η^6-Cycloparaphenylene Transition Metal Complexes: Synthesis, Structure, Photophysical Properties, and Application to the Selective Monofunctionalization of Cycloparaphenylenes

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S *Supporting Information*

ABSTRACT: The synthesis, structure, photophysical properties, and reactivity of cycloparaphenylenes (CPPs) coordinated to group 6 transition metal fragments are described. The η^6-coordination of [9]CPP or [12]CPP with $M(CO)_6$ (M = Cr, Mo, W) afforded the corresponding [n]CPP-$M(CO)_3$ complexes (n = 9, 12; M = Cr, Mo, W). In the ^{1}H NMR spectra of these complexes, characteristic upfield-shifted singlet signals corresponding to the four hydrogen atoms attached to the coordinated C_6H_4 ring of the CPPs were observed at 5.4−5.9 ppm. The complex [9]CPP-$Cr(CO)_3$ could be successfully isolated in spite of its instability. X-ray crystallographic analysis and computational studies of [9]CPP-$Cr(CO)_3$ revealed that chromium-CPP coordination occurs at the convex surface of [9]CPP both in the solid state and in solution. TD-DFT calculations suggested that the emerging high-wavenumber absorption peak upon coordination of [9]CPP to $Cr(CO)_3$ should be assigned to a weak HOMO−LUMO transition. Moreover, by using the complex [9]CPP-$Cr(CO)_3$, a rapid and highly monoselective CPP functionalization has been achieved. The established one-pot method, consisting of complexation, deprotonation, nucleophilic substitution, and decomplexation steps, yielded silyl-, boryl-, and methoxycarbonyl-substituted CPPs in up to 93% yield relative to reacted starting material.
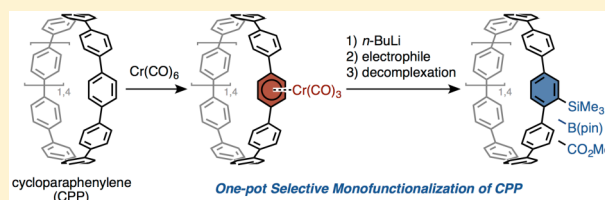
INTRODUCTION

The unusual properties and potential applications of organic molecules having cyclic π-conjugation have captivated the scientific community for decades.[1] In recent years, cycloparaphenylenes (CPPs), simple cyclic strings of benzene rings, have received great attention not only because this structure represents a shortest segment of armchair carbon nanotubes making it an ideal template for the bottom-up synthesis of carbon nanotubes,[2,3] but also due to its unique radial π-conjugation. Since the first isolation of CPPs in 2008, various ring sizes[4,5] and derivatives[6] have been synthesized. The effects of the radial conjugation mode in CPPs have been examined by photophysical measurements in combination with theoretical studies.[7]

However, the exact interaction modes between the radially conjugated π-orbitals of CPPs and organic or inorganic compounds still remain unclear. Figure 1 shows examples of noncovalent interactions of the CPP π-orbitals with various species. For example, van der Waals complexes of CPPs and fullerenes have been reported by the groups of Yamago and Jasti as well as by our group.[8] The binding constants of CPPs and fullerenes are very high, because the concave surface of CPPs provides excellent fit to the convex surface of fullerenes. Jasti and co-workers isolated the tetraanionic CPP $K_4([8]CPP)$, which showed ionic interactions between potassium and both
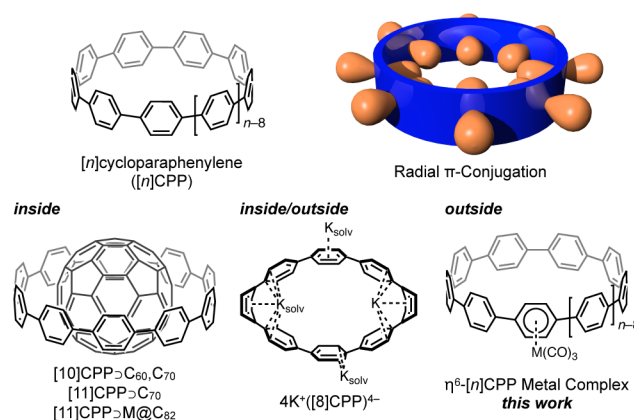

Figure 1. Radial π-conjugation system in CPPs.

the inside and outside surface of [8]CPP in the solid state.[9] However, neither van der Waals nor ionic interactions influence the CPP π-conjugation system substantially. Further investigations into the properties of CPP π-conjugation systems that result in the ability to tune the properties of CPPs, e.g., by

complexation of CPPs with transition metals, therefore present an interesting research target. The electronic properties and the reactivity of arenes can be easily adjusted by coordination to transition metals via η^6-coordination.[10] In this Article, we report the synthesis, characterization, and photophysical properties of group 6 transition metal η^6-complexes of CPPs. The application of η^6-complexation to the selective monofunctionalization of CPPs is also described.

