGi\text{-}Pr}H$, $Cp^{BIGn\text{-}Bu}H$, and $Cp^{BIGt\text{-}Bu}H$ were synthesized by the Pd-catalyzed reaction of zirconocene dichloride (Cp_2ZrCl_2) with the corresponding aryl bromides according to a literature method and characterized by ^1H NMR spectroscopy.[44-46] The compounds were purified by purified by flash column chromatography followed by recrystallization from different solvents (see experimental details). The ^1H NMR spectra show a free rotation of the aryl substituents, which is consistent with C_s symmetric structures in solution. Reactions of the cyclopentadienes with equimolar amounts of alkali metal amides $MN(SiMe_3)_2$ (M = Li, Na, K, Rb, Cs) at ambient temperature proceeded with elimination of bis(trimethylsilyl)amine ($HN(SiMe_3)_2$) and subsequent formation of the corresponding metal cyclopentadienyls, which were isolated in high yields as colorless, crystalline solids.

Scheme 2. Synthesis of 1 - 15.



R = 4-*n*-Bu-Ph, 4-*i*-Pr-Ph, 4-*t*-Bu-Ph
M = Li, Na, K, Rb, Cs

Table 1: Numbering scheme of pentaarylcyclopentadienyl alkaline metal compounds.

metal	R = 4-*i*-Pr-Ph	R = 4-*n*-Bu-Ph	R = 4-*t*-Bu-Ph
Li	**1**	**6**	**11**
Na	**2**	**7**	**12**
K	**3**	**8**	**13**
Rb	**4**	**9**	**14**
Cs	**5**	**10**	**15**

Compounds **1** to **15** are soluble in organic solvents such as acetonitrile, toluene and THF, respectively. ^1H (Table S1 **1**-**5**, S3 **6**-**10**, S5 **11**-**15**) and ^{13}C NMR spectra (Table S2 **1**-**5**, S4 **6**-**10**, S6 **11**-**15**) show the expected resonances of the cyclopentadienyl substituents. ^{13}C NMR resonances of the C_5 ring are almost identical for **1** - **15**, proving the ionic nature of the metal cyclopentadienyl groups. In addition, the metal cyclopentadienyls except for the potassium salts (**3**, **8**, **13**) were characterized by heteronuclear (^7Li, ^{23}Na, ^{87}Rb, ^{133}Cs) NMR spectroscopy.

Unfortunately, most of the metal cyclopentadienyl complexes could not be structurally characterized by single crystal X-ray diffraction due to severe disorder problems, most likely caused by the incompatibility of the 5-fold symmetry of the ligand with a gap-less periodic packing. The resulting voids leave enough room for disordered solvent molecules or allow the alkyl substituents to occupy more than one position, particularly in case of the *n*-Bu substituted complexes. In contrast, *i*-Pr and *t*-Bu groups have less degrees of conformational freedom, giving data sets of higher quality for the $Cp^{BIGi\text{-}Pr}M$ and $Cp^{BIGt\text{-}Bu}M$ complexes **5** (two different solvates **5a**: THF, **5b**: MeCN), **11**, and **13** (two different solvates **13a**: THF, **13b**: MeCN), respectively. In addition, a dataset of lower quality was obtained for **10**, which allowed the determination of the connectivity.

The Cs compounds crystallize in the monoclinic space group $P2_1/c$ with two (**5a**, figure 1; **10**, figure S72) and five (**5b**, figure 2) $Cp^{BIG}Cs$ units in the asymmetric unit, respectively. They form infinite one-dimensional chains via translational symmetry in the solid state, in which the Cs atom is fivefold coordinated by two Cp^{BIG} ligands. Similar chain-type structures were previously reported for alkali metal cyclopentadienyl (CpM) and pentamethylcyclopentadienyl complexes (Cp*M), respectively,[6] as well as $Cp^{BIGn\text{-}Bu}K$[16] and $Cp^{BIG3,5\text{-}di\text{-}t\text{-}Bu}Li$ ($^{CpBIG3,5\text{-}di\text{-}t\text{-}Bu}$ = $Cp(3,5\text{-}t\text{-}Bu_2\text{-}Ph)_5$).[20] The conformation of the polymer is determined by the number of additional solvent molecules coordinated to the Cs atoms. The $Cp_{centr.}$-Cs-$Cp_{centr.}$ angle was found to strongly depend on the number of additional solvent molecules coordinating to the Cs center. The bond angle decreases from 170° in case of solvent-free complexes to approximately 150° with one donor molecule, whereas bond angles of roughly 140° are observed for complexes in which the Cs atom is coordinated by two solvent molecules. Comparable values (136 - 146°) were reported for solvent-coordinated CpM and Cp*M complexes.[47]

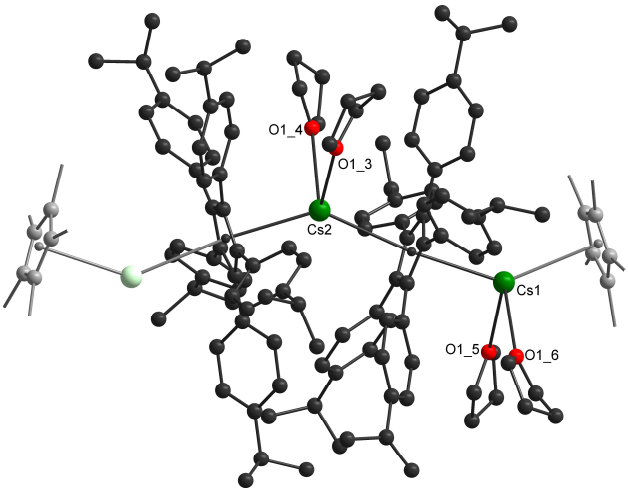


Figure 1. Solid state structure of thf-coordinated $Cp^{BIGi\text{-}Pr}Cs$ (**5a**); H atoms and disordered/non-coordinated solvent molecules are omitted for clarity; atoms displayed as spheres of arbitrary radii. The part in pale colors is generated via symmetry.

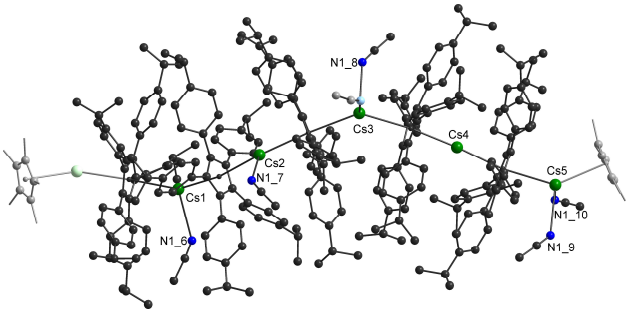


Figure 2. Solid state structure of MeCN-coordinated $Cp^{BIGi\text{-}Pr}Cs$ (**5b**); H atoms and disordered/non-coordinated solvent molecules are omitted for clarity; atoms displayed as spheres of arbitrary radii. The part in pale colors is generated via symmetry. The acetonitrile molecule in pale colors at Cs3 is disordered over a center of inversion and thus occupied by 0.5 only.

In contrast, the "solvent-free" Cs atom in $Cp^{BIGi\text{-}Pr}Cs$ **5b** shows an almost linear coordination ($Cp_{centr.}$-Cs4-$Cp_{centr.}$ 170°), which is rather surprising since solvent-free cyclopentadienyl complexes (CpM, M = Li 180°, Na 180°, K 137°, Rb 123°-136°, Cs 129°) and pentamethylcyclopentadienyl complexes (Cp*M, M =Li 180°, Na 180°, Rb 131° from powder data, Cs 129° from powder data) typically show a decreasing bond angle with increasing atomic number of the alkali metal. $Cp^{BIGn\text{-}Bu}K$ **8**, which is the only structurally characterized solvent free Cp^{BIG} complex, to date,[16] shows angles of 155° and 163°, respectively, proving that a bent structure is possible even in case of sterically extremely demanding Cp^{BIG} substituents. In $Cp^{BIGi\text{-}Pr}Cs$ **5a** and $Cp^{BIGn\text{-}Bu}Cs$ **10** the $Cp_{centr.}$-Cs-$Cp_{centr.}$-Cs torsion are – due to symmetry – exactly 180°. This is also true for all other structurally characterized Cp^RM complexes. The Z' of 5 in 5b allows deviations from torsion (torsions angle vary from 18° to 128°), resulting in a helical conformation of the chains.

