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Review

Probing the binding sites and coordination limits of buckybowls in a solvent-free environment: Experimental and theoretical assessment

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ABSTRACT

This work overviews the coordination properties of fullerene fragments or buckybowls, a new class of open geodesic polyaromatic hydrocarbons that map onto the surface of fullerenes but lack their full closure. In contrast to fullerenes, the bowl-shaped polyarenes have both the convex and concave unsaturated carbon surfaces open and available for coordination, which makes them unique and interesting π-ligands for metal binding reactions. Variable synthetic methods based on solution and solid-state reactions have been developed to access transition metal complexes of buckybowls and to reveal their coordination properties. These studies have been mainly focused on the smallest fragments of the C_{60}-fullerene, corannulene ($C_{20}H_{10}$) and sumanene ($C_{21}H_{12}$). In order to utilize directional metal–π-arene interactions effectively and to differentiate π-bonding sites of buckybowls, we have introduced a micro-scale gas-phase deposition method. We have proven this technique to be very effective for the preparation of metal complexes of buckybowls in a single crystalline form. Plus, it allowed us to expand the coordination studies to larger bowls, including dibenzo[*a*,*g*]corannulene ($C_{28}H_{14}$), monoindenocorannulene ($C_{26}H_{12}$), and the C_3-symmetric hemifullerene ($C_{30}H_{12}$). Specifically, several dimetal core complexes of varied electrophilicity have been used in the gas-phase coordination reactions to identify the preferential binding sites and to test the coordination limits of π-bowls in a solvent-free environment. The coordination preferences of several buckybowls having different surface area and bowl depth, as well as different curvature and strain are compared and discussed here based on the results of X-ray diffraction and DFT calculation studies.

1. Introduction

Transition metal complexes of fullerenes have attracted considerable attention since 1991, when Fagan et al. reported the synthesis and structure of the first complex, $[Pt(PPh_3)_2(\eta^2\text{-}C_{60})]$ [1]. A great number of *exo*-bound transition metal complexes of fullerenes, in which a metal coordinates to the junction of

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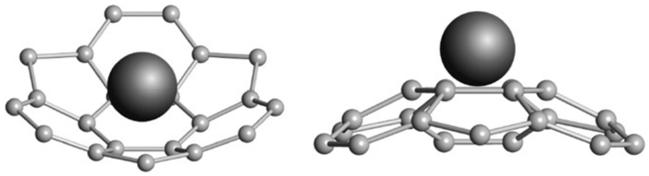


Fig. 1. Schematic representation for *endo*- and *exo*-coordination of a buckybowl.

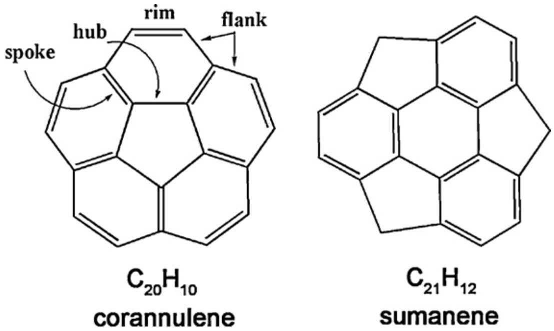
two six-membered rings of the fullerene surface [2] or to the five-membered ring of pentaalkyl- or pentaaryl-functionalized fullerenes [3] has been synthesized since then. Compared to the closed surface buckyballs, open geodesic polyaromatic hydrocarbons that constitute fragments of fullerenes [4] (and therefore referred to as buckybowls or π-bowls) represent even more interesting π-ligands from a coordination viewpoint. Buckybowls have multisite coordination possibilities, namely convex and concave interior polyaromatic faces, as well as edge and rim carbon atoms capped by hydrogen atoms. They share with fullerenes the convex three-dimensional unsaturated carbon surface but also have an open concave side that is readily accessible. The study of relative preferences of the convex and concave faces of buckybowls for binding metal centers (Fig. 1) has been a focus of considerable interest in the recent years due to its fundamental and practical importance.

First, the controlled positioning of metal centers inside the bowls can provide a direct route toward the inclusion complexes of fullerenes and nanotubes, still remaining challenging synthetic targets [5]. Second, the coordination of metal centers to the outside of the bowls should find applications in surface activation and the functionalization of fullerenes and nanotubes [6], which should greatly stimulate the use of curved and strained carbon-rich molecules in materials chemistry [7].

2. Buckybowls: Progress and challenges of metal binding reactions

Although substantial efforts have been directed toward studying the reactivity and ligating properties of buckybowls using various computational techniques [8], only a limited number of their metal complexes has been isolated and structurally characterized by single crystal X-ray diffraction. The latter technique is required to reveal which face of a bowl is directly involved in metal binding, as spectroscopic methods cannot clearly address this critical issue. In 2001, Bohme and co-workers studied the reactivity of the iron-corannulene complex, $[Fe^{+}\cdot C_{20}H_{10}]$, with several small inorganic and organic molecules, such as N_2, CO_2, SO_2 and simple hydrocarbons using a selected-ion flowtube (SIFT) mass spectrometer [9]. By comparing that with the bare Fe^{+}-ion, it was revealed that the presence of corannulene led to enhancements in reactivity of up to 5 orders of magnitude in room temperature reactions. A few years later, Duncan and co-workers [10] investigated the gas-phase corannulene complexes of transition (Ti, V, Cr, Fe) and actinide (U) metals, as well as their oxides produced by co-vaporization of materials by a laser plasma source. The time-of-flight mass spectra revealed that metals yield mono- and di-ligand complexes in the form of $[M(C_{20}H_{10})_n]^{+}$ ($n = 1$ or 2), while their oxides efficiently produce mono-adducts. Both studies could not provide experimental hints for elucidation of binding modes of corannulene or for identification of its *exo*/*endo* coordination preference.

