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# Pentaisopropyl Cyclopentadienyl: An Overview across the Periodic Table

Sergej Lauk[a] and André Schäfer*[a]

*Dedicated to Prof. Dr. Helmut Sitzmann in acknowledgment of his pioneering work in pentaisopropylcyclopentadienyl chemistry.*

Cyclopentadienide (Cp) groups are among the most popular ligands in organometallic chemistry. Sterically demanding substitution patterns on the Cp ring can have an important effect on the ligand properties and there are many examples of metal complex which are only stable and isolatable with sterically demanding Cp ligands, carrying alkyl or aryl groups. Among these sterically demanding Cp ligands, pentaisopropyl-cyclopentadienide is the bulkiest pentaalkyl derivative and has been utilized in main group, as well as transition metal and rare-earth element chemistry for several decades.

## Introduction

With the discovery of ferrocene and its structural elucidation,[1–7] cyclopentadienyl ligands have become indispensable ligands in organometallic chemistry. The parent compound cyclopentadienide ($C_5H_5$), which is commonly abbreviated with Cp, was quickly accompanied by substituted derivatives. Perhaps the best known example is that of the permethylated analog, pentamethylcyclopentadienide ($C_5Me_5$),[8,9] which is abbreviated with Cp* (Figure 1). Nowadays, there are countless examples of different substitution patterns on Cp groups, including alkyl, aryl and benzyl substituents, as well as different functional groups, and the steric demand of the substitution pattern often plays an important role in the synthesis, isolation and reactivity of a corresponding metal complex. In the quest for sterically "super-bulky" Cp groups, pentaaryl- and pentabenzyl-substituted Cp ligands, referred to as Cp$^{BIG}$ and Cp$^{Bn5}$, came into focus (Figure 1).[10–12] However, the corresponding complexes sometimes suffer from a rather poor solubility, especially in case of pentaphenylcyclopentadienide. Interestingly, while penta-sub-stitution is easily possible with benzyl and aryl groups, pentaalkyl-derivatives of Cp are less common. With *tert*-butyl groups, a maximum of trisubstitution is possible and the di-*tert*-butylcyclopentadienide and tri-*tert*-butylcyclopentadienide, commonly referred to as Cp′′ and Cp′′′ are well-appreciated as sterically demanding Cp groups.[13,14] However, sometime per-alkylation is desired to prevent reaction on the Cp ring scaffold. Here, the isopropyl-substitution pattern is of particular interest, as it allows for the preparation of the corresponding tetra- and, more importantly, pentaisopropylcyclopentadienide ligands,
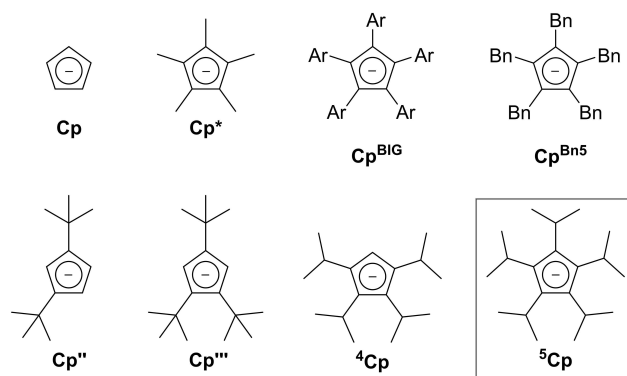


**Figure 1.** Different anionic cyclopentadienide ligands.

referred to as $^4$Cp and $^5$Cp (Figure 1). Thus, $^5$Cp is the sterically most demanding pentaalkyl-substituted Cp ligand (Figure 2), and has enabled a rich and in many ways peculiarly chemistry, both with transition metals as well as main-group and rare-earth elements.
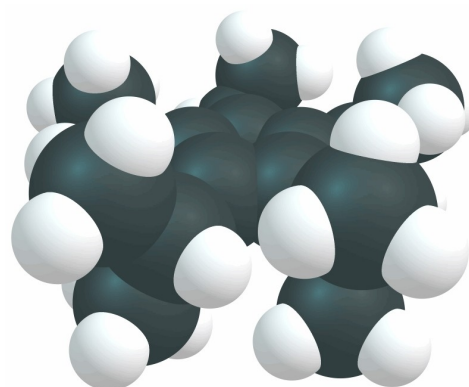
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**Figure 2.** Space-filling plot of pentaisopropylcyclopentadienide, $^5$Cp$^-$.

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This review aims to summarize the synthesis and properties of the $^5$Cp ligand and its compounds/complexes throughout the periodic table.
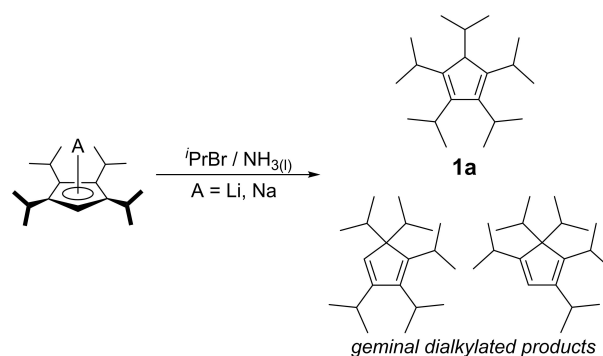
## Pentaisopropyl Cyclopentadiene and the Pentaisopropyl Cyclopentadienyl Radical

The first synthesis of pentaisopropyl cyclopentadiene was reported by Sitzmann in 1989.[15] In this synthesis, the authors used lithiated or sodiated tetraisopropyl cyclopentadienide and reacted it with 2-bromopropane in liquid ammonia (Scheme 1), to perform a Wurtz-type coupling reaction. While this reaction does result in the formation of pentaisopropyl cyclopentadienes, it gives predominantly a mixture of geminally dialkylated products, and only low yields of the desired 1,2,3,4,5-pentaisopropyl cyclopentadiene, **1a**.

The fact that the geminally dialkylated products do not contain an acidic C–H moiety could be used to separate the desired 1,2,3,4,5-pentaisopropyl cyclopentadiene, **1a**, by metalation with NaNH$_2$ in thf at 348 K. This route produced $^5$CpNa in 5% isolated yield starting from $^4$CpNa and 11% starting from $^4$CpLi and remained the only known synthetic route for several years. In the beginning, the chemistry of the pentaisopropyl cyclopentadienide ligand was therefore limited by its low availably. An improved synthetic route was introduced by Sitzmann et al. in 1997 and is discussed in more detail in the next chapter.

In addition to its interesting ligand properties, it was also recognized by Sitzmann et al. in 1991 that the neutral 5e$^-$ radical, **1b**, is remarkably stable and can be a useful synthon. Starting from $^5$CpNa and FeCl$_2$, the authors were able to obtain the radical in 36% yield.[16] This reaction was found to be slow and require careful temperature control. In 1993 and 1998, two improved syntheses were reported by Sitzmann.[17,18] $^5$CpNa can be reacted with bromine (2:1 stoichiometry) at 195 K in pentane, which gives radical **1b** in 70% yield, and $^5$CpLi(Et$_2$O) can be treated with AgCl in diethyl ether at room temperature to give radical **1b** in 76% yield (Scheme 2).