$Cp^{BIGt\text{-}Bu}Li$ **11** crystallizes in the monoclinic space group $C2/c$ with half a cation and half an anion in the asymmetric unit (figure 3), whereas both solvates of $Cp^{BIGt\text{-}Bu}K$ **13** crystallize in the triclinic space group $P\text{-}1$ (figure 4).

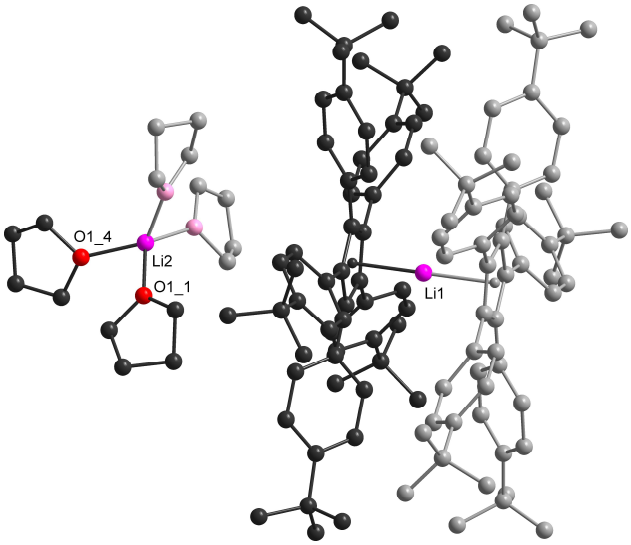


Figure 3. Solid state structure of thf-coordinated $Cp^{BIGt\text{-}Bu}Li$ (**11**); H atoms and disordered/non-coordinated solvent molecules are omitted for clarity; atoms displayed as spheres of arbitrary radii. The part in pale colors is generated via symmetry.

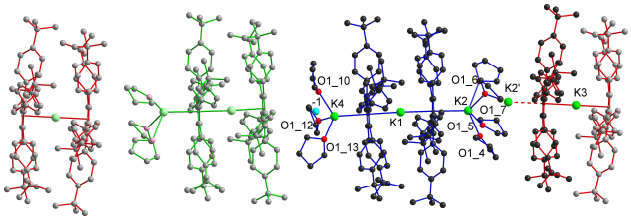


Figure 4. Solid state structure of thf-coordinated $Cp^{BIGt\text{-}Bu}K$ (**13a**); H atoms and disordered/non-coordinated solvent molecules are omitted for clarity; atoms displayed as spheres of arbitrary radii. The part in pale colors is generated via symmetry. The potassocene anion is displayed with red bonds, the cation with blue ones and the neutral moiety in green. K4 is disordered over the center of inversion (cyan dot). The alternate position of K2 leads to anion and cation changing places.

The chain-type structure as observed for **5a** and **10** is disrupted in both compounds by coordination of solvent molecules, resulting in the formation of ion pairs. The $[Li(thf)_4]^+$ cation and the lithocene $[Cp^{BIGt\text{-}Bu}_2Li]^-$ anion in **11** are located on special positions, 4*e* and 4*c*, respectively, which is most likely caused by the high steric demand of the $Cp^{BIGt\text{-}Bu}$ ligands. Bending of the linear chain upon coordination of a solvent molecule is disfavored, since this is expected to result in strong repulsive interactions between the $Cp^{BIGt\text{-}Bu}$ ligands. A comparable structure was observed for $Cp^{BIG3,5\text{-}di\text{-}t\text{-}Bu}Li$, in which the one-dimensional chain is separated into $[Cp^{BIG}_2Li]^-$ anions and $[Cp^{BIG}_2Li_3(solv)]^+/[Li(solv)]^+$ cations.[23] The formation of solvent separated ion pairs is typically observed for Cp complexes of light-weighted alkali metals, but several Cp-complexes including light-weighted alkali metals such as Na are known, in which the chain-like structure is retained upon coordination of additional solvent molecules.[48,49]

Two different solvent-coordinated potassium complexes (**13a**, **13b**) were structurally characterized. An inverse triple-decker potassocene cation $[(Cp^{BIGt\text{-}Bu})_2K_3(solv)_n]^+$ as well as potassocene anions $[Cp^{BIGt\text{-}Bu}_2K]^-$ were observed in both structures, and **13a** also indicates a neutral $[Cp^{BIGt\text{-}Bu}_2K_2(solv)_n]$ moiety (see experimental section for details). In the thf solvate **13a**, the potassocene $[Cp^{BIGt\text{-}Bu}_2K]^-$ anion is located on a center of inversion and the $(Cp^{BIGt\text{-}Bu})_2K_3(thf)_7^+$ cation on a general position. One of the potassium atoms and the coordinated thf molecules are disordered over a center of inversion, resulting in an occupation of 0.5, i.e. the cation shares its position with a $[Cp^{BIGt\text{-}Bu}_2K_2(solv)_n]$ moiety (see experimental section for details). The overall arrangement of the molecules/ions still resembles a chain. In **13b** both the cation and the anion are located on a center of inversion. In all moieties the $Cp_{centr.}$-M-$Cp_{centr.}$ angles are either close to linear or exactly linear due to symmetry. These findings agree very well to the calculated structure of the potassocene anion $[Cp_2K]^-$, which also showed a linear coordination geometry.[50] The phenyl rings of the Cp^{BIG} are as observed before not co-planar with the central five-membered ring allowing edge to face CH···π interaction within the Cp^{BIG}_2M units. The M···Cp_{centr} distance increases with the size of the alkali metal (**11**: 2.10 Å, **13a**: 2.62 Å, **13b**: 2.70 Å (anion) 2.72/3.00 Å (cation), **5b**: 2.94/2.95 Å (linear chain-link)). This matches well with values observed earlier in $Cp^{BIG3,5\text{-}di\text{-}t\text{-}Bu}Li$.[20]

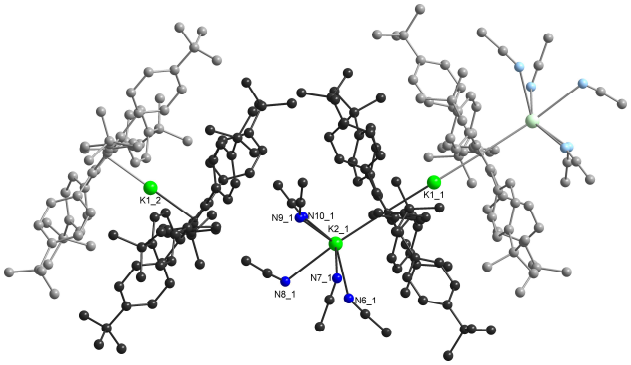
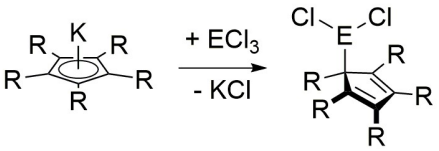


Figure 5. Solid state structure of MeCN -coordinated $Cp^{BIGt\text{-}Bu}K$ (**13b**); H atoms and disordered/non-coordinated solvent molecules are omitted for clarity; atoms displayed as spheres of arbitrary radii. The part in pale colors is generated via symmetry.

