Arene–Ruthenium Complexes

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Regioselective Synthesis and Characterization of Multinuclear Convex-Bound Ruthenium-[*n*]Cycloparaphenylene (*n* = 5 and 6) Complexes

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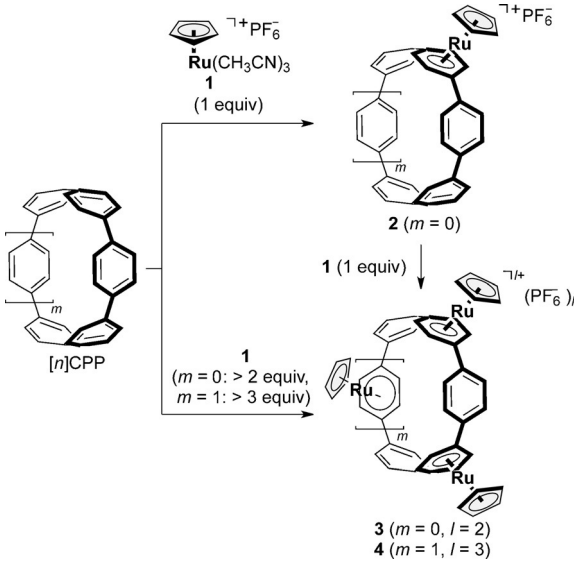
Abstract: *Mono- and multinuclear complexes of ruthenium and [n]cycloparaphenylene (CPP, n = 5 and 6) were synthesized in excellent yields through ligand exchange of the cationic complex [(Cp)Ru(CH$_3$CN)$_3$](PF$_6$) with CPP. In the multinuclear complexes, ruthenium selectively coordinated to alternate paraphenylene units to give bis- and tris-coordinated Ru complexes for [5] and [6]CPPs, respectively. Single-crystal X-ray analysis revealed the Ru was coordinated with η^6-hapticity on the convex surface of CPP.*

Transition-metal complexes of curved (nonplanar) π-carbon surfaces have attracted considerable interest since the initial report on the Pt and Ir complexes of C_{60}.[1] A variety of transition-metal complexes with different metals coordinated to curved π-molecules with different hapticities have been synthesized, and potential applications in catalysis and in the construction of supramolecular architectures have also been reported.[2] The same metal sometime coordinates to π-conjugated molecules with different hapticity for curved and planar π-conjugated molecules owing to differences in the nature of the π orbitals.[2d,3] Furthermore, the curved structure creates the novel issue of the concave/convex selectivity of coordination. Curved π-conjugated molecules are rare and up to now have been restricted to fullerenes,[1–3] corannulene,[4] sumanene,[5] and their derivatives.[6]

Recently, cycloparaphenylenes (CPPs) and other structurally related hoop-shaped, π-conjugated molecules have attracted considerable attention because of their aesthetically appealing structures, which represent the shortest sidewall segments of armchair carbon nanotubes.[7] The recent success in the bottom-up syntheses of CPPs[8–11] and their derivatives[12–15] has sparked a new area of research involving the elucidation of their unique physical properties, such as size-dependent photophysical[16] and redox properties,[11b,17] and size-complementary host–guest chemistry.[18] Analogous to the transition-metal complexes coordinated to curved π-carbon surfaces, the paraphenylene units of CPP should serve as ligands for transition metals. Such metal–CPP complexes would affect the properties of CPPs and would be useful for their selective functionalization.

Herein, we report the synthesis and characterization of cationic mono- and multinuclear convex-bound Ru–[*n*]CPP (*n* = 5 and 6) complexes through the ligand exchange of [*n*]CPP with the cationic ruthenium complex [(Cp)Ru(CH$_3$CN)$_3$](PF$_6$) (**1**; Scheme 1; Cp = cyclopentadienyl).[19] By



Scheme 1. Synthesis of mono- and multinuclear ruthenium [5]CPP and [6]CPP complexes.

varying the ratio of **1**/CPP, mono-, di-, and trinuclear Ru complexes were successfully synthesized for the first time in excellent yields. The results are in sharp contrast to the multinuclear Ru complexes of linear oligoparaphenylenes,[20] in which Ru coordinated to all paraphenylene units and selective coordination could not be achieved. Itami and co-workers recently reported the synthesis and monofunctionalization of a chromium tricarbonyl complex of [9]CPP, obtained in low yield through high-temperature complexation.[21] The present report is the first example of the synthesis of multinuclear transition-metal–CPP complex. Importantly, the di- and tri-incorporation of Ru occurred with complete regioselectivity and with high yields, thus providing a new route for the site-selective functionalization of CPPs.