Pentaisopropyl cyclopentadienyl radical **1b** is an air and moisture sensitive green-yellow solid which can be sublimed. It can be stored for years under an inert gas atmosphere. The isopropyl groups are arranged in a paddle-wheel-like manner in



**Scheme 1.** Synthesis of pentaisopropyl cyclopentadiene, **1a**, as reported by Sitzmann et al. in 1989.[15]
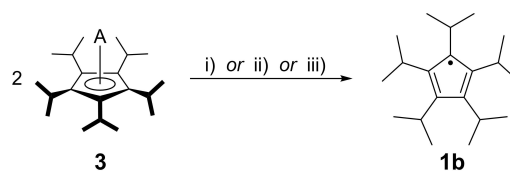


**Scheme 2.** Synthesis of pentaisopropyl cyclopentadieny radical, **1b**, as reported by Sitzmann et al. in 1991,[16] 1993[17] and 1998;[18] i): FeCl$_2$/thf, A=Na; ii): Br$_2$/pentane/195 K, A=Na; iii): AgCl/Et$_2$O/r.t., A=Li(OEt$_2$).

the crystal, with 50% of the isopropyl groups oriented to the left and 50% to the right. In the ESR spectrum of a toluene solution at ambient temperature a broad singlet (g-value: 2.0025) is observed, which splits into a multiplet with 20 lines due to hyperfine couplings at 190 K. The radical can be used for the synthesis of different $^5$Cp metal complexes, which is discussed in more detail in the next chapters.

## Main Group Compounds

In 1997, eight years are the first report, Sitzmann et al. reported an improved synthesis that yields $^5$CpLi directly from a corresponding fulvene via addition of methyl lithium to the exocyclic double bond.[19] The required fulvene can be obtained in good yields from the reaction of $^4$CpNa by reacting it with dimethylaminomethoxycarbenium methyl sulfate in thf at 258 K, producing 1,2,3,4-tetraisopropyl-6-dimethylaminofulvene,

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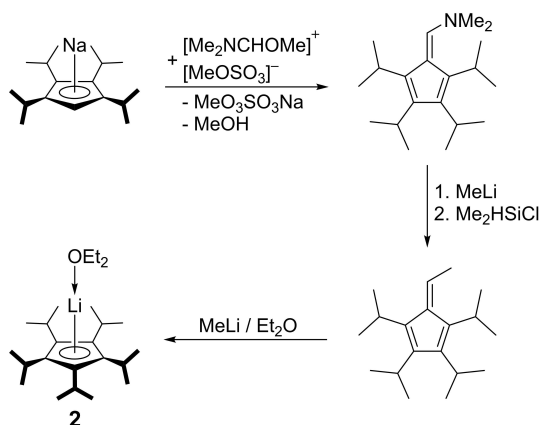
**André Schäfer** studied chemistry at the Carl von Ossietzky University of Oldenburg, where he graduated in 2009. Subsequently, he received his PhD in 2013, under the supervision Prof. Dr. Thomas Müller. After a two-year post-doctoral stay at Bristol University, in the group of Prof. Dr. Ian Manners, he began his independent career at Saarland University, where he was awarded an Emmy Noether grant in 2016. His research focuses on s- and p-block element cyclopentadienyl compounds.

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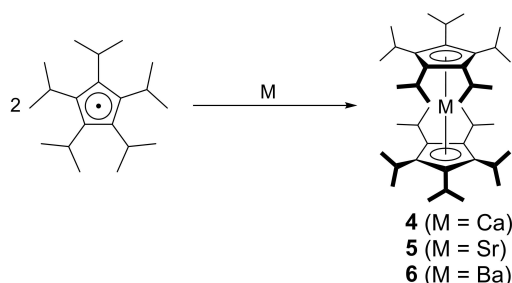European Chemical
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which is subsequently transformed into 1,2,3,4-tetraisopropyl-6-methylfulvene by treatment with methyl lithium and chloro(dimethyl)silane. The subsequent reaction with methyl lithium produces $^5$CpLi(Et$_2$O), **2**, in good yields (Scheme 3), with an overall yield of $^5$CpLi(Et$_2$O), **2**, from $^4$CpNa of 55%.

This synthetic route is vastly superior to the synthesis of $^5$CpH / $^5$CpNa described in the previous chapter, because of the much better yields.

In addition to the described complexes of group 1 metals, $^5$Cp has also been applied to several group 2 metals and p-block elements. The synthesis of the decaisopropyl metallocenes of calcium, strontium, and barium was reported by

Sitzmann et al. in 1998, starting from radical **1b** and the corresponding metal (Scheme 4).[18]

In this process the metal was dissolved in liquid ammonia and a diethyl ether solution of radical **1b** was added. Alternatively, the metal may be suspended in a thf solution of radical **1b** and sonicated at 333 K. Both routes yield the metallocenes **4**–**6** in around 80%, which were characterized in solution by NMR spectroscopy and in case of bariocene **6** also by single crystal X-ray diffraction in the solid-state. The solid-state structure of bariocene **6** displays two almost parallel oriented Cp rings. This structure is also predicted for calcocene **4** and strontocene **5** by DFT calculations.[20] The metal-Cp bond lengths increase with the size of the central atom, as to be expected (Table 1). Due to hindered rotation around the $^{Cp}$C–C$^{iPr}$ bond, different isomers of these metallocenes were observed in the $^1$H NMR spectrum, as well as in the crystal structure of bariocene **6**. The activation enthalpies for the rotation of the isopropyl groups was estimate by VT-NMR spectroscopy to be 70–75 kJ mol$^{-1}$. Due to the extremely bulky substitution pattern calcocene **4** and strontocene **5** were reported to be air stable for several weeks. In case of bariocene **6** slow decomposition was observed.

In addition to decaisopropyl metallocenes of group 2 metals, the first analogues group 14 derivatives were reported by Sitzmann et al. in 1995 and 1996. The reaction of $^5$CpLi(Et$_2$O), **2**, with tin(II) chloride gives decaisopropyl stannocene, **7**, in 37% yield and the reaction of $^5$CpNa, **3**, with lead(II) chloride gives decaisopropyl plumbocene, **8**, in 70% yield (Scheme 5).[21,22]

These compounds were characterized in solution by NMR spectroscopy and in the solid state by single crystal X-ray diffraction. Decaisopropyl stannocene **7** exhibits a $^{119}$Sn NMR chemical shift thst is similar to other stannocenes ($^{119}$Sn(**7**) = −2262;[22] $^{119}$Sn(Cp$_2$Sn) = −2199;[23] $^{119}$Sn(Cp*$_2$Sn) = −2129[23]), indicating that the isopropyl substitution pattern on the Cp rings has only a small influence on the electronic properties of the tin center. Similarly, plumbocene **8** exhibits a $^{207}$Pb NMR chemical shift in the same range to that of other plumbocenes ($^{207}$Pb(**8**) = −3293;[21] $^{207}$Pb(Cp$_2$Pb) = −5030;[23] $^{207}$Pb(Cp*$_2$Pb) = −4390[23]). The solid-state structure of stannocene **7** and plumbocene **8**,



**Scheme 3.** Improved synthesis of Lithium pentaisopropyl cyclopentadienide, **2**, as reported by Sitzmann et al. in 1997.[19]