In general, the smallest C_{5v} and C_{3v} symmetrical subunits of the C_{60}-fullerene, namely corannulene [11] and sumanene [4d, 4f, 7g, 12] (Scheme 1), have served as the primary models for theoretical and experimental coordination studies.



Scheme 1.

For corannulene, both σ and π metal complexes have been reported. It was found that the halogen substituted corannulene core can undergo standard organometallic reactions on the rim, similar to those with planar aromatic systems. In 2005, Lee and Sharp [13] showed that oxidative addition of bromocorannulene to $Ni(COD)_2/2PEt_3$ and $Pt(PEt_3)_4$ opens a route to σ-bonded organometallic corannulene derivatives. In 2009, these systems were substantially expanded by Siegel and co-workers [14] and others [15] to include reactions with multisubstituted halo- and ethynylcorannulenes.

The first π-metal complex of corannulene, $[(\eta^6\text{-}C_{20}H_{10})Ru(C_5Me_5)]^{+}$, was isolated and spectroscopically characterized in Siegel's group back in 1997 [8c]. The NMR evidence was also subsequently reported for the formation of η^6-coordinated complexes of corannulene and tetramethylcorannulene with $[Ir(C_5Me_5)]^{2+}$ [16]. Interestingly, the above iridium cation showed no reactivity toward the C_{60}-fullerene. Generally, many attempts to isolate corannulene complexes with metal units that show high reactivity toward the C_{60}-fullerene or planar aromatic hydrocarbons have been unsuccessful [16,17], illustrating the striking difference in their metal coordination preferences. Plus, the lability of corannulene complexes in solution may have hindered the early crystallization attempts. Thus, it was not until 2004, that Angelici and co-workers [18] finally succeeded in structural characterization of η^6-coordinated corannulene complexes for the first time (Fig. 2).

This X-ray crystallographic study revealed the dramatic impact that transition metals can have on bowl-shaped polyaromatic ligands. The observed differences in bond lengths of the six-membered rings of $C_{20}H_{10}$ involved in metal binding approach

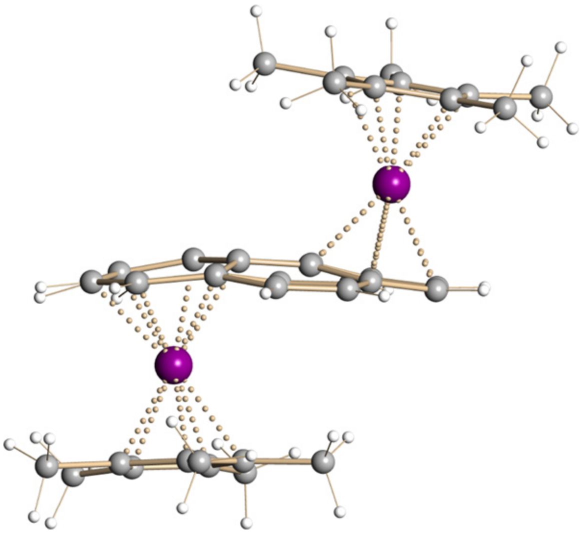


Fig. 2. Molecular structure of $[Ru(Cp^{*})_2(\mu_2\text{-}\eta^6{:}\eta^6\text{-}C_{20}H_{10})]^{2+}$.

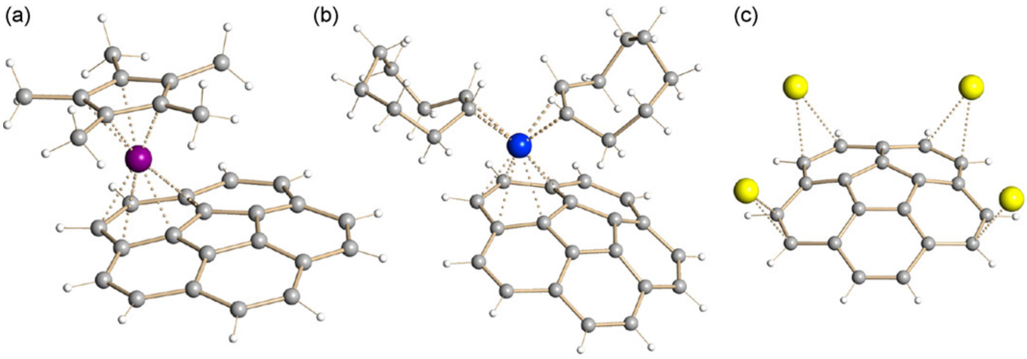


Fig. 3. Transition metal η^6-complexes of Ru^+ (a), Rh^+ and Ir^+ (b), and the η^2:η^2:η^2:η^1-bound Ag^+-cations (c).