■ RESULTS AND DISCUSSION

Synthesis of η^6-CPP Transition Metal Complexes. We began our study by investigating the complexation of [9]CPP with Cr(CO)$_6$. It was found that [9]CPP-Cr(CO)$_3$ (**1a**) could be isolated in 35% yield when [9]CPP was treated with an equimolar amount of Cr(CO)$_6$ in n-Bu$_2$O/THF mixed solvent system (n-Bu$_2$O/THF = 9:1) at 160 °C for 10 h (Scheme 1).

Scheme 1. Complexation of [9]CPP to Chromium Tricarbonyl
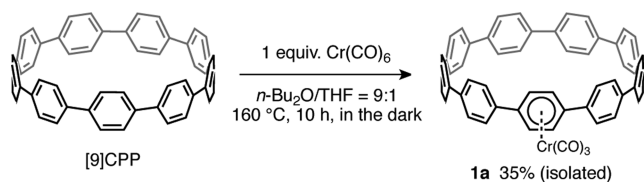
Prolonged reaction times and/or higher temperatures resulted in decomplexation of Cr from **1a**. As an alternative to Cr(CO)$_6$, Cr(CO)$_3$(MeCN)$_3$ could also be used as a precursor. Surprisingly, even when a small excess (1.5 or 2 equiv) of chromium complex was used, the main product was the 1:1 CPP-Cr complex and only trace amount of 1:2 and 1:3 CPP-Cr complexes were detected by ESI-MS. As **1a** was found to slowly decompose upon exposure to ambient light, the reaction tubes were covered with aluminum foil, and the reaction products were purified as quickly as possible by PTLC (preparative thin-layer chromatography) in the dark. The ^{1}H NMR spectrum of **1a** exhibited a characteristic singlet resonance at 5.46 ppm, which was assigned to the four hydrogen atoms attached to the C$_6$H$_4$ ring coordinated to chromium (illustrated by the red circle in Figure 2). Compared to uncoordinated, "free" [9]CPP
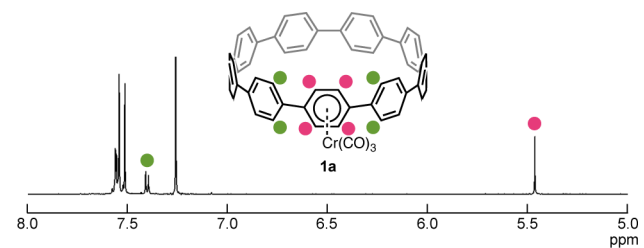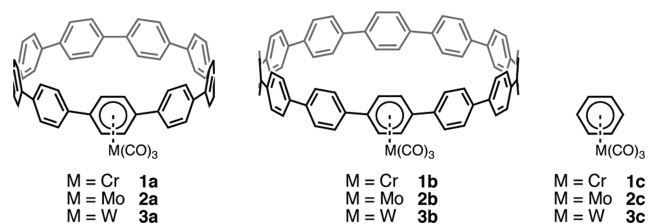

Figure 2. ^{1}H NMR spectrum of **1a** (600 MHz, CDCl$_3$).

(7.53 ppm), these hydrogen atoms experience a drastic upfield shift. The neighboring four hydrogen atoms (illustrated by the green circle in Figure 2) were also slightly upfield shifted (7.40 ppm). Considering a similar upfield shift in the ^{1}H NMR spectrum of the model complex (η^6-C$_6$H$_6$)-Cr(CO)$_3$ (**1c**; 7.36 → 5.33 ppm),[11,12] we concluded that one of the C$_6$H$_4$ rings of [9]CPP coordinates to the Cr(CO)$_3$ fragment in a η^6 fashion.