**Scheme 4.** Synthesis of decaisopropyl calcocene (M=Ca), **4**, strontocene (M=Sr), **5**, bariocene (M=Ba), **6**, as reported by Sitzmann et al. in 1998.[18]

**Table 1.** Selected structural parameters for compounds **4**–**9**.

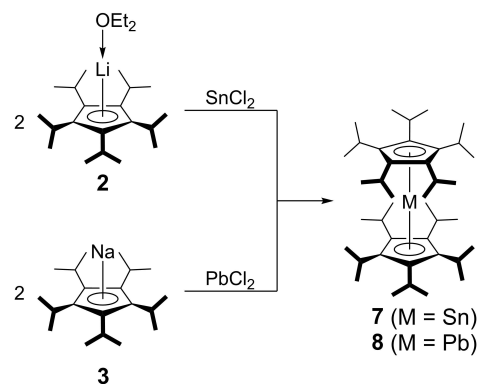| Compound | E–$^5$Cp[a] (exp.) [pm] | Cp–E–Cp[a] (exp.) [°] | E–$^5$Cp[a,c] (calc.) [pm] | Cp–E–Cp[c] (calc.) [°] |
|---|---|---|---|---|
| **4**[18] | – | – | 243 | 180 |
| **5**[18] | – | – | 255 | 180 |
| **6**[18] | 275 | 180 | 277 | 180 |
| **7**[22] | 249 | 180 | – | – |
| **8**[21][b] | 275 | 170 | – | – |
| **9**[24] | 219 | 179.7 | – | – |

[a] Relative to centroid of Cp. [b] Structure not completely resolved. [c] Data from calculated structure.[7]



**Scheme 5.** Synthesis of decaisopropyl stannocene (M=Sn), **7**, and plumbocene (M=Pb), **8**, as reported by Sitzmann et al. in 1995[21] and 1996.[22]

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with differently oriented isopropyl groups, is similar to what was discussed earlier for the analogues group 2 metallocenes. The activation enthalpies for isopropyl group rotations were estimated by VT-NMR and found to very similar to those of the group 2 metallocenes.
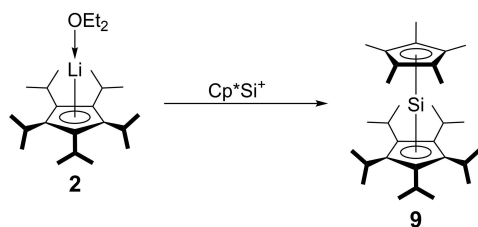
While decaisopropyl metallocenes of the lighter elements are unknown, the pentaisopropyl cyclopentadienide ligand was utilized in silicon chemistry in the synthesis of a pentaisopropyl pentamethyl silicocene, **9**, as reported by Jutzi et al. in 2006. Treatment of the pentamethyl cyclopentadienide silyliumylidene cation in form of its perfluorinated tetraphenylborate salt with lithium pentaisopropyl cyclopentadienide, **2**, in dichloromethane at 218 K gave the colorless, air and moisture sensitive heteroleptic silicocene **9** in almost quantitative yield (Scheme 6).[24]

Silicocene **9** was characterized by NMR spectroscopy in solution and single crystal X-ray diffraction in the solid state and exhibits a structure with parallel oriented Cp rings similar to decamethyl silicocene ($Cp^*_2Si$). The $^{29}Si$ NMR resonance of silicocene **9** was observed at $-420$ ppm, which is similar to that of decamethyl silicocene ($\delta^{29}Si(Cp^*_2Si) = 392.6^{[24]}/-398^{[25]}$) The pentaisopropyl cyclopentadienide silyliumylidene cation ($^5CpSi^+$) can be produced from **9** by protonation of the pentamethyl cyclopentadienide ligand with $[H(OEt_2)_2][Al[OC-(CF_3)_3]_4]$ and is obtained in a quantitative yield in form of its aluminate salt as a yellow, air and moisture sensitive solid. It exhibits a similar $^{29}Si$ NMR chemical shift as the pentamethyl cyclopentadienide derivative ($\delta^{29}Si(Cp^*Si^+) = -400.2;^{[24]}$ $\delta^{29}Si(^5CpSi^+) = -397.4^{[24]}$).
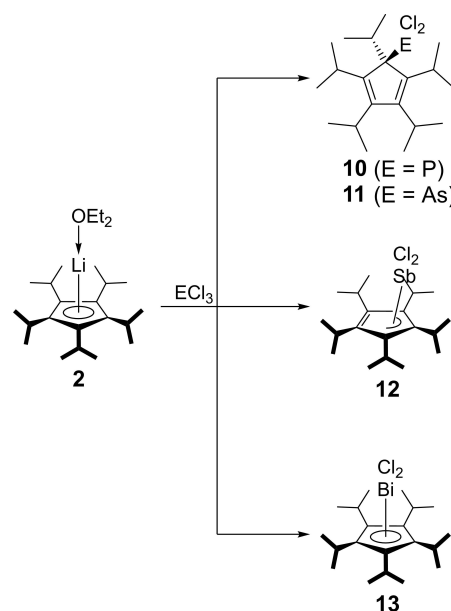
The following table lists selected structural features of the $^5Cp$-substituted metallocenes discussed in this chapter.

More recently, the $^5Cp$ ligand was also utilized in group 15 chemistry and several mono-Cp-substituted compounds were reported by Schäfer et al.[26] Treatment of $^5CpLi(Et_2O)$, **2**, with the corresponding pnictogen trichloride gives the matching cyclopentadienyl pnictogen dichloride (Scheme 7).

Here, the usual tendency of a hapticity increase, which is often observed in main-group chemistry going from lighter to heavier elements, is nicely illustrated. While the phosphorus and arsenic compounds exhibit $\eta^1/\sigma$ bonded pentaisopropylcyclopentadienyl groups, antimony exhibits an $\eta^3$ coordination and bismuth an $\eta^5$ coordination. Furthermore, the bismuth compound forms a chloro-bridged dimer in the solid state, which is a common motif for organobismuth halogenides. In case of the phosphorus, arsenic and antimony compounds,
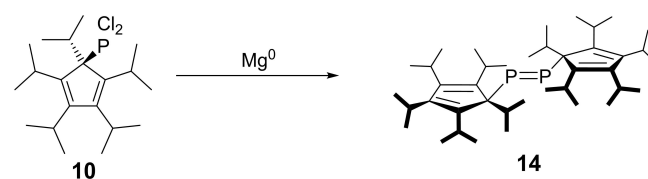
**Scheme 7.** Synthesis of pentaisopropylcyclopentadienyl phosphorus dichloride (E=P), **10**, pentaisopropylcyclopentadienyl arsenic dichloride (E=As), **11**, pentaisopropylcyclopentadienyl antimony dichloride (E=Sb), **12**, and pentaisopropylcyclopentadienyl bismuth dichloride (E=Bi), **13**, as reported by Schäfer et al. in 2021.[26]

rapid sigmatropic rearrangements of the pnictogenyl groups were observed, which were studied by VT-NMR and DFT calculations.