Alkali metal pentaarylcyclopentadienyl complexes **1** - **15** are of potential interest as Cp-transfer reagents in metal organic synthesis. Our interest in main group metal cyclopentadienyls prompted us to investigated reactions with group ECl_3 (E = P - Bi). To date, 39 pnictogen complexes of the type Cp^XEX_2, Cp^X_2EX or Cp^X_3E (Cp^X any kind of Cp ligand) have been structurally characterized.[51] Since the $Cp^{BIGt\text{-}Bu}$-substituent showed far less disorder problems compared to the *n*-Bu and *i*-Pr substituted analogues, $Cp^{BIGt\text{-}Bu}K$ **13** was used for salt metathesis reactions with pnictogen chlorides ECl_3 (E = P, As, Sb, Bi).

Reactions of $Cp^{BIGt\text{-}Bu}K$ **13** with ECl_3 (E = P, As, Sb, Bi) occurred with elimination of KCl and formation of $Cp^{BIGt\text{-}Bu}ECl_2$ (E = P **16**, As **17**, Sb **18**, Bi **19**), which were isolated after recrystallization from solutions in *n*-hexane as colorless crystalline solids in almost quantitative yields. Unfortunately, X-ray quality single crystals were only obtained for **17**. ^1H and ^{13}C NMR spectra (Tables S5, S6) of **16** - **19** recorded in THF-d_8 solution show the expected resonances of the cyclopentadienyl substituents. The ^{13}C NMR resonances of the C_5 ring clearly differ from those of the ionic alkali metal compounds **1** - **15**, shifting from 132.8 ppm for the arsenic compound **17** to 126.4 ppm for the bismuth compound **18**. These findings are in accordance with the decreasing electronegativity of the pnictogen atom. The ^{13}C NMR resonance of the cyclopentadienyl atoms of the phosphorus compound **16** could not be determined due to fast intramolecular conversion, resulting in substantial peak broadening. The [1,5]-sigmatropic rearrangement is also evident in the VT ^1H NMR spectra of **16** (Fig. S62).

Scheme 3. Synthesis of 16 - 19.



R = 4-*t*-Bu-Ph
E = P (**16**), As (**17**), Sb (**18**), Bi (**19**)

Crystals of **17** suitable for a single crystal X-ray diffraction study were obtained upon slow re-crystallization from a solution of **17** in *n*-hexane at ambient temperature. **17** crystallizes in the monoclinc space goup $P2_1/n$ with one molecule in the asymmetric unit.

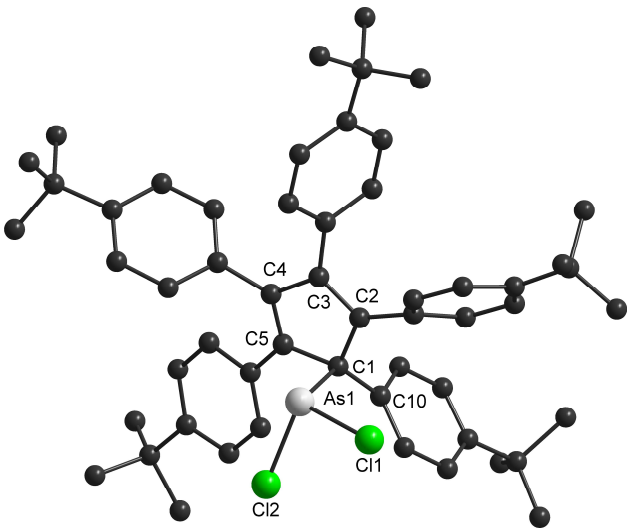


Figure 6. Solid state structure of **17.** H atoms and disordered parts are omitted for clarity; atoms displayed as spheres of arbitrary radii.

The arsenic atom in **17** adopts an almost perpendicular orientation to the central C_5 ring and the As1-C1 bond length of 2.0590(18) Å is typical for an As-C σ bond, whereas the As1-C1-C10 bond angle of 124.26(13)° is significantly larger than the expected value for a sp^3-hybridized carbon atom. The other As-C_{Cp} distances in **17** are substantially longer (As1-C2 2.5677(2) Å, As1-C5 2.6138(2) Å, As1-C3 3.0828(2) Å, As1-C4 3.0616(3) Å). Almost identical As1-C1 bond lengths have been reported for Cp^*AsX_2 complexes (X = F 2.026(10) Å, Cl 2.035(7) Å, Br 2.052(10) Å, I 2.066(10) Å),[52] Cp^*_2AsCl (2.038(3) Å, 2.045(3) Å)[53] as well as *i*-$Pr_4(H)C_5AsCl_2$ (2.056(6) Å),[54] whereas the As-C bond lengths in the sigma-bonded As_4 butterfly-type structure $(Cp^{BIGn\text{-}Bu})_2As_4$ (2.1003(25) Å, 2.0941(23) Å) are slightly elongated.[58] The As1-C2 and As1-C5 bond distances in the Cp^*AsX_2 complexes are slightly shorter compared to those in **17**, hence the bonding nature of the Cp* substituents was described as "pseudo η^3". Very recently, the solid state structures of Cp*-substituted arsenic mono- $[(\eta^2\text{-}Cp^*)AsCl][B(C_6F_5)_4]$ and dication $[(\eta^5\text{-}Cp^*)As(tol)][B(C_6F_5)_4]_2$ were reported by Stephan et al.,[55] whereas Krossing et al. previously reported on $[(\eta^2\text{-}Cp^*)AsCl][ClAl(OC\{CF_3\}_3)_3]$[56] and Jutzi et al. structurally characterized the arsenocene cation $[(Cp^*)_2As]^+$,[57] respectively. The $[(\eta^5\text{-}Cp^*)As(tol)]$ dication represents the only structurally characterized arsenic compound containing a η^5-coordinated Cp* substituent complexes, to date. The As-C bond lengths observed in $[(\eta^5\text{-}Cp^*)As(tol)][B(C_6F_5)_4]_2$ (2.190(3) to 2.246(3) Å) and $[(Cp^*)_2As]^+$ (2.186 Å) are roughly 10 pm elongated compared to those reported for the n^2-coordinated derivatives $[(\eta^2\text{-}Cp^*)AsCl][B(C_6F_5)_4]$ and $[(\eta^2\text{-}Cp^*)AsCl][ClAl(OC\{CF_3\}_3)_3]$, respectively, and about 15 pm longer than that observed in **17**. The central C_5 ring in **17** is almost flat (r.m.s. deviation from the best plane 0.038 Å) and the occurrence of well separated C-C single (C1-C2 1.507(2) Å, C1-C5 1.511(2) Å, C3-C4 1.452(2) Å) and C-C double bonds (C2-C3 1.375(2) Å, C4-C5 1.386(2) Å) further supports that the As1-C1 σ-bond is the dominant interaction. The C1–As1–Cl1/2 bond angles in **17** (103.84(5)°, 106.67(5)°) are substantially larger than the Cl1–As1–Cl2 angle (93.40(2)°), and the sum of the C-As-Cl and Cl-As-Cl bond angles in **17** (303.91°) is larger compared to that in Cp^*AsCl_2 (295.20°)[52] and *i*-$Pr_4(H)C_5AsCl_2$ (290.95°).[54] Moreover, intermolecular Cp···As interactions as was observed in Cp^*AsCl_2 were not observed in **17**, which can be attributed to the higher steric demand of the $Cp^{BIGt\text{-}Bu}$ ligand.

CONCLUSION

Alkali metal salts of sterically demanding cyclopentadienyls $Cp^{BIGi\text{-}Pr}M$, $Cp^{BIGn\text{-}Bu}M$, and $Cp^{BIGt\text{-}Bu}M$ are accessible in high yields by amine elimination reaction of the corresponding cyclopentadiene with alkali metal amides $MN(SiMe_3)_2$. Solvent-coordination to the metal center typically leads to the breakage of the infinite one-dimensional chain structure, resulting in the formation of solvent-separated ionic structures. In the solid state, $Cp^{BIGt\text{-}Bu}K$ (**13a**) forms an ionic structure containing an inverse triple-decker potassocene cation $[(Cp^{BIGt\text{-}Bu})_2K_3(solv)_n]^+$, a potassocene anion $[Cp^{BIGt\text{-}Bu}{}_2K]^-$ and there are also indications for a neutral $[Cp^{BIGt\text{-}Bu}{}_2K_2(solv)_n]$ moiety. Salt elimination reactions of $Cp^{BIGt\text{-}Bu}K$ **13** with ECl_3 (E = P - Bi), yielded the monosubstituted cyclopentadienyl compounds $Cp^{BIGt\text{-}Bu}ECl_2$.