0.05 Å. Furthermore, binding of two ruthenium atoms to corannulene in $[(Cp^*Ru)_2(\mu_2\text{-}\eta^6{:}\eta^6\text{-}C_{20}H_{10})]X_2$ ($X = PF_6^-$ and SbF_6^-) caused significant structural changes in the bowl shape and almost completely flattened its curved polyaromatic surface. This effect is noteworthy, because metal-ion binding may likewise change the shape of other non-planar carbon surfaces, such as the walls or caps of carbon nanotubes. The family of η^6-corannulene metal complexes has later been expanded to include several new members. The recently prepared complexes of the type $[(\eta^6\text{-arene})M(\eta^6\text{-}C_{20}H_{10})]X_2$ (M = Ru, Os; $X = BF_4^-$, PF_6^-, or SbF_6^-; arene = C_6HMe_5, C_6Me_6, C_6EtMe_5, cymene) [8s] showed an increased stability compared to the analogous η^6-corannulene complexes of $[Cp^*Ru]^+$, $[Cp^*Ir]^{2+}$, and $[(COE)_2M]^+$ (M = Rh or Ir) [8q].

Interestingly, the NMR investigations demonstrated that, in solution, the metal unit is moving around the curved surface of corannulene. The first observations of such metal migration were reported by Angelici and co-workers in 2003, but the mechanism could not be elucidated at that time [16]. It was found that the reaction of tetramethylcorannulene with $[Cp^*Ir]^{2+}$ initially affords the product where the cation is coordinated to a non-methylated ring. Within a short period of time, the isomerization occurs and the more stable isomer, in which the metal unit is coordinated to one of the methylated rings, is detected. In 2006, Siegel and co-workers ruled out the possibility for migration along the corannulene surface via the intermolecular dissociation/association mechanism based on their NMR and calculation data [8q]. They favored the inter-ring migration of metal cationic units by walking through the central five-membered ring over the migration from one arene ring to the next along the outer edge of corannulene.

Importantly, the single crystal X-ray diffraction studies revealed that all η^6-corannulene complexes having a single metal bound to a bowl exhibit exclusive convex metal coordination (Fig. 3a and b). A similar trend has been seen for the complexation of Ag^+-cations to $C_{20}H_{10}$ studied in solution [19]. In the three silver(I)-based extended networks built on η^2- and η^1-binding of Ag^+-ions to the rim sites of corannulene, a metal was always found at the outside of the bowl (Fig. 3c). These facts illustrated a general preference of the convex face of corannulene for metal coordination and thus for some time thwarted the idea of using buckybowls to access inclusion metal complexes.

In this regard, the first selective concave coordination reported by Hirao and co-workers in 2007 has been a breakthrough [20]. *Endo*-metal coordination (Fig. 4) has been successfully accomplished for sumanene (Scheme 1) that has a deeper and more rigid bowl than corannulene [4d,4f]. Prior to this work, which was recently expanded to include the chiral [Fe(Cp-(*S*)-*sec*-Bu]$^+$ [21] and the more flexible $[RuCp]^+$ complex showing a dynamic inversion behavior [22], no selective coordination of metal ions to the concave face of a π-bowl had been observed experimentally.

This discovery serves as the first step toward the elusive inclusion complexes of buckybowls and has several important implications. It confirms that bowl-shaped polyarenes are indeed excellent multisite models to reveal trends in metal binding to curved and strained unsaturated carbon surfaces. It proves, that, despite all prior examples of the preferential coordination of metal centers to the convex surfaces of buckybowls, their inside concave carbon faces can also be engaged in metal binding. It further stimulates research targeting π-bowls with larger and more strained surfaces than those of corannulene and sumanene. One additional outcome of this work should also be mentioned. In contrast to the solution preparation methods used to access the above corannulene complexes, Hirao's group took advantage of the solid-state synthesis to successfully place Fe and Ru cyclopentadienyl units into the sumanene bowl [20]. Since large polyarenes can be expected to show limited solubility, such novel preparative methods are clearly needed for further advancement of the coordination chemistry of buckybowls [23]. In this regard, our approach based on gas-phase co-deposition of complementary reactive units under

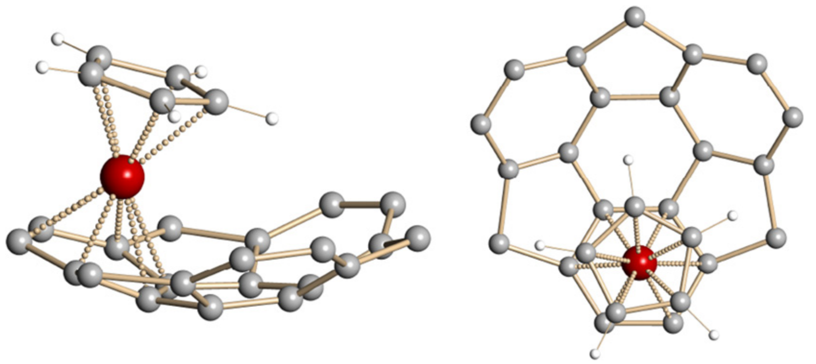


Fig. 4. *Endo*-bound $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_{21}H_{12})]^+$ cation: side (left) and top (right) views.