In addition, the capability of the $^5Cp$ ligand to kinetically stabilize low-valent main group compounds was also nicely demonstrated by the reduction of $^5CpPCl_2$, **10**, with magnesium metal to obtain the corresponding diphosphene $^5Cp_2P_2$, **14**, (Scheme 8).

Although diphosphenes are relatively common, this is a rare example of such a compound in which the phosphorus atoms are carrying cyclopentadienyl groups instead of bulky aryl or alkyl substituents. Like **10**, diphosphene **14**, also undergoes rapid sigmatropic rearrangements. Moreover, it was also demonstrated that the diphosphene can be used as a ligand for transition metal fragments and a corresponding dicationic disilver(I) complex was structurally characterized in form of its dodecabromo-closo-dodecaborate salt.

As discussed before, treatment of two equivalents of $^5CpNa$ with one equivalent of bromine in pentane at low temperatures yields the $^5Cp$ radical **1b**. If this reaction is however carried out with a 1:1 stoichiometry, pentaisopropyl cyclopentadienyl

**Scheme 6.** Synthesis of pantaisopropyl pentamethyl silicocene, **9**, as reported by Jutzi et al. in 2006.[24]

**Scheme 8.** Synthesis of bis(pentaisopropyl cyclopentadienyl)diphosphene, **14**, as reported by Schäfer et al. in 2021.[26]

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bromide **1d** can be obtained. Likewise, treatment of ⁵CpNa with hexachloroethane at 273 K in pentane gives pentaisopropyl cyclopentadienyl chloride **1c** (Scheme 9), as reported by Sitzmann et al. in 1993.[17]

⁵Cp chloride **1c** was obtained in a 72% yield as a light-yellow air and thermally stable compound. In contrast, **1d**, which was obtained as a yellow solid in 63% yield, is very sensitive to moisture and air, and only marginally stable at ambient conditions and decomposes under HBr elimination.
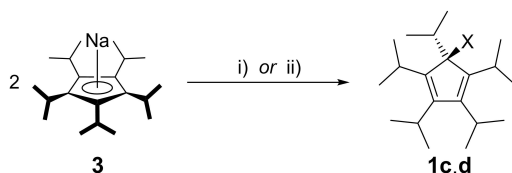
Reaction of **1c** or **1d** with $SbCl_5$ at 180 K in dichloromethane results in an immediate color change from yellow to red-brown. The EPR spectrum of this mixture suggest the presence of a radical species, which is believed to be the formally $4\pi$ electron pentaisopropyl cyclopentadienyl cation, which has a triplet ground state due to its antiaromatic character. The same species could also be observed by cyclovoltammetry experiments of an acetonitrile solution of ⁵CpNa with tetrabutylammonium perchlorate as electrolyte at room temperature vs ferrocene/ferrocenium.
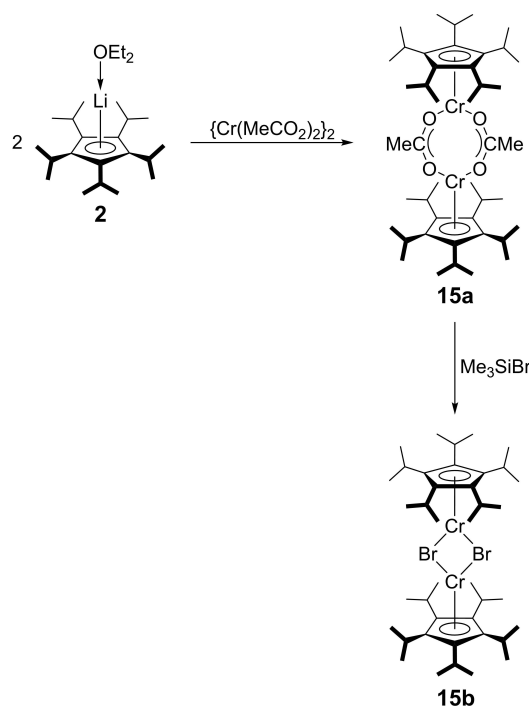
## Transition Metal Compounds

The ⁵Cp ligand has been widely employed in transition metal chemistry to various elements of group 6, 8, 9 and 10. The corresponding complexes in this subchapter will be discussed in the order of the element groups in the periodic table, but with the iron compounds last, since this is the largest group of compounds.

The first ⁵Cp chromium complexes were published in 2018 by Sitzmann et al. The dinuclear complex [⁵CpCr(μ-$O_2$CMe)]₂, **15**, was obtained from a reaction of ⁵CpLi($Et_2$O), **2**, with {Cr-(MeCO₂)₂}₂. Subsequent treatment of this complex with Me₃SiBr gave the dinuclear bromo-bridged analog {⁵CpCr(μ-Br)}₂, **15b** (Scheme 10).[27]
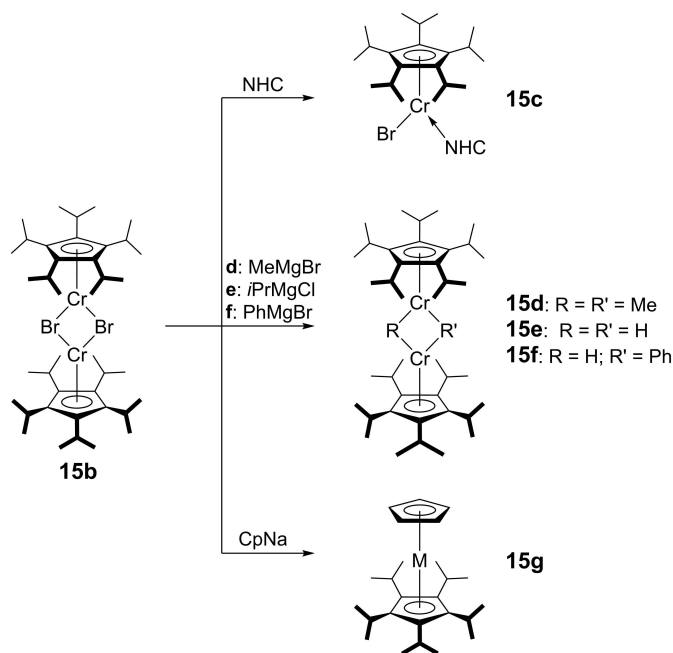
The pentaisopropylcyclopentadienide chromium bromide dimer, **15b**, proved to be an extremely useful synthon for several other ⁵Cp chromium complexes, as demonstrated by Sitzmann et al. in 2021 (Scheme 11).[28] For instance, treatment with methyl magnesium bromide Grignard-reagent yielded the methyl bridged analogue, **15d**. Interestingly, treatment of **15b** with the sterically more demanding isopropyl magnesium chloride Grignard-reagent resulted in the formation of the hydride bridged dimer, **15e**, and not the isopropyl bridged derivative, as one might expect. Similarly, the reaction of **15b**



**Scheme 10.** Synthesis of pentaisopropylcyclopentadienide chromium acetate dimer, **15**, as reported Sitzmann et al. in 2018.[27]



**Scheme 11.** Different reactions of pentaisopropylcyclopentadienide chromium bromide dimer, **15b**, as reported by Sitzmann et al. in 2021.[28]



**Scheme 9.** Synthesis of pentaisopropyl cyclopentadienyl chloride (X=Cl), **1c**, and pentaisopropyl cyclopentadienyl bromide (X=Br), **1d**, as reported by Sitzmann et al. in 1993;[17] i): C₂Cl₆/pentane/273 K, X=Cl; ii): Br₂/pentane/195 K, X=Br.

with phenyl magnesium bromide gave the phenyl-hydride-mixed-bridged dimer, **15f**, presumably via aryne elimination. The heteroleptic chromocene, **15g**, can be obtained by treating **15b** with sodium cyclopentadienide and is a rare example of such a species. Finally, the monomeric of pentaisopropylcyclo-

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pentadienide chromium bromide can be obtained in form of an N-heterocyclic carbene complex, **15c**. Furthermore, the magnetic susceptibilities of some of these complexes were investigated, highlighting interesting magnetic properties. Table 2 lists selected structural parameters of the $^5$Cp chromium complexes discussed.