The same reaction conditions were applied to [12]CPP, and the characteristic singlet signal of [12]CPP-Cr(CO)$_3$ (**1b**) was

observed at 5.61 ppm as expected. Similarly, reactions of [9]CPP or [12]CPP with Mo(CO)$_6$ or W(CO)$_6$ furnished the corresponding CPP η^6-complexes [n]CPP-M(CO)$_3$ (**2a**, n = 9, M = Mo; **2b**, n = 12, M = Mo; **3a**, n = 9, M = W; **3b**, n = 12, M = W) as summarized in Table 1. All reaction products were

Table 1. ^{1}H NMR Chemical Shifts for Reference Compounds 1c−3c and the Characteristic Singlet Resonances of the Coordinated C$_6$H$_4$ Rings in the [9]- and [12]CPP Complexes 1a,b−3a,b[a]

	M = Cr	**1a**
	M = Mo	**2a**
	M = W	**3a**

	M = Cr	**1b**
	M = Mo	**2b**
	M = W	**3b**

	M = Cr	**1c**
	M = Mo	**2c**
	M = W	**3c**

	[9]CPP (**a**)	[12]CPP (**b**)	benzene (**c**)
Cr (**1**)	5.46	5.61	5.33[c]
Mo (**2**)	5.72	5.86	5.58[d]
W (**3**)	5.56	5.69	5.36[c]
"free" arene	7.52[b]	7.61[b]	7.36[e]

[a]Chemical shifts (in CDCl$_3$) in ppm corresponding to the singlet signals associated with the hydrogen atoms indicated by the red circle in Figure 2. [b]References 4e, f. [c]Reference 11. [d]This work (see Supporting Information). [e]Reference 12.

identified by ^{1}H NMR and high-resolution mass spectrometry. However, isolation of **1b**, **2a,b**, and **3a,b** was unsuccessful due to their instability toward light and air, as well as their low crystallinity. Compared to the chemical shifts of the model compounds (η^6-C$_6$H$_6$)-M(CO)$_3$ (M = Mo, W), these complexes were reliably assigned as resulting from η^6 coordination of one aromatic ring of the CPP to the metal carbonyl fragment.

Structure of η^6-[9]CPP Chromium Carbonyl Complex 1a. Single crystals of [9]CPP-Cr(CO)$_3$ (**1a**) were obtained by the slow vapor diffusion of pentane into a solution of **1a** in THF. Although the obtained yellow crystals of **1a** suffered from cracks upon exposure to ambient light for ca. 1 h, the molecular structure of **1a** was unambiguously determined by X-ray crystallographic analysis, showing that the convex surface of [9]CPP coordinates to chromium (Figure 3a). Moreover, two molecules of pentane were incorporated in the cavity of **1a**. In contrast to the herringbone packing structure of "free" [9]CPP,[4f] the packing mode of these crystals showed the formation of pairs of **1a**, thereby eliminating the dipole moment of **1a** in the solid state (Figure 3b).