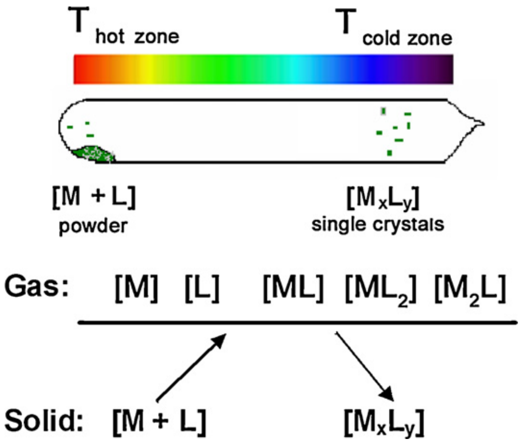


Fig. 5. Schematic representation of a co-deposition set-up.

solvent-free conditions stands out as a useful alternative to solution coordination methods [24].

3. Coordination in a solvent-free environment

For effective utilization of intermolecular metal–π-arene interactions, which in solutions may be thwarted by lability of complexes, solvent and ion-templating effects, or solvent competition for coordination [19,25], we introduced a micro-scale gas-phase technique that excludes the use of solvents. It is based [24b] on co-deposition of volatile complementary building units under reduced pressure (Fig. 5). Several experimental variables such as reaction temperature, temperature gradient, and the ratio of reactants are used to effectively modulate the reaction outcomes and to afford the product composition variations. While the composition of gas mixtures in these reactions cannot be easily monitored, the careful control of the above parameters permits the direct synthesis of compounds with a desired stoichiometry, as shown below. Importantly, products are likely to be obtained in the single crystalline form suitable for X-ray diffraction studies.

The deposition technique can utilize a variety of volatile organic donors spanning from planar molecules with isolated multiple carbon–carbon bonds [26] to conjugated planar polyarenes [27] to curved unsaturated π-bowls discussed here. As metal-containing units, a number of reactive and volatile complexes can be generally used, but in order to facilitate the formation of metal–π-arene interactions, the Lewis acidic complexes having one or multiple metal sites open for coordination are preferred. The synthetic availability, strong avidity for axial coordination, and ease of effective manipulation of electronic properties of dimetal core complexes [28a] make them a primary choice for solvent-free coordination reactions.

4. Dinuclear metal complexation: X-ray diffraction and DFT studies

Dimetal trifluoroacetates and trifluoromethyl-substituted benzoates (Fig. 6) were chosen for these studies due to the well-known ability of trifluoromethyl group to provide substantial Lewis acidity along with increased volatility of the resulting metal complexes [28b–d]. These electrophilic dirhodium(II,II) and diruthenium(I,I) complexes have been used to probe the reactivity and to identify the preferential binding sites of several buckybowls ranging in size and curvature. Importantly, excess of metal units can be readily created in the gas phase, and that allows us to test the coordination limits of carbon-rich bowl-shaped polyaromatic hydrocarbons in metal binding reactions.

4.1. *Corannulene*

The first crystalline complexes of corannulene have been successfully prepared and structurally characterized by single crystal X-ray diffraction in our laboratory back in 2003 [29]. Synthesis of the complexes was accomplished by sublimation-deposition reactions of $[Rh_2(O_2CCF_3)_4]$ and $C_{20}H_{10}$ at 160 °C. Different ratios of starting reagents in the solid state (1:1 and 3:2) resulted in the formation of two different products. The former exhibits an extended one-dimensional structure having alternating dirhodium units and corannulene molecules and built on directional η^2-coordination (Fig. 7). Both faces of $C_{20}H_{10}$ are involved in coordination with the average Rh–C separation being slightly longer for the convex side (2.580(4) Å for Rh–C_{concave} and 2.643(4) Å for Rh–C_{convex}). Only rim carbon atoms of a bowl are engaged in these interactions.

The X-ray diffraction analysis of the second product revealed a two-dimensional network consisting of large rhomboid cells built of six dimetal units and six corannulene molecules (Fig. 8a). As in the case of 1D polymer, each corannulene bowl uses its rim carbon atoms (η^2-mode) at both the convex and concave faces for Rh binding. One of the Rh–C_{convex} bond lengths is shorter (2.548(3) Å), while the other one is longer (2.636(3) Å) than the Rh–C_{concave} bond (2.570(3) Å).

The observed η^2-rim coordination of dimetal units does not perturb the geometrical parameters of the polyarene with the corannulene core being only slightly flattened in both cases (0.839(3), 0.861(3), and 0.875(2) Å in 1D, 2D, and free corannu-

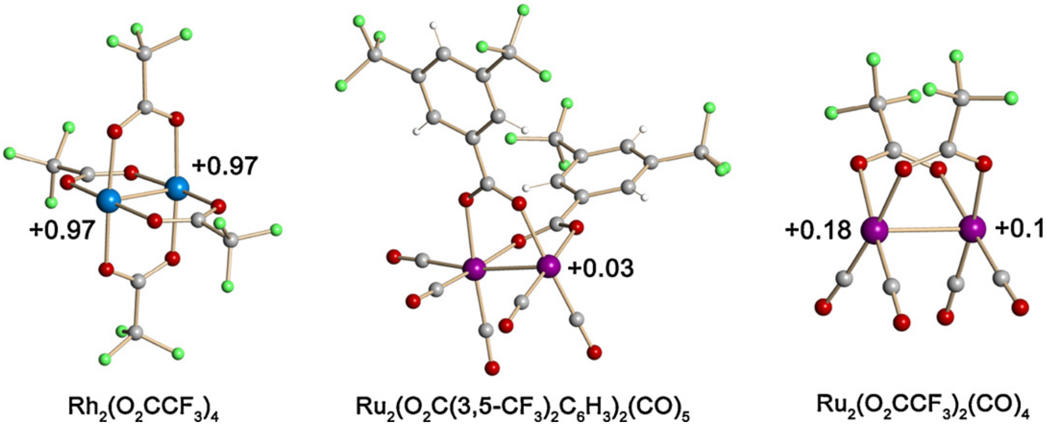


Fig. 6. Selected dimetal complexes with the computed charges on metal centers. Color scheme: Rh blue, Ru purple, O red, F green, C grey, H white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