EXPERIMENTAL SECTION

General Procedures. All experiments were performed in a Glovebox (MBraun) under an Ar atmosphere or with standard Schlenk techniques. Solvents were carefully dried either over Na/K or CaH_2 and degassed prior to use. $Cp^{BIGi\text{-}Pr}H$, $Cp^{BIGn\text{-}Bu}H$, and $Cp^{BIGt\text{-}Bu}H$ were prepared according to literature procedures reported for the synthesis of comparable pentaaryl-substituted Cp derivatives[44-46] and purified by flash column chromatography with *n*-hexane:DCM 4:1 on silica ,giving R_f values of 0.43 ($Cp^{BIGi\text{-}Pr}H$), 0.47 ($Cp^{BIGn\text{-}Bu}H$) and 0.39 ($Cp^{BIGt\text{-}Bu}H$). $Cp^{BIGi\text{-}Pr}H$ was further re-crystallized from acetone, $Cp^{BIGn\text{-}Bu}H$ was re-crystallized from *n*-hexane:isopropanol 1:10 and $Cp^{BIGt\text{-}Bu}H$ was re-crystallized from toluene:methanol 1:1. $Cp^{BIGn\text{-}Bu}Na$ **7**[58] and $Cp^{BIGn\text{-}Bu}K$ **8**[16] were previously reported, but analytical details (^1H, ^{13}C, EA, XRD) were only given for **8**. NMR spectra were recorded on a Bruker Avance 300 spectrometer at 25 °C at 300 MHz (^1H), 75 MHz (^{13}C), 117 MHz (^7Li), 79 MHz (^{23}Na), 122 MHz (^{31}P), 98 MHz (^{87}Rb) and 39 MHz (^{133}Cs) and referenced to internal toluene-d_8 (^1H: δ = 2.08 ppm; ^{13}C: δ = 20.4 ppm), CD_3CN (^1H: δ = 1.94; ^{13}C: δ = 1.32), thf-d_8 (^1H: δ = 1.72; ^{13}C: δ = 25.3) and external 9.7 M LiCl in D_2O (^7Li: δ = 0 ppm), 0.1 M NaCl in D_2O (^{23}Na: δ = 0 ppm), 85 % H_3PO_4 in H_2O (^{31}P: δ = 0 ppm), 0.01 M RbCl in D_2O (^{87}Rb: δ = 0 ppm) and 0.1 M $CsNO_3$ in D_2O (^{133}Cs: δ = 0 ppm).[59] IR spectra were recorded on a Bruker ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. Melting points were measured in sealed capillaries and were not corrected. Elemental analyses were determined by the Elementaranalyse Labor of the University of Duisburg-Essen.

General synthesis of $Cp^{BIGi\text{-}Pr}M$ (1-5). $Cp^{BIGi\text{-}Pr}H$ (131 mg, 0.2 mmol) and $MN(SiMe_3)_2$ (0.2 mmol) were dissolved in acetonitrile (3 mL) and the resulting light-yellow solution was

stirred for 1 h at ambient temperature. All volatiles were removed under reduced pressure at 100 °C, yielding **1** - **5** as colorless crystalline solids.

Cp$^{BIGi\text{-}Pr}$Li 1. $LiN(SiMe_3)_2$ (33 mg, 0.2 mmol); Yield: 118 mg (0.178 mmol, 89 %). Mp. 189 °C (dec.). Anal. Calcd. for $C_{50}H_{55}Li$: C, 90.59; H, 8.36 %. Found: C, 90.56; H, 8.31 %. ^{1}H NMR (300 MHz, CD_3CN, 25 °C): δ 1.17 (d, $^3J_{HH}$ = 6.9 Hz, 30 H, C*H*$_3$), 2.69-2.83 (m, 5 H, C*H*), 6.70 (d, $^3J_{HH}$ = 8.3 Hz, 10 H, Ar-*H*), 6.77 (d, $^3J_{HH}$ = 8.1 Hz, 10 H, Ar-*H*). ^{13}C NMR (75.5 MHz, CD_3CN, 25 °C): δ 24.52 (*C*H$_3$), 34.19 (*C*H), 121.13 (Cp-*C*), 125.17 (Ar-*C*H), 132.50 (Ar-*C*H), 141.96 (Ar-*C*), 142.43 (Ar-*C*). ^{7}Li NMR (117 MHz, CD_3CN, 25 °C): δ –2.26. ATR-IR: ν = 3022, 2958, 2928, 2868, 1504, 1460, 1410, 1382, 1362, 1053, 1018, 833, 787, 600, 566, 442 cm^{-1}.

Cp$^{BIGi\text{-}Pr}$Na 2. $NaN(SiMe_3)_2$ (37 mg, 0.2 mmol); Yield: 132 mg (0.194 mmol, 97 %). Mp. 202 °C (dec.). Anal. Calcd. for $C_{50}H_{55}Na$: C, 88.45; H, 8.17 %. Found: C, 87.25; H, 8.07 %. ^{1}H NMR (300 MHz, CD_3CN, 25 °C): δ 1.19 (d, $^3J_{HH}$ = 6.9 Hz, 30 H, C*H*$_3$), 2.73-2.82 (m, 5 H, C*H*), 6.72 (d, $^3J_{HH}$ = 7.7 Hz, 10 H, Ar-*H*), 6.79 (d, $^3J_{HH}$ = 7.9 Hz, 10 H, Ar-*H*). ^{13}C NMR (75.5 MHz, CD_3CN, 25 °C): δ 24.55 (*C*H$_3$), 34.21 (*C*H), 121.13 (Cp-*C*), 125.17 (Ar-*C*H), 132.53 (Ar-*C*H), 141.93 (Ar-*C*), 142.45 (Ar-*C*). ^{23}Na NMR (79 MHz, CD_3CN, 25 °C): δ –7.82. ATR-IR: ν = 3024, 2958, 2931, 2870, 1514, 1459, 1148, 1051, 1014, 851, 836, 773, 692, 567 cm^{-1}.

Cp$^{BIGi\text{-}Pr}$K 3. $KN(SiMe_3)_2$ (40 mg, 0.2 mmol); Yield: 130 mg (0.188 mmol, 94 %). Mp. 267 °C (dec.). Anal. Calcd. for $C_{50}H_{55}K$: C, 86.40; H, 7.98 %. Found: C, 84.95; H, 7.97 %. ^{1}H NMR (300 MHz, CD_3CN, 60 °C): δ 1.21 (d, $^3J_{HH}$ = 6.9 Hz, 30 H, C*H*$_3$), 2.72-2.86 (m, 5 H, C*H*), 6.69 (d, $^3J_{HH}$ = 8.1 Hz, 10 H, Ar-*H*), 6.77 (d, $^3J_{HH}$ = 8.2 Hz, 10 H, Ar-*H*). ^{13}C NMR (75.5 MHz, CD_3CN, 60 °C): δ 24.70 (*C*H$_3$), 34.45 (*C*H), 121.37 (Cp-*C*), 125.51 (Ar-*C*H), 132.71 (Ar-*C*H), 141.49 (Ar-*C*), 143.12 (Ar-*C*). ATR-IR: ν = 3013, 2959, 2931, 2869, 1515, 1459, 1361, 1149, 1051, 1013, 851, 833, 773, 689, 567 cm^{-1}.