**Table 2.** Selected structural parameters for compounds **15a,c–g**.

| Compound | Cr–$^5$Cp[a] [pm] | Cr–X [pm] | Cr–Cr [pm] |
|---|---|---|---|
| **15a**[27] | 197.08(5), 198.05(6) | (X=O₂CMe); 196.66(38), 197.35(41), 198.10(45), 197.29(43) | 423.67(8) |
| **15c**[28] | 199.70(5) | (X=Br); 248.52(7), (X=C$^{NHC}$), 214.90(32) | – |
| **15d**[28] | 197.96(4), 199.50(3) | (X=Me); 216.10(18), 220.07(18) | 239.14(4) |
| **15e**[28] | 192.59(5) | (X=H); 177.35(32) | 245.75(4) |
| **15f**[28] | 220.13(25), 221.66(25) | (X=H); 151.08(3), 153.31(2) (X=Ph); 202.13(25), 221.66(25) | 258.23(6) |
| **15g**[28] | 174.75(3) | (X=Cp$^{cent}$); 180.78(3) | – |

[a] Relative to centroid of Cp.
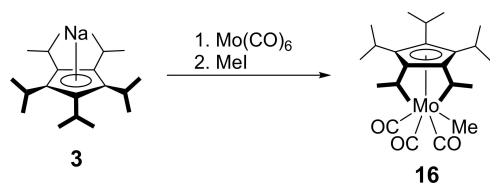


**Scheme 12.** Synthesis of pentaisopropylcyclopentadienide tricarbonylmethyl molybdenum, **16**, as reported by Sitzmann in 1990.[29]
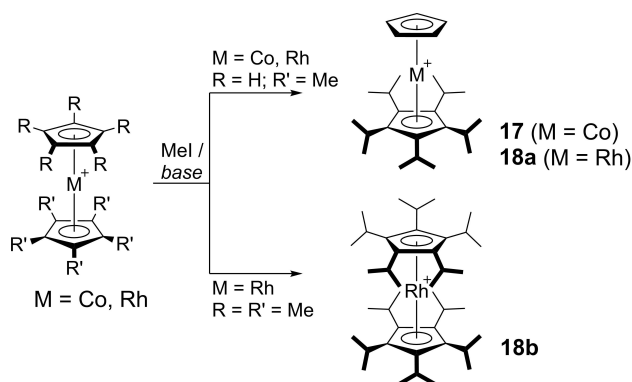


**Scheme 13.** Synthesis of pentaisopropyl cobaltocenium, **17**, rhodocenium, **18a**, and decaisopropyl rhodocenium, **18b**, as reported by Astruc et al. in 1990,[30] 1994[31] and 1995.[32]

The first $^5$Cp molybdenum complexes were published in 1990 by Sitzmann et al. The half-sandwich tricarbonyl complex $^5$Cp(CO)$_3$MoMe, **16**, was obtained by the reaction of $^5$CpNa, **3**, and Mo(CO)$_6$ and subsequent addition of MeI (Scheme 12). For this complex, an energy barrier for the isopropyl group rotation of $55.6 \pm 4$ kJ/mol was determined experimentally, using the Eyring equation.[29]

In 1990, the first one-pot synthesis for [$^5$CpCpCo]PF$_6$, **17**, was published by Astruc et al. (Scheme 13). Starting from [Cp*CpCo]PF$_6$ with an excess of KOH and MeI, **17** was obtained by Cp-substituent-functionalization – a rather uncommon synthetic route – and structurally characterized ($^5$Cp$^{cent}$–Co 168.4(2) pm, Cp$^{cent}$–Co 165.6(2) pm). Electrochemical studies of this compound revealed an E$^0$ value (Hg, DMF, n-Bu$_4$NBF$_4$ 0.1 M, 20 °C, V vs. ESC) of −0.96 V for the reversible Co$^{II}$–Co$^{III}$ ion pair and −2.11 V for the Co$^I$–Co$^{II}$ pair.[30]

The first decaisopropylmetallocene – a metallocene-type compound with two $^5$Cp groups – was [$^5$Cp$_2$Rh]PF$_6$, **18b**, which was prepared by Astruc et al. in 1994 via a similar route starting from [Cp*$_2$Rh]PF$_6$ with an excess of KOH and MeI.[31] A year later, Astruc et al. also reported [$^5$CpCpRh]PF$_6$, **18a**.[32]
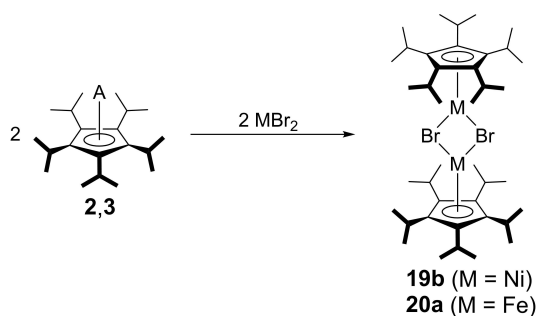
In 1995, Sitzmann et al. reported the first $^5$Cp nickel complexes, by utilizing the previously discussed $^5$Cp radical, **1b**, as the Cp source and reacting it with Ni(CO)$_4$ (Scheme 14). The dinuclear complex {$^5$CpNi(μ–CO)}$_2$, **19a**, was obtained as a diamagnetic compound in good yields.[33]

The analogues bromo-bridged dinuclear complexes of nickel and iron could be obtained starting from either of $^5$CpLi (Et$_2$O), **2**, or $^5$CpNa, **3** and the corresponding dibromide (Scheme 15). While {$^5$CpFe(μ-Br)}$_2$, **20a**, can be obtained from FeBr$_2$(dme) and $^5$CpNa, treatment of $^5$CpLi(Et$_2$O) and FeBr$_2$(dme) and a subsequent gassing with CO yields the monomeric dicarbonyl complex $^5$CpFeBr(CO)$_2$, **20b**, (Scheme 16). The related nickel derivative {$^5$CpNi(μ-Br)}$_2$, **19b**, can also be obtained by the reaction of $^5$CpLi(Et$_2$O) with nickel dibromide (Scheme 15), and was reported to be paramagnetic with two unpaired electrons at each nickel center.[34]