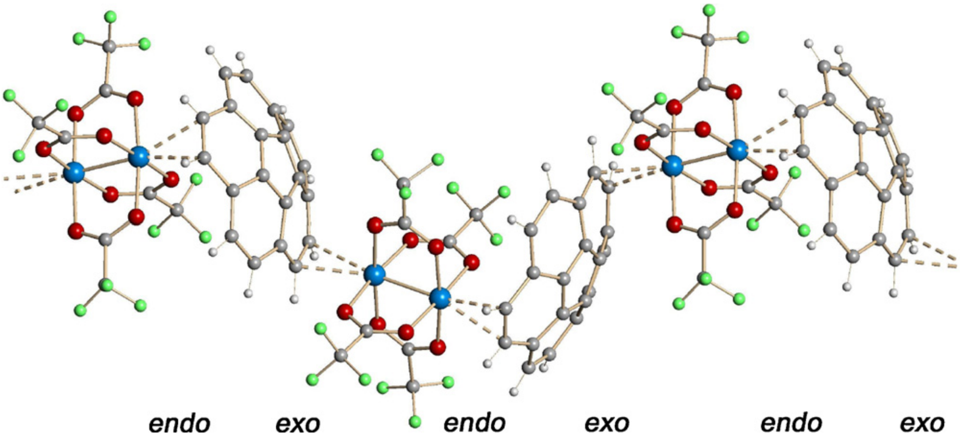


Fig. 7. A fragment of a 1D polymeric chain in $[Rh_2(O_2CCF_3)_4{\cdot}(C_{20}H_{10})]_\infty$.

lene [30], respectively). At the same time, the Rh–Rh bond distance (averaged at 2.43 Å in both complexes) is substantially elongated compared to that of 2.38 Å in the unligated dirhodium(II,II) tetratrifluoroacetate [28b].

The π-orbital axis vector (POAV) analysis of Haddon [31] is commonly used as a quantitative evaluation method for the degree of pyramidalization of trigonal C-atoms. As reference points, the planar trigonal atoms are taken with a POAV angle of 0.0°, whereas the pyramidalized carbon atoms of the C_{60}-fullerene have POAV angles of 11.6°. The pyramidalization of the hub C-atoms of free corannulene is 8.3°. In the 1D polymer, the average POAV angle for four hub C-atoms of the 6-membered rings involved in metal complexation is decreased to 7.9°, while the POAV for the fifth hub C-atom is the same as in $C_{20}H_{10}$. In the 2D layered structure, POAV angles remain essentially unchanged, which is consistent with almost the same bowl depth of $C_{20}H_{10}$ in the coordinated and free forms. DFT calculations of the mono-adduct having $[Rh_2(O_2CCF_3)_4]$ bound at the rim of corannulene [8z] also showed that the rim coordination mostly affects the 6-membered ring involved in metal binding. The values of POAV angles of the hub C-atoms of the coordinated ring are decreased to 8.0°, while remaining the same for other hub-atoms. In contrast, theoretical modeling of the corresponding spoke-adduct revealed that the coordination noticeably increases the bowl depth of the corannulene core (from 0.870 to 0.908 Å). Plus, the POAV angle of the hub C-atom in this isomer is greatly increased to 10.8°, while the pyramidalization of all other hub-atoms is slightly decreased.

The experimentally observed exclusive coordination of Rh centers at the rim of corannulene shows some similarities with the complexation of planar polycyclic aromatic hydrocarbons (PAHs), where η^2-rim coordination has been previously seen [27]. For planar polyarenes such as naphthalene and acenaphthylene calculations indicate [8z] that the preference of rim- over spoke-binding in coordination of $[Rh_2(O_2CCF_3)_4]$ is greater in comparison with corannulene (8.1, 4.7, and 2.2 kcal/mol, respectively). Thus, the donor–acceptor ability of the internal spoke site of $C_{20}H_{10}$ is noticeably increased compared to planar PAHs, which makes the spoke complexes of π-bowls a feasible experimental target. On the basis of Hückel calculations, we have noticed that the electrophilic dirhodium units tend to coordinate to CC bonds of PAHs having the highest π-bond order [27]. We have later demonstrated that the direction of this interaction depends on topology of the frontier molecular orbitals (FMOs) for aromatic ligands and dimetal complexes (Fig. 9) [8z,26].