Cp$^{BIGi\text{-}Pr}$Rb 4. $RbN(SiMe_3)_2$ (50 mg, 0.2 mmol); Yield: 134 mg (0.176 mmol, 90 %). Mp. 381 °C (dec.). Anal. Calcd. for $C_{50}H_{55}Rb$: C, 81.00; H, 7.48 %. Found: C, 80.85; H, 7.37 %. ^{1}H NMR (300 MHz, thf-*d*$_8$, 25 °C): δ 1.16 (d, $^3J_{HH}$ = 6.9 Hz, 30 H, C*H*$_3$), 2.65-2.79 (m, 5 H, C*H*), 6.66 (d, $^3J_{HH}$ = 8.4 Hz, 10 H, Ar-*H*), 6.72 (d, $^3J_{HH}$ = 8.3 Hz, 10 H, Ar-*H*). ^{13}C NMR (75.5 MHz, thf-*d*$_8$, 25 °C): δ 24.61 (*C*H$_3$), 34.48 (*C*H), 120.89 (Cp-*C*), 125.07 (Ar-*C*H), 132.27 (Ar-*C*H), 140.34 (Ar-*C*), 142.42 (Ar-*C*). ^{87}Rb NMR (98 MHz, CD_3CN, 25 °C): δ –14.77. ATR-IR: ν = 3013, 2958, 2931, 2869, 1514, 1460, 1149, 1052, 1013, 850, 833, 773, 689, 566 cm^{-1}.

Cp$^{BIGi\text{-}Pr}$Cs 5. $CsN(SiMe_3)_2$ (58 mg, 0.2 mmol); Yield: 147 mg (0.187 mmol, 93 %). Mp. >400 °C. Anal. Calcd. for $C_{50}H_{55}Cs$: C, 76.13; H, 7.03 %. Found: C, 76.15; H, 6.95 %. ^{1}H NMR (300 MHz, Tol-*d*$_8$, 25 °C): δ 1.17 (d, $^3J_{HH}$ = 6.8 Hz, 30 H, C*H*$_3$), 2.65-2.74 (m, 5 H, C*H*), 6.59 (s, br., 20 H, Ar-*H*). ^{13}C NMR (75.5 MHz, Tol-*d*$_8$, 25 °C): δ 24.25 (*C*H$_3$), 33.94 (*C*H), 121.90 (Cp-*C*), 126.54 (Ar-*C*H), 131.07 (Ar-*C*H), 136.75 (Ar-*C*), 143.95 (Ar-*C*). ^{133}Cs NMR (39.4 MHz, Tol-*d*$_8$, 25 °C): δ –226.30. ATR-IR: ν = 3015, 2956, 2929, 2866, 1607, 1512, 1456, 1362, 1148, 1051, 851, 830, 808, 771, 688, 567 cm^{-1}.

5 was re-crystallized from thf at –30 °C and from acetonitrile at –30 °C, yielding colorless crystals of **5a** and **5b**.

Cp$^{BIGn\text{-}Bu}$Li 6. A light-yellow solution of Cp$^{BIGn\text{-}Bu}$H (73 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (17 mg, 0.1 mmol) in benzene (1 mL) was stirred for 1 h at ambient temperature. All volatiles were removed under reduced pressure at 100 °C, yielding a colorless crystalline solid. Yield: 65 mg (0.090 mmol, 90 %). Mp. 154 °C (dec.). Anal. Calcd. for $C_{55}H_{65}Li$: C, 90.12; H, 8.94 %. Found: C, 90.10; H, 8.89 %. ^{1}H NMR (300 MHz, CD_3CN, 25 °C): δ 0.92 (t, $^3J_{HH}$ = 7.3 Hz, 15 H, C*H*$_3$), 1.25-1.38 (m, 10 H, C*H*$_2$), 1.47-1.57 (m, 10 H, C*H*$_2$), 2.46 (t, $^3J_{HH}$ = 7.7 Hz, 10 H, C*H*$_2$), 6.64 (d, $^3J_{HH}$ = 8.1 Hz, 10 H, Ar-*H*), 6.70 (d, $^3J_{HH}$ = 8.2 Hz, 10 H, Ar-*H*). ^{13}C NMR (75.5 MHz, CD_3CN, 25 °C): δ 14.31 (*C*H$_3$), 23.12 (*C*H$_2$), 34.61 (*C*H$_2$), 35.79 (*C*H$_2$), 120.96 (Cp-*C*), 127.27 (Ar-*C*H), 132.42 (Ar-*C*H), 136.32 (Ar-*C*), 141.75 (Ar-*C*). ^{7}Li NMR (117 MHz, CD_3CN, 25 °C): δ –2.73. ATR-IR: ν = 2955, 2926, 2870, 2857, 1504, 1458, 1412, 1018, 830, 750, 569 cm^{-1}.

Cp$^{BIGn\text{-}Bu}$Na 7. Cp$^{BIGn\text{-}Bu}$H (145 mg, 0.2 mmol) and $NaN(SiMe_3)_2$ (37 mg, 0.2 mmol) were suspended in benzene (3 mL) and stirred for 3 h at 60 °C. All volatiles were removed under reduced pressure at 100 °C, yielding a colorless solid. Yield: 139 mg (0.186 mmol, 93 %). Mp. 162 °C (dec.). Anal. Calcd. for $C_{55}H_{65}Na$: C, 88.18; H, 8.75 %. Found: C, 87.90; H, 8.70 %. ^{1}H NMR (300 MHz, CD_3CN, 25 °C): δ 0.93 (t, $^3J_{HH}$ = 7.3 Hz, 15 H, C*H*$_3$), 1.27-1.39 (m, 10 H, C*H*$_2$), 1.49-1.59 (m, 10 H, C*H*$_2$), 2.48 (t, $^3J_{HH}$ = 7.6 Hz, 10 H, C*H*$_2$), 6.66 (d, $^3J_{HH}$ = 8.1 Hz, 10 H, Ar-*H*), 6.72 (d, $^3J_{HH}$ = 8.0 Hz, 10 H, Ar-*H*). ^{13}C NMR (75.5 MHz, CD_3CN, 25 °C): δ 14.35 (*C*H$_3$), 23.13 (*C*H$_2$), 34.63 (*C*H$_2$), 35.82 (*C*H$_2$), 120.95 (Cp-*C*), 127.29 (Ar-*C*H), 132.45 (Ar-*C*H), 136.36 (Ar-*C*), 141.72 (Ar-*C*). ^{23}Na NMR (79 MHz, CD_3CN, 25 °C): δ –7.80. ATR-IR: ν = 3023, 2955, 2925, 2854, 1513, 1463, 1438, 1116, 1015, 847, 833, 763, 686 cm^{-1}.

Cp$^{BIGn\text{-}Bu}$K 8. A solution of Cp$^{BIGn\text{-}Bu}$H (73 mg, 0.1 mmol) and $KN(SiMe_3)_2$ (20 mg, 0.1 mmol) in acetonitrile (2 mL) was stirred for 1 h at ambient temperature. All volatiles were removed under reduced pressure at 100 °C, yielding a colorless solid. Yield: 70 mg (0.091 mmol, 91 %). The product was identified by ^{1}H NMR spectroscopy. Analytical data were identical to those published by Harder and coworkers.[16]

Cp$^{BIGn\text{-}Bu}$Rb 9. Cp$^{BIGn\text{-}Bu}$H (73 mg, 0.1 mmol) and $RbN(SiMe_3)_2$ (25 mg, 0.1 mmol) were suspended in acetonitrile (3 mL) and stirred for 4 h at 60 °C. All volatiles were removed under reduced pressure at 100 °C, yielding a colorless solid. Yield: 76 mg (0.094 mmol, 94 %). Mp. 217 °C (dec.). Anal. Calcd. for $C_{55}H_{65}Rb$: C, 81.40; H, 8.07 %. Found: C, 81.33; H, 7.97 %. ^{1}H NMR (300 MHz, thf-*d*$_8$, 25 °C): δ 0.92 (t, $^3J_{HH}$ = 7.3 Hz, 15 H, C*H*$_3$), 1.27-1.39 (m, 10 H, C*H*$_2$), 1.52 (s, br., 10 H, C*H*$_2$), 2.44 (s, br., 10 H, C*H*$_2$), 6.62 (s, br., 20 H, Ar-*H*). ^{13}C NMR (75.5 MHz, thf-*d*$_8$, 25 °C): δ 14.39 (*C*H$_3$), 23.20 (*C*H$_2$), 34.79 (*C*H$_2$), 36.14 (*C*H$_2$), 120.83 (Cp-*C*), 127.30 (Ar-*C*H), 132.23 (Ar-*C*H), 136.29 (Ar-*C*), 140.18 (Ar-*C*). ^{87}Rb NMR (98 MHz, CD_3CN, 25 °C): δ –9.22. ATR-IR: ν = 3014, 2957, 2923, 2854, 1608, 1514, 1457, 1378, 1140, 1115, 1016, 847, 831, 760, 683, 564, 548 cm^{-1}.