When [5]CPP was treated with **1** (1.0 equiv) in THF at room temperature (RT), the clear solution immediately turned into a suspension. After 5 min, the precipitate was

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filtrated and the filtrate was concentrated. Recrystallization of the residue from 1:1 THF/hexane gave the mononuclear Ru-[5]CPP complex [(Cp)Ru]([5]CPP)(PF_6) (**2**), as a red-brown solid in 77% yield. From the initially separated precipitate, dinuclear Ru–[5]CPP complex **3** was isolated as a pale red solid in 9% yield. The fast atom bombardment (FAB) mass spectra of **2** and **3** showed peaks at $m/z =$ 547.1006 and 714.0473, respectively. Treatment of [5]CPP with 2.0 equivalents of **1** in 1,1,2,2-tetrachloroethane, on the other hand, gave the dinuclear complex **3** as a single product in 82% yield. The reaction of **2** with **1** (1.0 equiv) also afforded **3** in 83% yield as a single product. The dinuclear Ru complex **3** was selectively obtained in 77% yield even with 3 equivalents of **1** relative to [5]CPP.

[6]CPP was next selected as a ligand. When it was treated with 3.0 equivalents of **1** in acetone at RT for 0.5 h, trinuclear Ru–[6]CPP complex **4** was obtained as the sole product as a yellow powder in 91% yield. Complex **4** was selectively obtained even when [6]CPP was treated with more than 4 equivalents of **1**. The FAB mass spectrum of **4** ($m/z =$ 956.0241) was fully consistent with the trinuclear Ru. Treatment of [6]CPP with 1 or 2 equivalent(s) of **1**, on the other hand, afforded a mixture of mono-, di-, and tri-Ru–[6]CPP complexes as judged by electrospray ionization mass spectrometry and ^{1}H NMR spectroscopy. However, isolation of the desired mono- and dinuclear complexes has so far been unsuccessful.

The structures of the complexes were characterized first in solution by ^{1}H NMR spectroscopy. In the spectrum of **2** (Figure S5 in the Supporting Information), the chemical shift of the paraphenylene unit coordinated to the Ru appeared at $\delta = 6.66$ ppm as a singlet, which is upfield-shifted from that of the parent [5]CPP (8.04 ppm) and is similar to that of [(Cp)Ru(η^6-C_6H_6)](PF_6) (6.44 ppm).[22] The hydrogen atoms of uncomplexed paraphenylene resonated as a set of doublets at 7.89, 7.93, 7.99, and 8.10 ppm and those of the Cp ring appeared at 5.34 ppm. In the spectrum of **3** (Figure S7), the hydrogen atoms of the Ru-coordinated paraphenylenes resonated as a set of doublets at 6.67 and 6.70 ppm, the uncomplexed paraphenylene hydrogen atoms at 7.96 ppm (doublet), 8.00 ppm (doublet), and 8.15 ppm (singlet), and the Cp hydrogens at 5.47 ppm. The ^{1}H NMR spectrum of **4** only showed three singlet peaks at 5.63 ppm (Cp), 6.55 ppm (Ru-C_6H_4), and 7.91 ppm (C_6H_4) (Figure S9). In the ^{13}C NMR spectra, eleven signals were observed for both **2** and **3** and five signals for **4**, in which the Ru-coordinated paraphenylene carbons resonated at 78.94 and 116.86 ppm for **2**, at 79.52, 79.72, 116.56, and 119.66 ppm for **3**, and at 81.80 and 114.47 ppm for **4**. All these spectra are consistent with the proposed structures.

Structures of the multi-Ru complexes were unambiguously determined by X-ray diffraction experiments performed on single crystals of **3** and **4** (Figure 1). Suitable single crystals for analysis were obtained by slow evaporation of a solution of **3** in CH_2Cl_2 and by vapor diffusion of CH_2Cl_2 into a solution of **4** in acetone. The analyses clearly show that the convex surface of CPP coordinates to the (Cp)Ru^+ fragments with η^6-hapticity. In the solid state of **3** (Figure 1a), the Ru–C distances from the Ru center to the *ortho* carbons

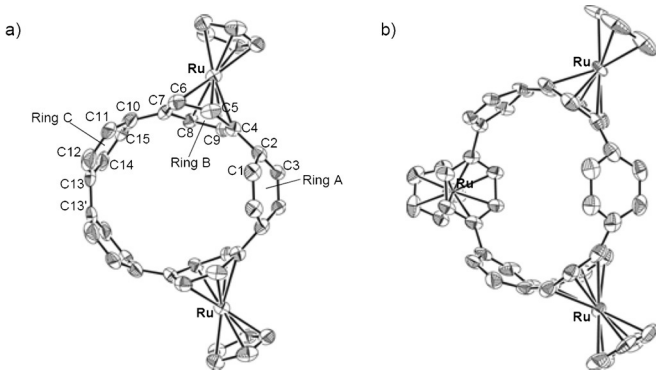

Figure 1. ORTEP drawings of a) **3** and b) **4**. Thermal ellipsoids are shown at 50% probability, and all hydrogen atoms, counteranions PF_6^-, and solvent are omitted for clarity.