The FMOs of corannulene are primarily localized at the rim and spoke sites. The former results in η^2-coordination and the latter affords η^1-binding to the hub C-atom due to a substantially greater atomic coefficient at this site. The rim coordination should be preferred over the spoke one (bond orders are 1.63 and 1.33, respectively). Calculation of bonding energies of adducts having $[Rh_2(O_2CCF_3)_4]$ units coordinated at the rim and spoke sites confirmed this prediction but showed only a small difference between the two isomers (18.8 and 16.6 kcal/mol, respectively). The higher bonding energy of the rim isomer is mainly provided by a notice-

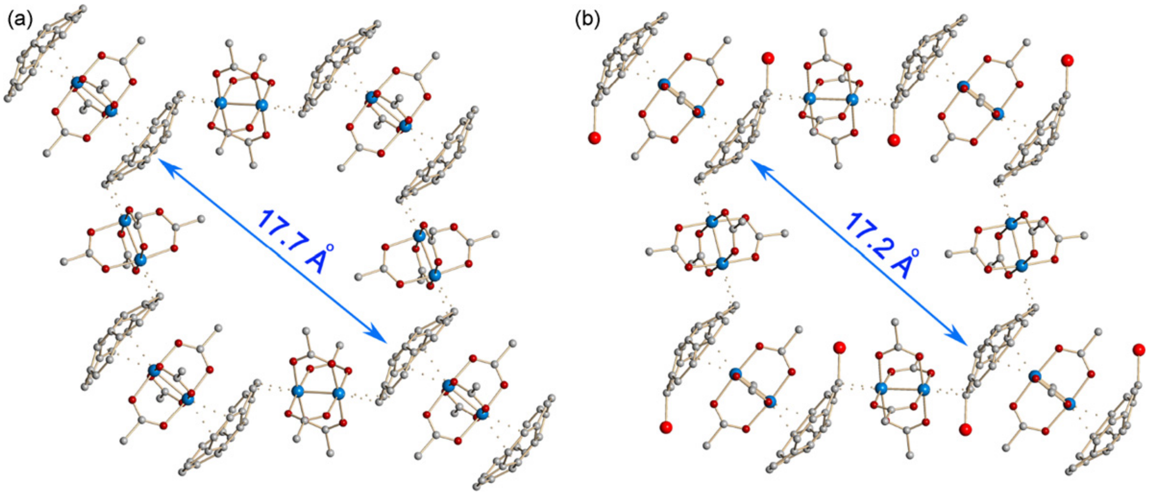


Fig. 8. Fragments of the 2D layers in $[(Rh_2(O_2CCF_3)_4)_3{\cdot}(C_{20}H_{10})_2]_\infty$ (a) and $[(Rh_2(O_2CCF_3)_4)_3{\cdot}(C_{20}H_9Br)_2]_\infty$ (b). Fluorine and hydrogen atoms are omitted for clarity.

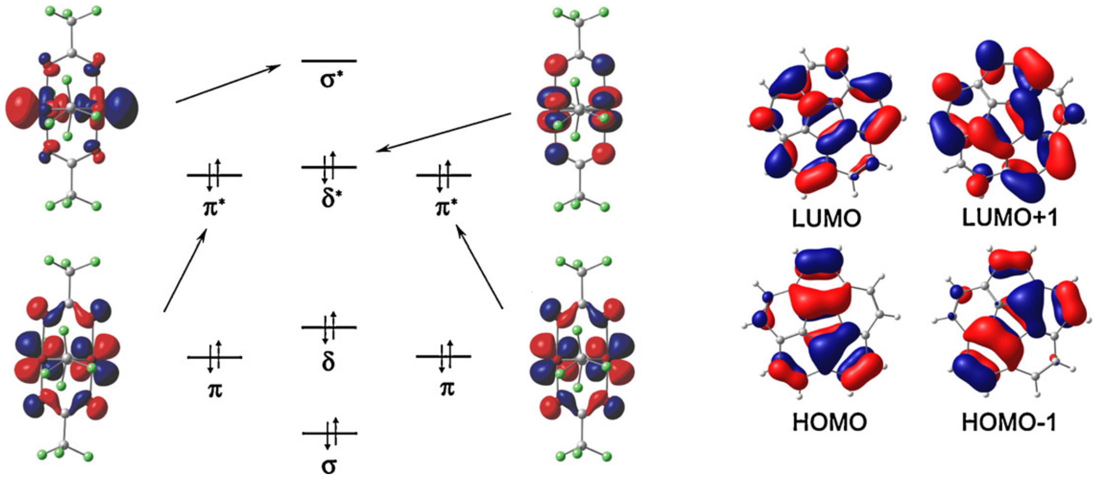


Fig. 9. DFT computed FMOs in $[Rh_2(O_2CCF_3)_4]$ (metal-based, left) and $C_{20}H_{10}$ (right).

ably greater L → M contribution (40.8 *vs.* 28.2 kcal/mol), since the back-donation (M → L) components are close in these adducts (10.5 and 8.5 kcal/mol). The small total energy preference between the rim and the spoke isomers again implies the feasibility of the spoke complexes of corannulene. In order to access those experimentally, one would need to increase the orbital control of the coordination reaction and consequently to exploit much softer Lewis acids than $[Rh_2(O_2CCF_3)_4]$. In this regard, a one-end diruthenium(I,I) unit, $[Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_5]$ (Fig. 6), has been chosen. It has a proven record of reactivity toward planar aromatic systems [32] and is expected to behave as a very soft Lewis acid, having the smallest charge on Ru(I) atom among the selected dimetal units (+0.03 *vs.* +0.97 on Rh(II) in $[Rh_2(O_2CCF_3)_4]$). The experimental results on co-deposition of corannulene with the above diruthenium unit confirmed our expectations as the first η^1-hub coordinated complex was isolated along with the co-crystallized η^2-rim-bound isomer (Fig. 10, [33]).