Reduction of **20b**, with sodium amalgam gives mixed iron mercury complex {$^5$CpFe(CO)$_2$}$_2$(Hg) in almost quantitative yield. A reduction of the same reactant with two equivalents of potassium gives the potassium analog K[$^5$CpFe(CO)$_2$] in good yields. This iron fragment, Cp(CO)$_2$Fe, is also well-known for unsubstituted Cp, and sometimes abbreviated as "Fp". In
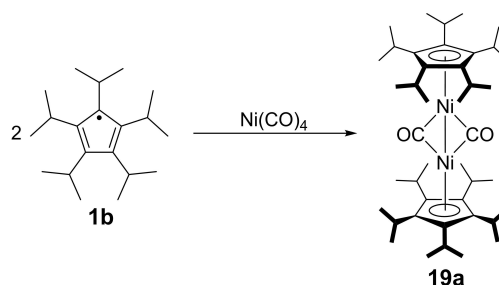


**Scheme 14.** Synthesis of pentaisopropylcyclopentadienide carbonyl nickel dimer, **19a**, as reported by Sitzmann et al. in 1995.[33]

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**Scheme 15.** Synthesis of pentaisopropylcyclopentadienide iron bromide dimer (A=Na; M=Fe), **20a**, pentaisopropylcyclopentadienide nickel bromide dimer (A=Li(OEt$_2$); M=Ni), **19b**, as reported Sitzmann et al. in 1996[35] and 2011.[34]
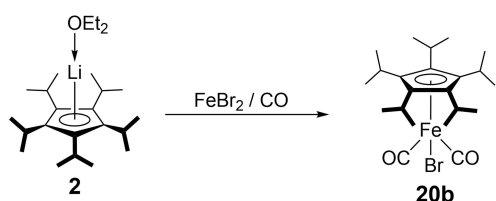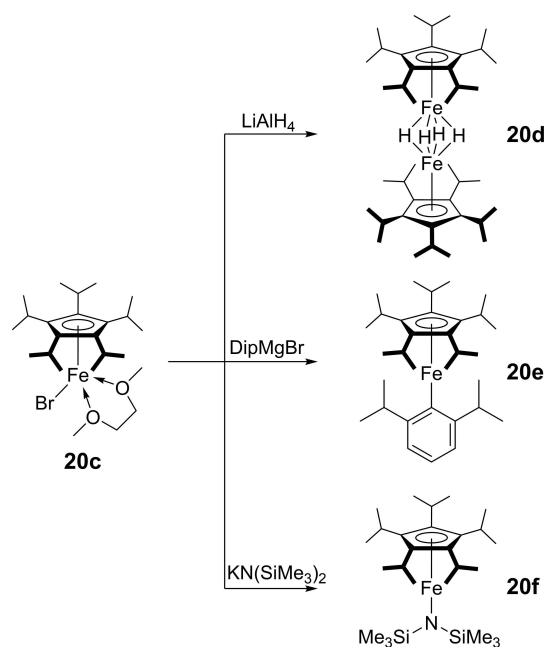


**Scheme 16.** Synthesis of pentaisopropylcyclopentadienidedicarbonyl iron bromide, **20b**, as reported by Sitzmann et al. in 1996.[35]



**Scheme 17.** Different reactions of pentaisopropylcyclopentadienide iron bromide dme-adduct, **20c**, as reported by Sitzmann et al. in 2011,[39] 2017[44] and 2019.[38]

addition to the anion iron fragments, the [⁵CpFe(CO)$_2$]$_2$ radical can be obtained either by a careful reduction of [⁵CpFeBr(CO)$_2$] with potassium or by the reaction of K[⁵CpFe(CO)$_2$] with AgBF$_4$ in almost quantitative yields. Investigations of the magnetic moment of this complex by the Evans' method gave $\mu B = 1.7$.[35] In addition, the tetraphosphorus-bridged complex {⁵Cp-(CO)$_2$Fe}$_2$($\mu$-P$_4$)[36] is also known and its reaction with diphenylacetylene results in phosphorus-functionalization and yields [⁵Cp($\eta^5$-P$_3$C$_2$Ph$_2$)Fe]. Furthermore, the related trinuclear complex {⁵Cp$_3$(CO)$_4$Fe$_3$}P$_{11}$ has likewise been reported, although only obtained in low yields.[37]

When ⁵CpLi(Et$_2$O), **2**, is reacted with FeBr$_2$(dme) in dme in the absence of CO, the half-sandwich iron bromide **20c** can be obtained as a dme-complex. This is a versatile synthon for a variety of other ⁵Cp iron complexes (Scheme 17).

Starting from **20c** and LiAlH$_4$, tetrahydride-bridged dinuclear complex **20d**, could be obtained. This complex was investigated with Valence-to-core X-ray emission spectroscopy (vtc-XES) and high-energy-resolution fluorescence detected X-ray absorption near edge structure (HERFD-XANES) in combination with DFT calculations. This provided information on the bonding situation and oxidation state of the iron centers, suggesting that both iron centers are in the low-spin state in the oxidation state +II and there is no Fe—Fe bonding interaction.[38] Reaction of half-sandwich iron bromide **20c** with 2,6-diisopropylphenylmagnesium bromide Grignard-reagent gives the diorgano iron complex ⁵CpFeDip (Dip=2,6-diisopropylphenyl), **20e**. This mononuclear high-spin Fe(II) complex is quite remarkable, as it has properties of a single-molecule magnet (SMM).[39,40] **20e** is sensitive to oxidation and treatment
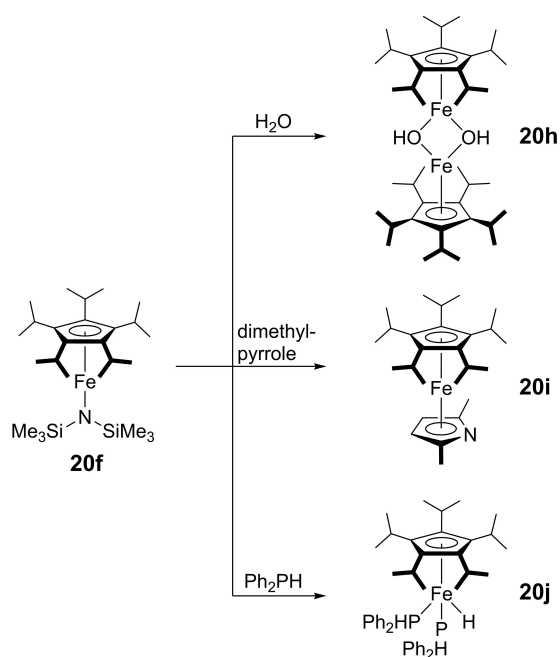
with hexachloroethane gives ⁵CpFeDipCl,[41] while treatment with trimethylaluminum results in substitution of the *ipso*-carbon atom of the phenyl ring by the AlMe$_3$ moiety and rearrangement of the Dip moiety from $\sigma$-bonding to $\eta^6$-coordination to the iron center, giving sandwich complex **20g** (Scheme 18).[42]

Finally, the half-sandwich amido complex ⁵CpFeN(SiMe$_3$)$_2$, **20f**, can be obtained by the reaction of **20c** with KN(SiMe$_3$)$_2$. This iron amino species, **20f**, also exhibits interesting magnetic properties and magnetic susceptibility measurements showed $U_{eff} = 113$ cm$^{-1}$ and $\tau_0 = 4.8 \times 10^{-10}$ s. Thus, **20f** is a rare example of a cyclopentadienyl iron complex which exhibits a relatively slow relaxation of magnetization. Furthermore, **20f** is also a very potent synthon for a variety of other half-sandwich complexes (Scheme 19).