of the coordinated paraphenylene ring (C5, C6, C8, C9 in Ring B) were in the range of 2.189(1)–2.197(8) Å, distances similar to those in [(Cp)Ru(C_6H_6)](PF_6) (2.19–2.22 Å).[23] The distances of Ru to the *ipso* carbons (C4 and C7) are slightly longer (2.344(8)–2.370(9) Å) due to the boat conformation of the paraphenylene units as discussed below. The values are still in the range of Ru–C distances observed in the η^6-coordinated Ru complexes with other curved polyarenes such as corannulene[4c] and sumanene.[5a] The counteranion PF_6^- was located on the exterior of **3**, the cavity of which was occupied by CH_2Cl_2 molecules.

Each paraphenylene unit adopts a shallow boat conformation with two *ipso* carbons lying above the mean plane defined by the four *ortho* carbons. The out-of-plane bending angles of the *ipso* carbons in the Ru-complexed ring B was 12.39° and those of the uncomplexed rings A and C were 17.40°and 17.97°, respectively, while that of neutral [5]CPPs was 15.40°.[9f] This means that the ring B of the paraphenylene unit flattens out upon complexation to (Cp)Ru^+. The same behavior was also reported in a Ru–coranulene complex.[4c] This in turn leads to a stronger bending of the uncomplexed rings A and C and a pyramidilization of the *ipso* carbons. The sums of the three bond angles around the *ipso* carbons (351.98°, 357.31°, 358.25°, 353.99°, and 355.38° around C2, C4, C7, C10, and C13, respectively, and 355.35° for [5]CPP) and the π-orbital axis vector angles[24] at the *ipso* carbons (10.59°, 6.09°, 4.89°, 9.11°, and 7.98° at C2, C4, C7, C10, and C13, respectively, and 6.55–7.45° for [5]CPP) reflect the difference of the degree of planarity of each paraphenylene unit in complex **3** and the parent [5]CPP.

To clarify the highly regioselective formation of multinuclear Ru complexes, DFT calculations using the B3LYP/6-31G(d)(C, H) and LANL2DZ(Ru) were examined for all possible regioisomers. Between two possible [(Cp)Ru]$_2$-[5]CPP isomers, the alternated Ru dimer **3** is thermodynamically more stable than the other isomer **3′** by 32 kJ mol^{-1} (Figure 2a). Among the three possible [(Cp)Ru]$_3$[6]CPP isomers, the fully alternated isomer **4** is thermodynamically most stable, followed by **4′**, which has one alternated Ru-paraphenylene unit, and then **4″** with no alternating structure by 33 and 90 kJ mol^{-1}, respectively (Figure 2b). These results

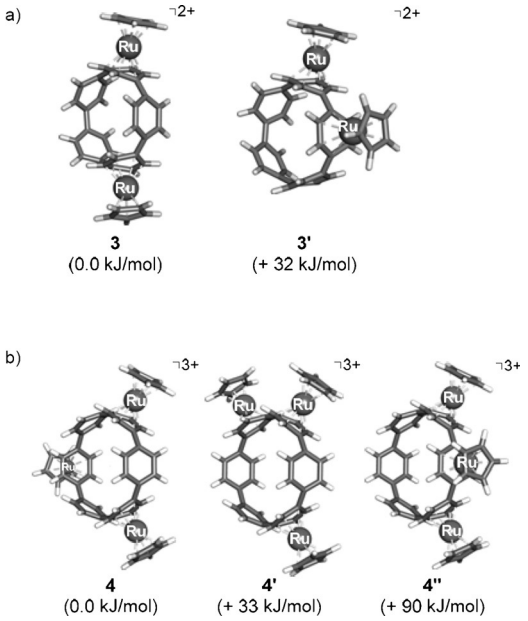

Figure 2. Calculated regioisomers of a) $[(Cp)Ru]_2([5]CPP)^{2+}$ and b) $[(Cp)Ru]_3([6]CPP)^{3+}$ obtained by DFT calculations using B3LYP/6-31G(d) (C, H) and LANL2DZ (Ru). The relative energies ($kJ\,mol^{-1}$) with respect to the most stable isomer are shown in parentheses. Black and white represent carbon and hydrogen atoms, respectively. Black balls represent the ruthenium atom.

clearly indicate that thermodynamic stability determines the regioselectivity.