The compelling experimental evidence for a bonding interaction between the Ru(I) center and the interior site of $C_{20}H_{10}$ stems from the fact that the pyramidalization of the complexed hub-atom increases by nearly 30%, while the pyramidalization of the remaining C-atoms is indistinguishable from that of uncoordinated corannulene (10.6 *vs.* 8.3°). Consequently, the bowl depth is also increased from 0.875(2) Å in free corannulene [30] to 0.940(4) Å in the η^1-hub ruthenium(I) complex. DFT calculations showed a slightly weaker effect of the η^1-complexation on the corannulene core: the POAV angle is 10.3° and the bowl depth is only 0.895 Å. Noteworthy, the overall effect of coordination is noticeably less pronounced in the Ru(I) η^1-hub complex compared with that in the computed η^2-spoke complex with Rh(II). In contrast to the η^1-hub isomer, coordination of $[Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_5]$ at the rim of corannulene does not perturb its core with the POAV angles averaged over all hub C-atoms being 8.2°.

Co-crystallization of both hub and rim isomers of $[Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_5\cdot(C_{20}H_{10})]$ suggests that they should be close in energy. In fact, the same small energetic preference for the rim-bound structure over the hub complex was revealed, as it was found in dirhodium tetratrifluoroacetate corannulene complexes (*ca.* 2.5 kcal/mol, [33]). Plus, an increase in softness of the dimetal core led to a greater orbital control of the donor-acceptor contributions to bonding. A direct comparison of the Rh(II) and Ru(I) binding to the rim and spoke sites of $C_{20}H_{10}$ showed that the calculated energies of the L → M contribution for the significantly softer Ru(I) complexes are much lower than for the very Lewis acidic Rh(II) units. For example, these values for the spoke and rim Ru(I) isomers are 19.1 and 25.2 kcal/mol [33] compared to 28.2 and 40.9 kcal/mol in the Rh(II) case [8z]. At the same time, the energies of the M → L back-donation are greater in the above Ru(I) complexes, being 8.6 and 16.9 kcal/mol *vs.* 8.5 and 10.5 kcal/mol in the Rh(II) adducts.

All η^2-rim complexes discussed above revealed that coordination properties of $C_{20}H_{10}$ are more reminiscent of those for

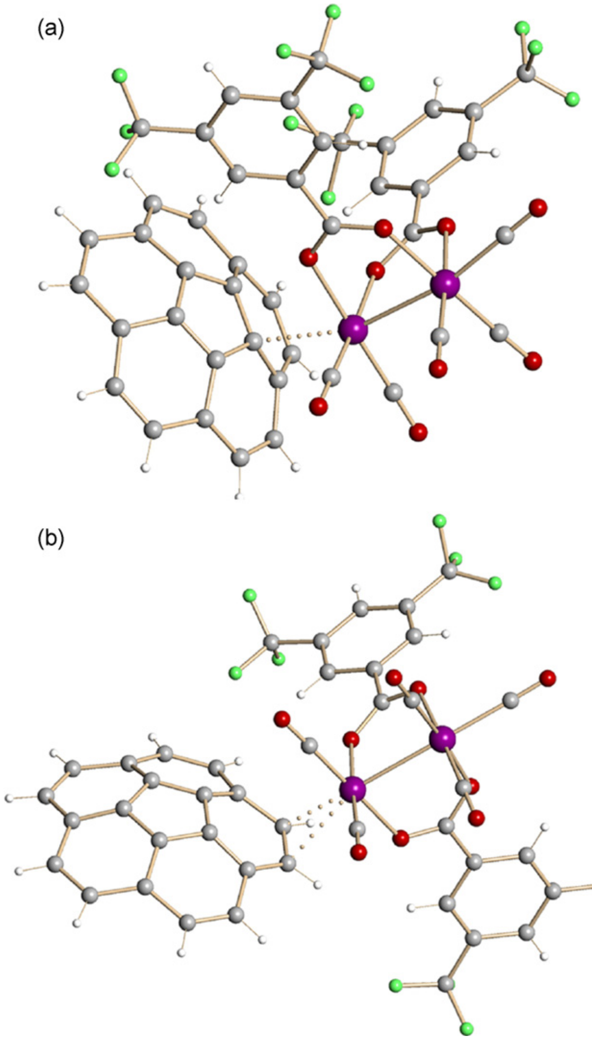


Fig. 10. The η^1-hub (a) and η^2-rim (b) coordinated complexes of $[Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_5]$ with corannulene.