$Cp^{BIGn\text{-}Bu}Cs$ 10. A solution of $Cp^{BIGn\text{-}Bu}H$ (291 mg, 0.4 mmol) and $CsN(SiMe_3)_2$ (117 mg, 0.1 mmol) in toluene (5 mL) was stirred for 3 h at ambient temperature. All volatiles were removed under reduced pressure at 100 °C, yielding a colorless solid, which was re-crystallized from acetonitrile at –30 °C. Yield: 312 mg (0.363 mmol, 91 %). Mp. 253 °C (dec.). Anal. Calcd. for $C_{55}H_{65}Cs$: C, 76.90; H, 7.63 %. Found: C, 76.40; H, 7.63 %. ^1H NMR (300 MHz, Tol-d_8, 25 °C): δ 0.92 (t, $^3J_{HH}$ = 7.2 Hz, 15 H, CH_3), 1.25-1.36 (m, 10 H, CH_2), 1.45-1.55 (m, 10 H, CH_2), 2.41 (s, br., 10 H, CH_2), 6.61 (s, br., 20 H, Ar-*H*). ^{13}C NMR (75.5 MHz, Tol-d_8, 25 °C): δ 14.29 (*C*H_3), 23.10 (*C*H_2), 34.11 (*C*H_2), 35.81 (*C*H_2), 121.84 (Cp-*C*), 128.56 (Ar-*C*H), 130.94 (Ar-*C*H), 136.72 (Ar-*C*), 138.11 (Ar-*C*). ^{133}Cs NMR (39.4 MHz, Tol-d_8, 25 °C): δ –225.65. ATR-IR: ν = 3016, 2955, 2925, 2855, 1607, 1514, 1456, 1377, 1140, 1115, 1016, 847, 831, 761, 684, 547 cm^{-1}.

$Cp^{BIGt\text{-}Bu}Li$ 11. $Cp^{BIGt\text{-}Bu}H$ (218 mg, 0.3 mmol) and $LiN(SiMe_3)_2$ (50 mg, 0.3 mmol) were dissolved in acetonitrile (3 mL) and stirred for 1 h at ambient temperature. All volatiles were removed under reduced pressure at 100 °C, yielding a colorless solid. Single crystals of this product were obtained by layering a concentrated solution in THF with hexane. This procedure is not suitable for preparative purposes, since **11** partially decomposes in the presence of THF even under vigorously dry conditions, yielding varying amounts of $Cp^{BIGt\text{-}Bu}H$. Yield: 185 mg (0.253 mmol, 84 %). Yield: 208 mg (0.284 mmol, 95 %). Mp. >400 °C (dec.). Anal. Calcd. for $C_{55}H_{65}Li$: C, 90.12; H, 8.94 %. Found: C, 90.78; H, 9.19 %. The broad ^1H and ^{13}C NMR signals of **11** do not allow a reliable assignment and integration. ^1H NMR (300 MHz, CD_3CN, 25 °C): δ 1.24, 5.78-8.15. ^{13}C NMR (151 MHz, CD_3CN, 25 °C): δ 20.16-49.98, 107.31-160.36. ^7Li NMR (112 MHz, CD_3CN, 25 °C): δ -2.52. ATR-IR: ν = 3032, 2955, 2901, 2866, 1513, 1361, 1286, 1149, 1039, 852, 834, 693, 569, 558 cm^{-1}.

General synthesis of $Cp^{BIGt\text{-}Bu}M$ (12-14). A light-yellow solution of $Cp^{BIGt\text{-}Bu}H$ (218 mg, 0.3 mmol) and $MN(SiMe_3)_2$ (0.3 mmol) in THF (3 mL) was stirred for 1 h at ambient temperature. The solvent was partly removed under reduced pressure until a crystalline solid began to precipitate. Gentle heating to 60 °C yielded a clear solution, which was either cooled to 0 °C (**12**, **13**) or layered with 3 mL of hexane (**14**). Colorless crystals of **12** - **14** formed within 16 h, which were isolated from the mother liquor by decantation. Removing all volatiles from the mother liquor under reduced pressure at 100 °C gave a second fraction of **12** - **14**. Yields are given for the isolated crystals.

$Cp^{BIGt\text{-}Bu}Na$ 12. $NaN(SiMe_3)_2$ (55 mg, 0.3 mmol); Yield: 158 mg (0.212 mmol, 71 %). Mp. >400 °C (dec.). Anal. Calcd. for $C_{55}H_{65}Na$: C, 88.19; H, 8.75 %. Found: C, 87.82; H, 8.39 %. The broad ^1H NMR signals of **12** do not allow a reliable assignment and integration. ^1H NMR (600 MHz, thf-d_8, 25 °C): δ 0.62-1.75, 6.15-7.36. ^{13}C NMR (126 MHz, thf-d_8, 25 °C): δ 32.27 (*C*H_3), 34.67 (*C*$(CH_3)_3$), 119.41 (Cp-*C*), 123.56 (Ar-*C*H), 132.59 (Ar-*C*H), 138.39 (Ar-*C*), 144.41 (Ar-*C*). ^{23}Na NMR (79 MHz, thf-d_8, 25 °C): δ – 13.67. ATR-IR: ν = 3032, 2958, 2903, 2866, 1513, 1460, 1361, 1270, 1151, 1015, 852, 834, 776, 694, 569 cm^{-1}.

$Cp^{BIGt\text{-}Bu}K$ 13. $KN(SiMe_3)_2$ (60 mg, 0.3 mmol); Yield: 217 mg (282 mmol, 94 %). Mp. >400 °C. Anal. Calcd. for $C_{55}H_{65}K$: C, 86.33; H, 8.56 %. Found: C, 86.5; H, 8.57 %. ^1H NMR (500 MHz, thf-d_8, 25 °C): δ 1.23 (s, 45 H, CH_3), 6.58 (d, $^3J_{HH}$ = 7.6 Hz, 10 H, Ar-*H*), 6.78 (d, $^3J_{HH}$ = 7.6 Hz, 10 H, Ar-*H*). ^{13}C NMR (126 MHz, thf-d_8, 25 °C): δ 32.09 (*C*H_3), 34.65 (*C*$(CH_3)_3$), 120.63 (Cp-*C*), 123.90 (Ar-*C*H), 131.91 (Ar-*C*H), 139.37 (Ar-*C*), 144.71 (Ar-*C*). ATR-IR: ν = 3018, 2961, 2930, 2866, 1516, 1461, 1361, 1270, 1152, 1119, 1012, 851, 833, 774, 690, 571 cm^{-1}.