In the calculated structure of **3**, the C–C bond lengths on the CPP fragment were in good agreement with those obtained from X-ray analysis, but the Ru–C distances between Ru and the coordinated paraphenylene unit, Ru–C_{ipso} (C4 or C7) and Ru–C_{ortho} (C5, C6, C8, or C9), were significantly longer than those obtained from X-ray analysis. The differences must have originated from using effective core potential (LANL2DZ) on the Ru atom. Therefore, detailed comparisons between the calculated and X-ray structures have not been made here. Since the effect of the basis set used for Ru is the same for each isomer and the energy differences between each isomer are significant, the relative stability of each isomer should remain unchanged even when a more expensive basis set for Ru is applied.

To estimate the origin of the difference in the stabilities of the regioisomers **3** and **3′**, deformation energies were calculated, which correspond to the energies required for the structural changes from [5]CPP to the CPP fragments of **3** and **3′** upon complexation. The CPP fragments of **3** and **3′** were 20 and 31 $kJ\,mol^{-1}$ more strained than [5]CPP, respectively. On the other hand, the nearest distance between two (Cp)Ru moieties in **3′** was 5.97 Å, thus implying that steric repulsion between the metal moieties was unlikely.

The electronic effects were then analyzed by Mulliken population analysis, because the π-acidic (Cp)Ru fragment prefers the more electron-rich ring(s).[19] Indeed, the *ipso* carbon of Ru-coordinated paraphenylene in mononuclear complex **2** becomes more electron positive (0.27) than that of parent [5]CPP (0.11) upon complex formation (see the Supporting Information). In complex **3**, the Mulliken charges of the Ru-coordinated *ipso* carbons are 0.22–0.26, values are similar to those of **2**. On the contrary, in complex **3′**, while the Mulliken charge of the Ru-coordinated *ipso* carbons (C10, Table S11 in the Supporting Information) adjacent to the non-coordinated paraphenylnene unit is 0.28, that of the other *ipso* carbon (C13) adjacent to the Ru-coordinated carbon is 0.16, which is significantly smaller. The results are consistent with the previous results.[19] The same electronic effect is observed among tris-Ru–[6]CPP complexes **4**, **4′**, and **4″** in Mulliken population analysis. These results clearly indicate that the electronic effect mainly dictates the stability of the complexes.

The UV/Vis spectra of complexes **2** and **3** were obtained in CH_2Cl_2 solution at 25 °C (Figure 3). The complexes show

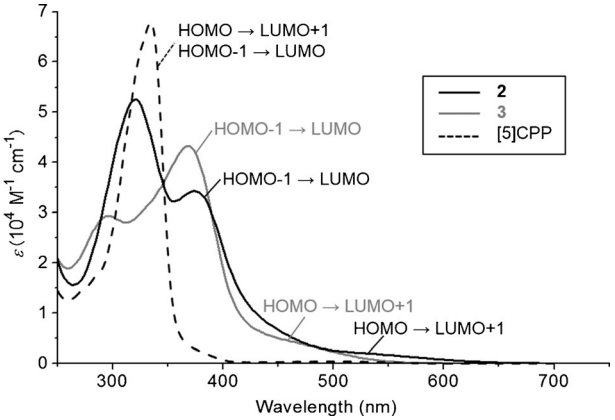

Figure 3. UV/Vis spectra of **2**, **3**, and [5]CPP in CH_2Cl_2.

two intense absorptions; low-energy bands (λ_{abs1}) at 374 nm for **2** and at 367 nm for **3** and high-energy bands (λ_{abs2}) at 320 nm for **2** and at 296 nm for **3**. The shapes of the spectra are significantly different from that of parent [5]CPP.[11e] The intensities of λ_{abs1} and λ_{abs2} increase and decrease, respectively, when the number of coordinated $(Cp)Ru^+$ units increases. Time-dependent density functional theory calculations indicate that the λ_{abs1} values of complexes **2** and **3** mainly derive from HOMO-1→LUMO transitions, together with a small contribution from HOMO→LUMO + 1 transitions. Since HOMO-1 and LUMO mainly comprise Ru center(s) and CPP, respectively, the transition can be assigned as metal-to-ligand charge transfer (MLCT). On the other hand, calculations suggested that λ_{abs2} values of **2** and **3** comprise several transitions. The UV/Vis spectrum of **4** (Figure S3 in the Supporting Information) shows a single absorption band with an absorption maximum at 329 nm, which is mainly ascribed to the MLCT transition from the nearly degenerate HOMO-1 and HOMO-2 to LUMO.

In summary, regioselective and high-yield synthesis of mono- and multinuclear Ru–[*n*]CPP complexes was achieved through the reaction of $(Cp)Ru^+$ with CPP under mild conditions. In view of the diverse use of $(Cp)Ru^+$–arene complexes in organic, organometallic,[19,25] coordination, and materials chemistry, these complexes would be applicable to the syntheses of functionalized CPPs and metal-coordinated carbon-based materials.

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Keywords: arene ligands · cycloparaphenylenes · regioselecitivity · ruthenium · X-ray diffraction

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