In order to elucidate the structure of **1a** in solution, DFT calculations were carried out using the B3LYP method with LANL2DZ (Cr) and 6-31G(d) (C, H, O) basis sets. According to previous NMR studies and DFT calculations,[6a] the benzene rings in "free" CPPs rotate freely. In the case of [9]CPP, the rotation barrier (ΔG) from the ground state **A** to the transition state (TS) **B** was calculated to be 10.4 kcal mol^{-1}, which is low enough to permit free rotation (Figure 4a). Our calculations showed that the ground state of **1a** corresponds to conformation **C**, which is similar to the solid-state structure of **1a**. The TS (**D**) of the rotation of the (C$_6$H$_4$)-Cr(CO)$_3$ moiety in **1a** was almost identical to conformation **B** in the case of "free" [9]CPP. The rotation barrier was determined to be
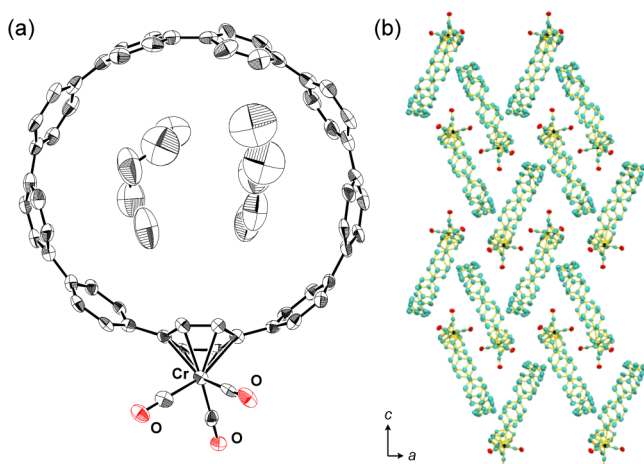
Figure 3. (a) ORTEP drawing of **1a**·2pentane with 50% probability; all hydrogen atoms omitted for clarity. (b) Packing mode of **1a**·2pentane.
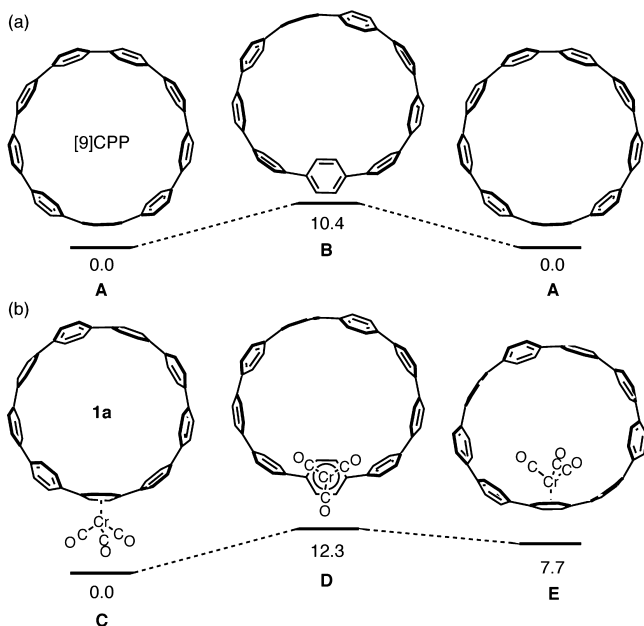

Figure 4. Rotational barriers (ΔG/kcal mol^{-1}) of an uncoordinated C_6H_4 ring in [9]CPP (a), and the corresponding coordinated C_6H_4 ring in **1a** (b) calculated at B3LYP/LANL2DZ (Cr) and B3LYP/6-31G(d) (C, H, O).

12.3 kcal mol^{-1}, which suggested that the coordinated C_6H_4 ring of **1a** should be able to rotate at ambient temperature in solution. Moreover, **1a** should potentially be able to form a rotamer **E**, in which the CPP-Cr coordination occurs at the concave surface (Figure 4b). However, judging from the higher ΔG of **E** relative to **C** (7.7 kcal mol^{-1}), it is likely that the coordination with chromium fragment in **1a** takes place at the convex surface of [9]CPP in solution.

Photophysical Properties of η^6-[9]CPP Chromium Carbonyl Complex 1a. The effect of transition metal coordination on the π-electrons of [9]CPP was investigated by a combination of photophysical measurements and TD (time-dependent) DFT calculations. Figure 5 shows the UV−vis absorption spectra of [9]CPP and **1a** in THF. The absorption maxima (λ_{max}), determined by the peak separation method, are summarized in Table 2. Compared to the spectrum
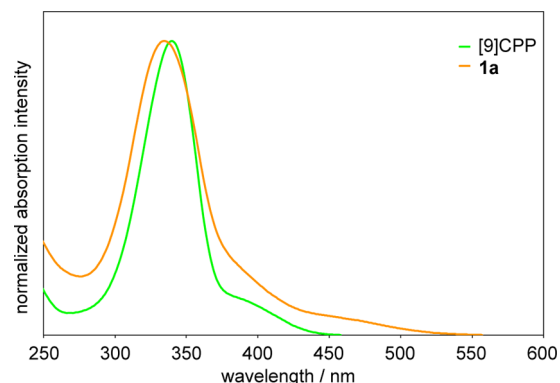

Figure 5. UV−vis absorption spectra of [9]CPP and **1a** in THF.