$Cp^{BIGt\text{-}Bu}Rb$ 14. $RbN(SiMe_3)_2$ (74 mg, 0.3 mmol); Yield: 197 mg (244 mmol, 81 %). Mp. >400 °C. Anal. Calcd. for $C_{55}H_{65}Rb$: C, 81.40; H, 8.07 %. Found: C, 81.08; H, 8.12 %. ^1H NMR (300 MHz, thf-d_8, 25 °C): δ 1.24 (s, 45 H, CH_3), 6.62 (d, $^3J_{HH}$ = 7.0 Hz, 10 H, Ar-*H*), 6.84 (d, $^3J_{HH}$ = 7.0 Hz, 10 H, Ar-*H*). ^{13}C NMR (75 MHz, thf-d_8, 25 °C): δ 32.09 (*C*H_3), 34.88 (*C*$(CH_3)_3$), 121.01 (Cp-*C*), 124.02 (Ar-*C*H), 131.94 (Ar-*C*H), 139.64 (Ar-*C*), 144.82 (Ar-*C*). ^{78}Rb NMR (98 MHz, CD_3CN, 25 °C): δ 1.66. ATR-IR: ν = 3016, 2958, 2903, 2865, 1515, 1361, 1268, 1151, 1012, 851, 832, 690, 871 cm^{-1}.

$Cp^{BIGt\text{-}Bu}Cs$ 15. $Cp^{BIGt\text{-}Bu}H$ (218 mg, 0.3 mmol) and $CsN(SiMe_3)_2$ (74 mg, 0.3 mmol) were dissolved in THF (3 mL) and the resulting light-yellow solution was stirred for 1 h at ambient temperature. All volatiles were removed under reduced pressure at 100 °C, yielding a colorless solid. The product was re-crystallized from pyridine at ambient temperature. Yield: 242 mg (282 mmol, 94 %). Mp. >400 °C. Anal. Calcd. for $C_{55}H_{65}Cs$: C, 76.90; H, 7.63 %. Found: C, 76.96; H, 7.11 %. ^1H NMR (600 MHz, thf-d_8, 25 °C): δ 1.22 (s, 45 H, CH_3), 6.57 – 6.77 (m, 10 H, Ar-*H*), 6.77 – 6.98 (m, 10 H, Ar-*H*). ^{13}C NMR (126 MHz, thf-d_8, 25 °C): δ 31.53 (*C*H_3), 34.18 (*C*$(CH_3)_3$), 120.91 (Cp-*C*), 123.43 (Ar-*C*H), 131.47 (Ar-*C*H), 139.45 (Ar-*C*), 144.15 (Ar-*C*). ^{133}Cs NMR (39 MHz, thf-d_8, 25 °C): δ – 143.71. ATR-IR: ν = 3020, 2959, 2904, 2866, 1515, 1361, 1268, 1151, 1013, 851, 832, 690, 572 cm^{-1}.

General synthesis of $Cp^{BIGt\text{-}Bu}ECl_2$ (16-19). Solutions of $Cp^{BIGt\text{-}Bu}K$ **13** (38 mg, 0.05 mmol) and ECl_3 (0.05 mmol) in THF (0.25 mL) were combined at ambient temperature and stirred for 1 h. The resulting greenish solution was centrifuged and the clear, greenish supernatant solution was decanted. All volatiles were removed under reduced pressure at ambient temperature, yielding a yellow powder, which was dissolved in 1 mL of *n*-hexane and again centrifuged to remove possible traces of KCl. The supernatant solution was decanted, and all volatiles were removed under reduced pressure at ambient temperature, yielding yellow (**16**-**18**) and brownish (**19**) crystalline solids.

$Cp^{BIGt\text{-}Bu}PCl_2$ 16. PCl_3 (6.9 mg, 4.4 µL, 0.05 mmol); Yield: 37.6 mg (45.4 mmol, 91 %). Mp. 181 °C (dec.). Anal. Calcd. for $C_{55}H_{65}PCl_2$: C, 79.78; H, 7.91 %. Found: C, 78.95; H, 7.57 %. ^1H NMR (300 MHz, thf-d_8, 60 °C): δ 1.21 (s, 45 H, CH_3), 6.97 (d, $^3J_{HH}$ = 8.4 Hz, 10 H, Ar-*H*), 7.09 (d, $^3J_{HH}$ = 8.4 Hz, 10 H, Ar-*H*). ^{13}C NMR (151 MHz, thf-d_8, 25 °C): δ 31.56 (*C*H_3), 35.03 (*C*$(CH_3)_3$), 125.20 (Ar-*C*H), 130.62 (Ar-*C*H), 133.53 (Ar-*C*), 150.52 (Ar-*C*). The signal of the Cp-*C* atom could not be observed. ^{31}P NMR (122 MHz, thf-d_8, 25 °C): δ 46.47. ATR-IR: ν

= 3033, 2958, 2903, 2867, 1503, 1461, 1393, 1363, 1268, 1120, 1018, 830, 567, 487 cm^{-1}.

$Cp^{BIG\textit{t}\text{-}Bu}AsCl_2$ 17. $AsCl_3$ (9.1 mg, 4.2 µL, 0.05 mmol); Yield: 41.8 mg (47.9 mmol, 96 %). Mp. 154 °C (dec.). Anal. Calcd. for $C_{55}H_{65}AsCl_2$: C, 75.76; H, 7.51 %. Found: C, 76.14; H, 7.66 %. ^{1}H NMR (600 MHz, thf-d_8, 25 °C): δ 1.26 (s, 45 H, CH_3), 7.00 (d, $^3J_{HH}$ = 8.7 Hz, 10 H, Ar-*H*), 7.14 (d, $^3J_{HH}$ = 8.7 Hz, 10 H, Ar-*H*). ^{13}C NMR (151 MHz, thf-d_8, 25 °C): δ 31.54 (*C*H_3), 35.08 (*C*$(CH_3)_3$), 125.21 (Ar-*C*H), 131.22 (Ar-*C*H), 132.29 (Ar-*C*), 133.80 (Cp-*C*), 150.95 (Ar-*C*). ATR-IR: ν = 3031, 2961, 2903, 2868, 1495, 1462, 1363, 1268, 1118, 1016, 852, 833, 686, 567 cm^{-1}. **17** was crystallized from *n*-hexane at −30 °C.

$Cp^{BIG\textit{t}\text{-}Bu}SbCl_2$ 18. $SbCl_3$ (11.4 mg, 0.05 mmol); Yield: 40.0 mg (43.5 mmol, 87 %). Mp. 134 °C (dec.). Anal. Calcd. for $C_{55}H_{65}SbCl_2$: C, 71.9; H, 7.13 %. Found: C, 74.3; H, 7.46 %. ^{1}H NMR (600 MHz, thf-d_8, 25 °C): δ 1.24 (s, 45 H, CH_3), 6.93 (d, $^3J_{HH}$ = 8.4 Hz, 10 H, Ar-*H*), 7.09 (d, $^3J_{HH}$ = 8.4 Hz, 10 H, Ar-*H*). ^{13}C NMR (151 MHz, thf-d_8, 25 °C): δ 31.60 (*C*H_3), 35.05 (*C*$(CH_3)_3$), 124.97 (Ar-*C*H), 131.02 (Cp-*C*), 131.43 (Ar-*C*), 132.12 (Ar-*C*H), 150.50 (Ar-*C*). ATR-IR: ν = 3034, 2962, 2904, 2867, 1462, 1362, 1269, 1016, 851, 833, 691, 569 cm^{-1}. **18** was re-crystallized from *n*-hexane at −30 °C.