For example, careful hydrolysis with stoichiometric amounts of water yields the hydroxy-bridged dimeric complex **20h**, in quantitative yields. Using nuclear inelastic scattering (NIS), both **20a** and **20h**, were investigated and Lamb-Mössbauer factors
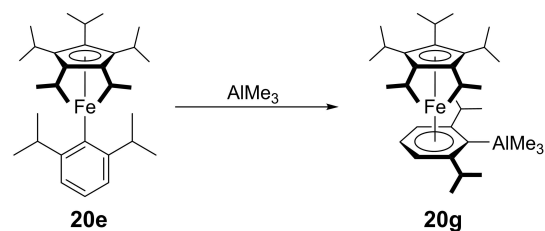


**Scheme 18.** Synthesis of trimethylaluminum complex, **20g**, as reported by Sitzmann et al. in 2014.[42]

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**Scheme 19.** Different reactions of pentaisopropylcyclopentadienide-(bis (trimethylsilyl)amido iron, **20 f**, as reported by Sitzmann et al. in 2017.[44]

**Table 3.** Selected structural parameters for compounds **20 a**, **20 d–i**.

| Compound | Fe–⁵Cp[a] [pm] | Fe–X [pm] | Fe–Fe [pm] |
|---|---|---|---|
| **20 a**[42] | 194.00(6), 194.34(6) | (X=Br); 250.20(15), 252.00(18), 250.15(16), 252.37(18) | 357.72(8) |
| **20 d**[38] | 167.31(4) | (X=H); 153.84(31), 155.20(39), 163.58(41), 166.10(48) | 221.45(6) |
| **20 e**[39] | 192.56(1) | (X=C$^{ipso}$); 204.27(9) | – |
| **20 f**[44] | 192.40(3) | (X=N); 192.00(18) | – |
| **20 g**[42] | 172.42(2) | (X= DIP$^{cent}$); 165.52(2) | – |
| **20 h**[44] | 194.35(3) | (X=OH); 193.89(52) | 299.58(4) |
| **20 i**[44] | 167.55(2) | (X=pyrrole$^{cent}$); 169.00(2) | – |
| **20 j**[44] | 172.61(3) | (X=P); 215.45(6), 216.05(5) (X=H); 145.54(29) | – |

[a] Relative to centroid of Cp.

as well as other thermodynamic parameters could be determined.[43] Treatment of **20 f** with 2,5-dimethylpyrrole gives the azaferrocene **20 i** in almost quantitative yields and reacting **20 f** with an excess of diphenylphosphane results in single P–H bond activation and the formation of bis(phosphine)-hydrido-iron complex **20 j**, as well as the dehydrocoupling product ⁵CpFe(H)(P₂Ph₄).[44] Table 3 lists selected structural features of the iron complexes discussed.

## Rare-Earth Element Compounds

The ⁵Cp ligand has also been applied to a series of rare-earth elements. Initially metallocene-type compounds of samarium, europium and ytterbium were investigated by Bosnich et al. in 1993, by DFT calculations. In this contribution, a linear geometry was predicted for ⁵Cp₂Ln (Ln=Sm, Eu, Yb) due to interligand methyl-methyl repulsions.[20] Following these initial theoretical investigations, Sitzmann et al. published the first ⁵Cp lanthanoid complexes, **21–23**, of the type ⁵Cp₂Ln (Ln = Sm, Eu, Yb), in 2000. They were obtained by the reaction of the corresponding metal with the ⁵Cp radical, **1 b**, (Scheme 20).[45]
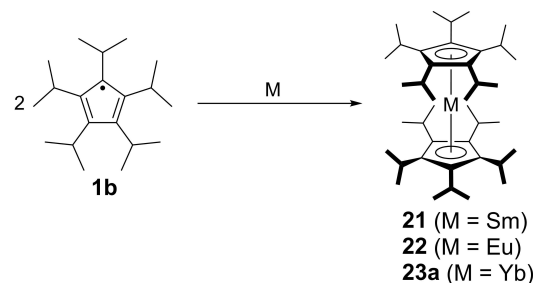
Noteworthy, ⁵Cp₂Eu, **22**, was described to show fluorescence in daylight and UV irradiation (336 nm).

A few years later, the first triple-decker sandwich complex with the ⁵Cp ligand was published by Sitzmann et al. in 2005. ⁵Cp₂Yb₂(COT) was obtained in good yields, starting from ytterbium metal and the ⁵Cp radical, **1 b**, in the presence of cyclooctotetraene (Scheme 21).[46]
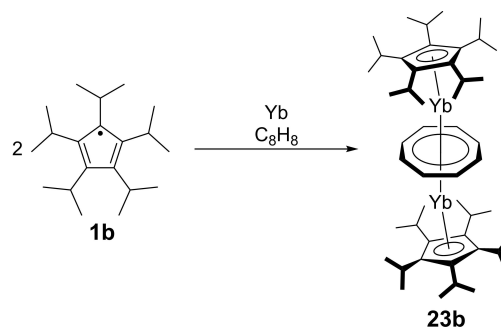
After these reports, ⁵Cp lanthanoid chemistry was dormant for several years, until Layfield et al. published the first ⁵Cp–Dy



**Scheme 20.** Synthesis of decaisopropyl samariocene (M = Sm), **21**, europiocene (M=Eu), **22**, and ytterbiocene (M=Yb), **23**, as reported by Sitzmann et al. in 2000.[45]



**Scheme 21.** Synthesis of a ⁵Cp₂Yb₂(COT) triple-decker sandwich complex, **23 b**, as reported by Sitzmann et al. in 2005.[46]

complexes in 2018.[47] Starting from ⁵CpNa, **3**, and Dy-(BH₄)₃(THF)₃, the corresponding half-sandwich complex, **24 a**,

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could be obtained in good yields. A subsequent reaction with Cp*K followed by abstraction of the $BH_4^-$ anion with the superelectrophile $[Et_3Si(\mu-H)SiEt_3]^+$ gave the cationic metal-locenium complex **24b** in form of its tris(pentafluorophenyl) borate salt (Scheme 22).