of [9]CPP, the spectrum of **1a** exhibited a new, broad absorption peak at 440 nm. The other major peaks observed for **1a** (λ = 397, 334 nm) were similar to the absorption bands in the spectrum of [9]CPP (λ = 395, 339 nm). TD-DFT calculations of **1a** were carried out by using the same method and basis sets as for the geometry optimization, i.e., B3LYP/LANL2DZ for Cr, and 6-31G(d) for C, H, and O. As already reported,[7b] the highest absorption band of [9]CPP (λ_{max} = 339 nm) was assigned to the HOMO − 1 → LUMO and HOMO → LUMO + 1 transitions, whereas the small shoulder at higher wavenumbers (λ_{max} = 395 nm) was assigned to a forbidden HOMO → LUMO transition. The TD-DFT study of **1a** indicated that the absorption peaks at 440 and 397 nm should be assigned to the HOMO → LUMO and HOMO − 1 → LUMO transitions, respectively. The absorption band around 334 nm contained several transitions, due to the lower symmetry of **1a** relative to "free" [9]CPP. The frontier molecular orbitals of [9]CPP and **1a** are shown in Figure 6, which clearly illustrate the effect of the coordination with the $Cr(CO)_3$ fragment onto the π-orbital of [9]CPP: (1) the energy levels of both the HOMO and LUMO decrease due to the electron-withdrawing effect of $Cr(CO)_3$ fragment; (2) the HOMO of [9]CPP splits into HOMO and HOMO − 1 in **1a** by the interaction with the $d_{x^2-y^2}$-orbital of Cr. The HOMO of **1a** consists mainly of the $d_{x^2-y^2}$-orbital, whereas the HOMO − 1 of **1a** remains predominantly the HOMO orbital of [9]CPP.
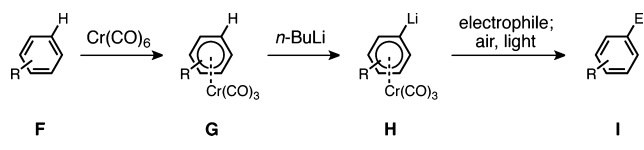
Selective Monofunctionalization of CPPs via η^6-CPP Chromium Carbonyl Complexes. The reactivity of arenes is drastically changed upon η^6-coordination to metals.[10] Scheme 2 shows the deprotonation of arenes facilitated by the η^6-coordination to a chromium fragment: coordination of arene **F** to $Cr(CO)_3$ affords complex **G**, in which the acidity of the hydrogen atoms is increased. Subsequent deprotonation of **G** using common strong bases such as n-butyllithium leads to the formation of **H**, which can be treated with suitable electrophiles, before being subjected to decomplexation under ambient conditions (room temperature, atmospheric air, ambient light). This convenient one-pot procedure yields functionalized arenes **I**. We envisioned that this method should also be applicable to CPPs.

The selective monofunctionalization of CPPs is usually difficult, as all C−H bonds of CPPs are chemically equivalent. Common electrophilic substitution reactions (S_EAr) occur randomly affording a complex mixture of functionalized CPPs as shown in Scheme 3. For example, when [9]CPP was treated with Br_2 and Fe, mixtures of Br_m[9]CPP (m = 1−7) and unreacted [9]CPP were obtained as judged by MALDI-TOF

Table 2. Experimental Results for the UV−Vis Absorption of [9]CPP and 1a and TD DFT-Generated Values for Vertical One-Electron Excitations

|	$\lambda_{max}{}^{a}$ [nm]	description[b]
[9]CPP	395	HOMO → LUMO
	339	HOMO − 1 → LUMO, HOMO → LUMO + 1
1a	440	HOMO → LUMO
	397	HOMO − 1 → LUMO
	334	HOMO − 1 → LUMO + 1, HOMO − 1 → LUMO + 2, etc.

[a]Absorption maxima (λ_{max}) were determined by the peak separation method. [b]B3LYP/LANL2DZ (Cr), 6-31G(d) (C, H, O).
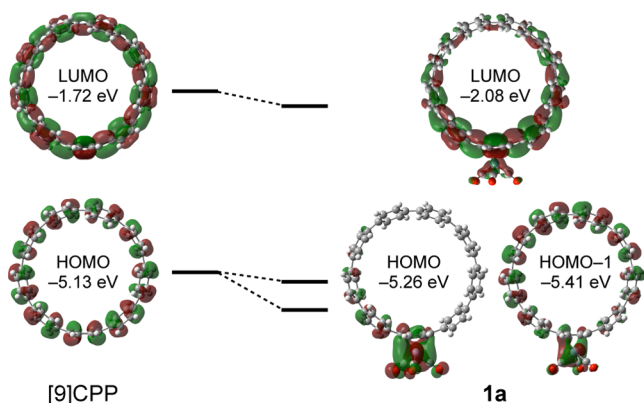
Figure 6. Frontier molecular orbitals of [9]CPP (left) and 1a (right).