$Cp^{BIG\textit{t}\text{-}Bu}BiCl_2$ 19. $BiCl_3$ (15.8 mg, 0.05 mmol); Yield: 46.2 mg (45.9 mmol, 92 %). Mp. 179 °C (dec.). Anal. Calcd. for $C_{55}H_{65}BiCl_2$: C, 65.67; H, 6.51 %. Found: C, 67.0; H, 6.62 %. ^{1}H NMR (600 MHz, thf-d_8, 25 °C): δ 1.23 (s, 45 H, CH_3), 6.90 (d, $^3J_{HH}$ = 8.3 Hz, 10 H, Ar-*H*), 7.04 (d, $^3J_{HH}$ = 8.3 Hz, 10 H, Ar-*H*). ^{13}C NMR (151 MHz, thf-d_8, 25 °C): δ 31.78 (*C*H_3), 34.96 (*C*$(CH_3)_3$), 124.68 (Ar-*C*H), 127.40 (Cp-*C*), 132.57 (Ar-*C*), 132.70 (Ar-*C*H), 149.26 (Ar-*C*). ATR-IR: ν = 3031, 2958, 2904, 2868, 1362, 1268, 1016, 851, 834, 570 cm^{-1}.

Single-crystal X-ray analyses. The crystals were mounted on nylon loops in inert oil. Data were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (monochromated Mo$_{K\alpha}$ radiation, λ = 0.71073 Å) at 100(2) K. The structures were solved by Direct Methods (SHELXS-97).[60] and refined anisotropically by full-matrix least-squares on F^2 (SHELXL-2014).[61,62] Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups. In **5a** an isopropyl group is disordered over two positions. This disorder is correlated with a partial occupation of a THF molecule and the occupations were matched accordingly. A second THF molecule is disordered over two positions. ISOR and RIGU restraints were applied to the ADP of the non-coordinating THF molecules. The corresponding bond lengths in all THF molecules were restrained to be equal (SADI). The bond lengths within the disordered isopropyl group were also restrained to be equal (SADI). In **5b** all atoms were refined with RIGU restraints. Additional ISOR restraints were used for atoms of disordered parts and all atoms of the acetonitrile molecules. All corresponding bond lengths of the isopropyl groups were restrained to be equal. The 1,2 and 1,3 distances of the acetonitrile molecules were restrained to be equal. Because of the large amount of restraints necessary bond lengths and angles may be of limited validity. Attempts to refine methyl groups as rigid rotating groups did not converge. Where possible the methyl H atoms were placed ideally staggered to the neighboring group. One methyl group of the acetonitrile molecules did not settle to a final position in the refinement thus a final parameter shift of 0 was not achievable. Several isopropyl and phenyl groups were disordered. They were refined using two alternate positions although the ADP suggest that in some cases more components might be present. Further alternate positions could not be resolved. In **10** one acetonitrile is disordered over a center of inversion. A second is coordinated in two different orientations of which one is accompanied by another non-coordinated molecule. Two of the n-butyl groups are disordered over two positions. The atoms of the orientation with the smaller occupancy could only be refined with isotropic displacement parameters. All ADPs were refined using RIGU restraints, for the disordered parts additional ISOR restraints were applied. The bond lengths of the disordered n- butyl group in residue 2 were restrained to be equal (SADI). Poor crystal quality: The (best) crystal was of poor quality and diffracted weakly. The intensities at resolutions > 1 Å were very weak and a high percentage < $2\sigma(I)$. Consequently, the model should be carefully interpreted, and any conclusions draw from it supported by other means. Quantitative results may be unreliable and only the connectivity should be taken for certain. In **11** the cation is strongly disordered. Two components for each THF ligand could be identified. The ADP of the atoms suggest that they are disordered over even more positions. SADI restraints were applied to all THF 1,2 and 1,3 distances. RIGU restraints were applied to all THF atoms of the cation. The structure contains an uncertain amount of THF solvent molecules (likely three) whose contribution to the electron density was removed by a SQUEEZE run (For details see:[63]). Since the amount of the solvent is not clear it was not included in the sum formula. In **13a** two *t*-Bu groups and five THF molecules were disordered and modeled with two alternate positions. The ADP suggest possible other orientations which could not be modeled. Several other ADP and the residual density hint further disorder. Any attempts to resolve it failed. All 1,2 and 1,3 distances of the THF molecules were restrained to be equal (SADI). So were the bond lengths of the disordered t-Bu groups. RIGU and ISOR restraints were applied to the ADP of the THF molecules' atoms. A neutral K_2L_2 moiety and a L_2K_3 cation share the same position thus K4 is only occupied by 0.5. The anionic L_2K moiety on a special position ensures the charge balance. K2 is disordered over two position which causes anion and cation to change place in the alternate position (K2'). Since K2' is only occupied by about 8% no THF associated with it could be identified in the residual density. An equal occupation of K2 and K2' would result in unit cell half the size. It is possible to solve and refine the structure with this unit cell however R values are substantially worse, and all ADP are elongated in the same direction. In this model no neutral unit is present but anion and cation are disordered over the same position. Weak but present reflection justify the use of the larger unit cell. In general, the crystal diffracted rather weakly and quantitative results should be carefully interpreted. In **13b** two of the t-Bu groups were disordered over two positions each. Their ADPs were refined using RIGU restraints. For residue 1 additional ISOR

restraints were necessary and the bond lengths and angle were restrained with SADI. RIGU and ISOR restraints were applied to the ADP of the non-coordinating acetonitrile molecules. In **17** two *t*-Bu groups are disordered over two positions each. The ADPs of C17' C18' and C19' (smaller component of one of the groups) were refined using RIGU and ISOR restraints.

CCDC-1904448 (**5a**), -1904449 (**5b**), -1904450 (**10**), -1904451 (**11**), -1904453 (**13a**), -1904454 (**13b**), and -1904455 (**17**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

ASSOCIATED CONTENT

Supporting Information

Electronic Supplementary Information (ESI) available: A CIF file giving X-ray crystallographic data of **5**, **10**, **11**, **13** and **17**. In addition, ^{1}H, ^{7}Li, ^{13}C, ^{23}Na, ^{31}P, ^{87}Rb and ^{133}Cs NMR spectra and IR spectra of **1** - **19** as well as the crystallographic details of of **5**, **10**, **11**, **13** and **17** are given. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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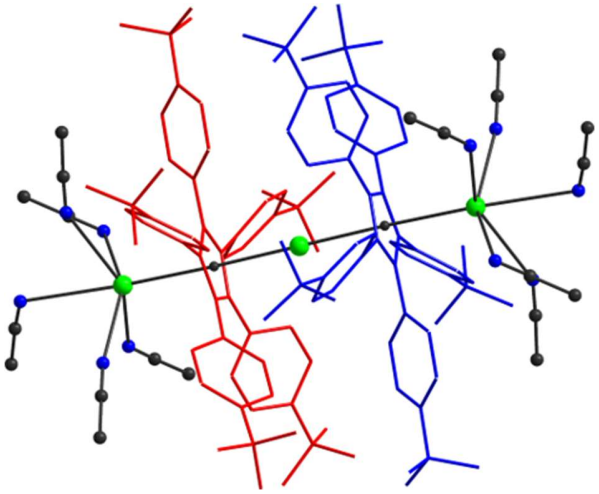
Table of Content

15 alkali metal complexes containing sterically extremely demanding pentaarylcyclopentadienyl Cp^{AR} ligands (Ar = 4-*i*-Pr-Ph, 4-*n*-Bu-Ph, and 4-*t*-Bu-Ph) were synthesized and characterized by IR and heteronuclear NMR spectroscopy. While the solvents-coordinated complexes typically form infinite chain-type structures in the solid state, $Cp(4\text{-}t\text{-Bu-Ph})_5K$ **13** forms a rather ionic structure with an inverse triple-decker potassocene cation $[(Cp^{BIGt\text{-}Bu})_2K_3(solv)_n]^+$, potassocene anion $[Cp^{BIGt\text{-}Bu}{}_2K]^-$ and a neutral $[Cp^{BIGt\text{-}Bu}{}_2K_2(solv)_n]$ moiety. $Cp(4\text{-}t\text{-Bu-Ph})_5K$ **13** is a valuable Cp-transfer reagent as was demonstrated in reactions with ECl_3, yielding the cyclopentadienyl complexes $Cp(4\text{-}t\text{-Bu-Ph})_5ECl_2$ (E = P **16**, As **17**, Sb **18**, Bi **19**).



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