This remarkable compound, **24b**, possesses fascinating single-molecule magnet propertied with $U_{eff} = 1541$ cm$^{-1}$ and $T_B = 80$ K, so far the highest values for a monometallic Dy$^{3+}$ complex.[48–50]

Almost simultaneously, Harvey et al. reported the synthesis of related metallocenium salts carrying two $^5$Cp ligands $[^5Cp_2M][B(C_6F_5)_4]$.[51] These compounds were obtained by the reaction of $^5$CpNa with the metal triiodide and subsequent halide abstraction. Magnetic studies of $[^5Cp_2Dy][B(C_6F_5)_4]$ revealed $U_{eff}$ 1334 cm$^{-1}$ and $T_B = 56$ K. Furthermore, by comparing $[^5Cp_2Dy]^+$ and $[^5CpCp*Dy]^+$, it was found that more bulky Cp groups lead to a larger Cp–Dy-Cp angle and that a large Cp–Dy–Cp angle and a short Cp$^{cent}$–Dy distance lead to an increase in $U_{eff}$ and $T_B$.
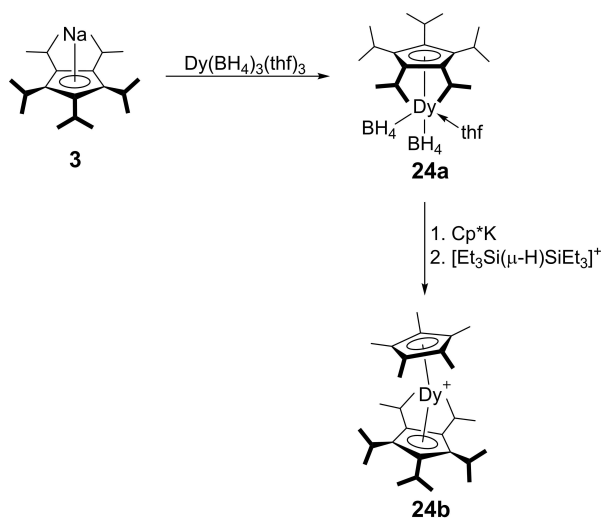
Shortly after, Long et al. reported the synthesis of a corresponding terbiocenium salt, as well as of the neutral terbiocene and dysprosiocene.[52] These neutral complexes, **24c**, **25**, carrying two $^5$Cp ligands, were obtained by treatment of

$^5$CpNa, **3**, the corresponding metal triiodide and subsequent reduction with potassium graphite (Scheme 23).

XRD analysis, DFT calculations and magnetic susceptibility measurements of **24c** and **25** reveal a 4f$^n$5d$^1$ electron configuration with strong s/d mixing. A comparison between the cationic complexes $[^5Cp_2Ln]^+$ and the neutral $[^5Cp_2Ln]$ reveals opposite effect for dysprosium and terbium. For terbium, a reduction from Tb(III) to Tb(II) leads to an increase in the magnetic relaxation time, whereas for dysprosium it leads to a decrease. For **25**, an effective thermal barrier for magnetic relaxation $U_{eff} = 1205$ cm$^{-1}$ and a 100-s-blocking temperature $T_B = 52$ K were measured; the highest values for a non-dysprosium single-molecule magnet.[52] Furthermore, using ab initio calculations for **25**, 4f-shell and valence magnetism (FV-magnetism) was investigated. Additional $^5$Cp$_2$Ln (Ln=Gd, Dy, Ho, Er, Tm) complexes were calculated and a close similarity of the molecular and electronic structure across the row was found.[53] Moreover, complete active space self-consistent field (CASSCF) studies of **25** showed a strong Fermi contact interaction between the Tb nuclear spin and the electron spin density at the nucleus arising from the occupation of the (6s,5d) orbitals.[53,54]

In 2019, Layfield et al. reported the preparation of $^5$Cp uranocene iodid, **26**, obtained from $^5$CpNa and UI$_3$ (Scheme 24).[55]

Subsequent iodide abstraction with $[Et_3Si(\mu-H)SiEt_3]^+$ gave the cationic complex $[^5Cp_2U]^+$. Bonding analysis of $[^5Cp_2U]^+$ indicated a strong splitting of the 5f orbitals of uranium, which are mixed with the ligand orbitals.[55] Similarly, to the afore mentioned terbium and dysprosium complexes, the neutral $^5$Cp$_2$U was obtained by reduction of **26** with potassium graphite. The electron configuration was investigated by UV-VIS-NIR spectroscopy and DFT calculations and suggested to be 5f36d1.[56] Table 4 lists selected structural features of the afore discussed rare-earth element complexes.

## Summary and Outlook

In summary, the pentaisopropylcyclopentadienide, $^5$Cp, ligand has seen widespread application in main-group, transition metal and rare-earth elements chemistry in the last few decades. The most commonly used Cp transfer reagents are the lithium and sodium compounds, as well as the neutral radical. In p-block chemistry, the $^5$Cp ligand has been used in metal-



**Scheme 22.** Synthesis of pentaisopropyl pentamethyl dysprosiocenium cation, **24b**, as reported by Layfield et al. in 2018.[47]
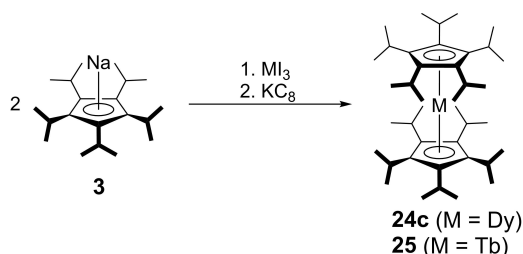


**Scheme 23.** Synthesis of decaisopropyl dysprosiocene (M=Dy), **24c**, and terbiocene (M=Tb), **25**, as reported by Furche, Harvey and Long et al. in 2019.[52]
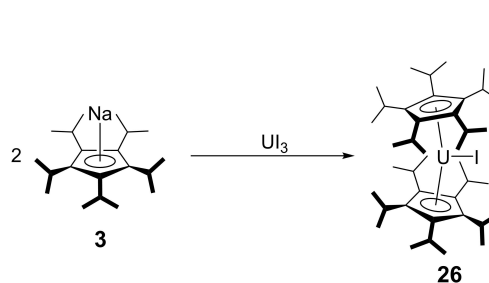


**Scheme 24.** Synthesis of decaisopropyl uranocene iodide, **26**, as reported by Tong, Mansikkamäki and Layfield et al. in 2019.[55]

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**Table 4.** Selected structural parameters for compounds **21, 24a–c, 25, 26**.

| Compound | 5Cp–E[a] [pm] | 5Cp–E–Cp[a] [°] |
|---|---|---|
| **22**[46] | 256.71 | 180 |
| **24a**[48] | 236.58(6) | – |
| **24b**[48] | 228.39(5) | 162.5(2) |
| **24c**[53] | 238.5(1) | 180 |
| **25**[53] | 241.6(1) | 180 |
| **26**[55] | 253.23(15), 254.08(15) | 152.63(6) |

[a] Relative to centroid of Cp.

locenes of group 14 elements and has enabled the isolation of low-valent group 15 diphosphenes. In transition metal chemistry, a variety of compounds is known, often possessing an interesting reactivity and some having unique magnetic properties. Rare-earth element chemistry with the 5Cp ligand has seen increasing interest in recent years, due to some complexes having single-molecule magnet properties.

Noteworthy, the 5Cp has not yet been applied to early transition metals from groups 3, 4, and 5, nor have complexes of group 7, 11 or 12 metals been reported. Furthermore, although some 5Cp transition metal complexes might hold great potential in bond activation processes, for instance small molecule activation or homogenous catalysis, this area also remains almost unexplored.

In summary, one can expect to see many more applications of the 5Cp ligand in the future, especially utilizing it in the stabilization of unusual low-valent compounds, both in transition metal chemistry, as well as main-group and rare earth element chemistry.

## Acknowledgements

## Conflict of Interest

The authors declare no conflict of interest.

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