Scheme 2. Functionalization of Arenes via Complexation to a Chromium Carbonyl Fragment

Scheme 3. Synthesis of Monofunctionalized CPPs
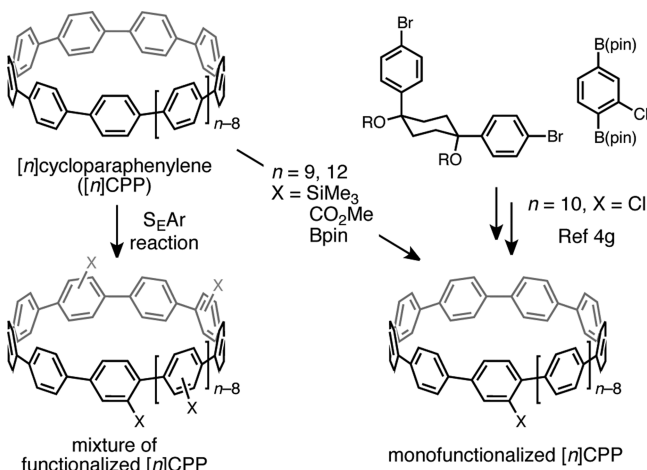
MS (see Supporting Information). To circumvent this obstacle, we previously designed a bottom-up approach for the synthesis of Cl[10]CPP (Scheme 3).[4g] While this approach selectively afforded Cl[10]CPP, the multistep nature of the method hampers its application to the synthesis of many other monofunctionalized CPPs. There is an obvious need for selective, postsynthetic modifications of CPPs, not only because these can produce a number of CPP derivatives in a step-economical manner, but also because CPPs can now be

obtained on gram scale,[8b] and some CPPs are commercially available.[13]

As a proof of concept, we employed η^6-complexation as a tool to effect the clean silylation, borylation, and methoxycarbonylation of [9]CPP and [12]CPPs. Because complexes 1a,b are unstable toward ambient light and/or air, we decided to carry out the four-step CPP functionalization (complexation, deprotonation, nucleophilic substitution, and decomplexation) consecutively without purification (Table 3). The CPP-Cr

Table 3. Selective Monofunctionalization of CPPs via Complexation to a Chromium Carbonyl Fragment
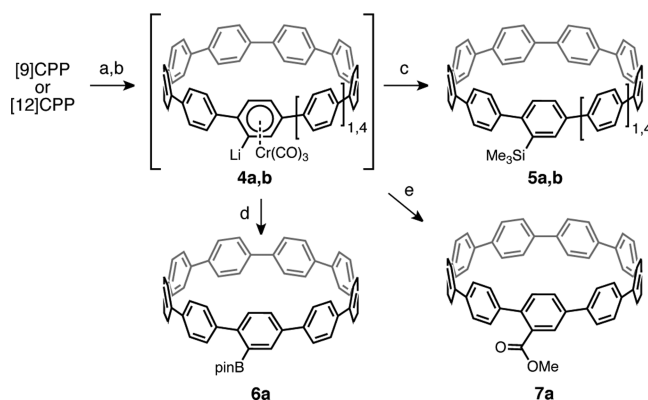
entry	product	absolute yield	recovered CPP	relative yield[f]
1	5a	40%	46%	74%
2[g]	5a	47%	35%	72%
3	5b	31%	60%	78%
4	6a	21%	70%	70%
5	7a	38%	59%	93%

[a][n]CPP (n = 9, 29 μmol; n = 12, 22 μmol), Cr(CO)$_6$, n-Bu$_2$O/THF = 9:1, 160 °C, 1 or 1.5 h, in the dark. [b]n-BuLi, THF, −78 °C, 30 min. [c]Me$_3$SiCl, rt, 1 h; THF/water, rt, 24 h, ambient light. [d]MeOBpin, rt, 1 h; THF/water, rt, 24 h, ambient light. [e]ClCO$_2$Me, rt, 1 h; THF/water, rt, 24 h, ambient light. [f]Relative yields are based on reacted CPP. Relative yield (%) = [absolute yield/(100 − recovered CPP)] × 100%. [g]146 μmol scale.

complexation conditions are identical to those described in Scheme 1. After complexation, all volatiles were removed, and THF was added for the subsequent steps. The reaction vessel was kept in the dark until the respective electrophile was added. Decomplexation proceeded readily once the samples were exposed to ambient conditions (room temperature, air, light) for 24 h. All products (5a−7a, 5b) and the starting materials were isolated by PTLC, and the results are summarized in Table 3. Monofunctionalized CPPs were obtained in low to moderate yields (21−47%) accompanied by substantial amounts of CPP starting materials were recovered (44−70%). The low yield of boryl-CPP 6a may be attributed to the low

reactivity of 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (MeOBpin) toward the lithiated arene. However, the yields relative to reacted CPP starting material were very high (70−93%), even when the reaction scale was increased to 5 times (entry 2, Table 3). Though the absolute yields remain to be improved, excellent selectivities for monofunctionalization over multifunctionalization were achieved.

Single crystals of **5a**, suitable for X-ray diffraction experiments, were obtained by recrystallization from THF. The molecular structure and the packing mode of **5a** are shown in Figure 7. Similar to [9]CPP, two molecules of THF were found
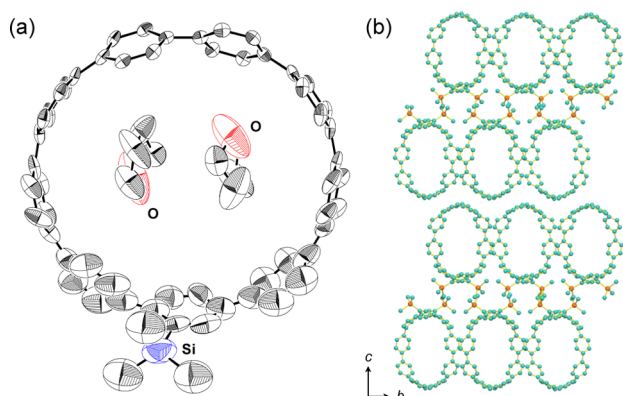

Figure 7. (a) ORTEP drawing of **5a·2THF** with 50% probability; minority parts of disordered moieties and hydrogen atoms are omitted for clarity. (b) Packing mode of **5a·2THF**.

to be incorporated in the cavity of **5a**. The trimethylsilyl substituent of **5a** was highly disordered. For the packing mode of **5a** in the *ab* plane, a herringbone structure was observed, which is similar to that of [9]CPP. Interestingly, the trimethylsilyl-substituted sides of the herringbone packing sheets face each other to form a layer-by-layer assembly.

CONCLUSION

The synthesis, structure, photophysical properties, and reactivity of CPPs coordinated to group 6 transition metal carbonyl fragments were investigated. Complexation of [n]CPPs (n = 9, 12) with M(CO)$_6$ (M = Cr, Mo, W) was accomplished to afford the corresponding [n](CPP)-M(CO)$_3$ complexes. In all complexes, characteristic singlet signals, associated with the four hydrogen atoms on the coordinated benzene rings, were observed at 5.4−5.9 ppm. Although the purification of several complexes proved to be unsuccessful, likely due to their instability toward ambient light and/or oxygen, complex [9]CPP-Cr(CO)$_3$ (**1a**) could be successfully isolated. X-ray crystallographic analysis and computational studies of [9]CPP-Cr(CO)$_3$ revealed that the chromium-CPP coordination occurs at the convex surface of [9]CPP both in the solid state and in solution. The emerging high-wavenumber absorption peak in **1a** upon coordination of [9]CPP to Cr(CO)$_3$ was assigned to a weak HOMO−LUMO transition, which was supported by TD-DFT calculations. Moreover, by using CPP-Cr(CO)$_3$ complexes, a rapid and highly mono-selective CPP functionalization has been achieved. Through a one-pot, four-step operation (complexation, deprotonation, nucleophilic substitution, and decomplexation), CPPs were functionalized to give silyl-, boryl-, and methoxycarbonyl-CPPs (**5−7a,5b**). As silyl, boryl, and ester groups can be easily transformed into various functional groups, this new method is extremely valuable for the construction of interesting and unprecedented nanocarbon structures.

ASSOCIATED CONTENT

⑤ Supporting Information

Experimental procedures and spectral data for all new compounds including scanned images of ^{1}H and ^{13}C NMR spectra, details of computational studies, photophysical measurements, and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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