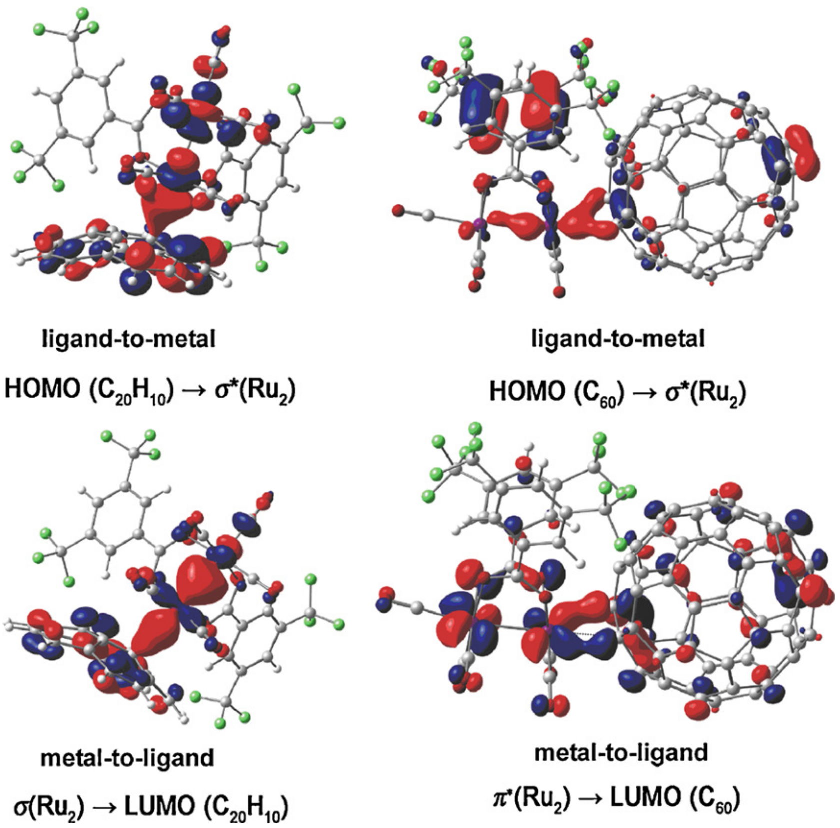


Fig. 11. Bonding molecular orbitals of $[Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_5]$ with $C_{20}H_{10}$ and C_{60}.

planar polyarenes and contrast to the reactivity of C_{60} in its exohedral metal complexes. Only the hub-corannulene Ru(I) complex, while representing the first example of metal coordination to the bowl interior, has also demonstrated some degree of similarity between the convex carbon surfaces of buckybowls and buckyballs in metal binding reactions. Interestingly, when $[Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_5]$ reacted with C_{60}, the η^2-coordinated complex to the (6:6) site on the surface of fullerene was obtained [8t]. Bonding metal–carbon orbitals clearly show the involvement of both C-atoms of C_{60} and only one hub C-atom of $C_{20}H_{10}$ in coordination (Fig. 11). It is also noteworthy that the bonding energy of the $C_{20}H_{10}$-complex is five times smaller than that of the analogous C_{60}-complex. This remarkable difference is attributed to the noticeably weaker acceptor abilities of $C_{20}H_{10}$ in metal binding reactions compared with that of the C_{60}-fullerene.

In addition to the above dimetal units, we have also tested the diruthenium(I,I) $[Ru_2(O_2CCF_3)_2(CO)_4]$ complex that has both axial positions open for coordination and a slightly increased charge on metal atoms (+0.18, Fig. 6) compared to +0.03 in $[Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_5]$. Plus, it is less volatile than $[Rh_2(O_2CCF_3)_4]$, and that allows creation of excess organic substrate over the diruthenium units in the gas phase. This resulted in the formation of the first bis-corannulene transition metal complex, $[Ru_2(O_2CCF_3)_2(CO)_4{\cdot}(C_{20}H_{10})_2]$ (Fig. 12, [34]).

Its central diruthenium(I,I) core has two terminally η^2-rim-coordinated $C_{20}H_{10}$ molecules with both metals bound to the *exo* face of corannulene. The average Ru–C distance (2.51 Å) is noticeably shorter than those in the aforementioned 1D and 2D dirhodium(II,II) complexes (averaged at 2.60 Å). Similarly, there is a little perturbation of the corannulene core upon ruthenium complexation with a small bowl depth flattening effect (0.860(1) *vs.* 0.875(2) Å in free corannulene) and a noticeable elongation of the Ru–Ru bond distance (from 2.627 to 2.665 Å). DFT calculations show that the η^2-*exo*-rim corannulene complex is favored over the η^2-*endo*-rim-bound one by 2 kcal/mol [34]. Although the energetic difference between these two isomers is rather small, we have not seen experimental evidence of *endo* coordination in this system.

Summing up the coordination properties of corannulene in the above complexes, it can be seen that Rh(II) and Ru(I) centers approach the bowls from both the *exo* and *endo* sides, interacting with the rim CC bonds or interior hub C-atom. The preferential mode of coordination is η^2-rim for all dimetal units except one case, where the Ru(I)-center is bound to the interior part of the bowl in an η^1-fashion. All Rh(II) complexes crystallize as extended coordination polymers (1D or 2D), while Ru(I) complexes exhibit discrete mono- or bis-adduct structures.

4.2. Other bowls

For the next step, we have extended these studies to buckybowls having substituents on the rim or larger surface areas than corannulene (Scheme 2).

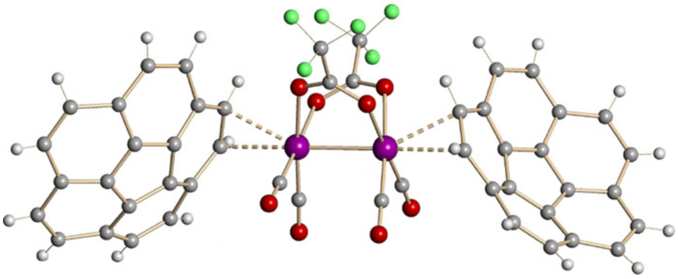
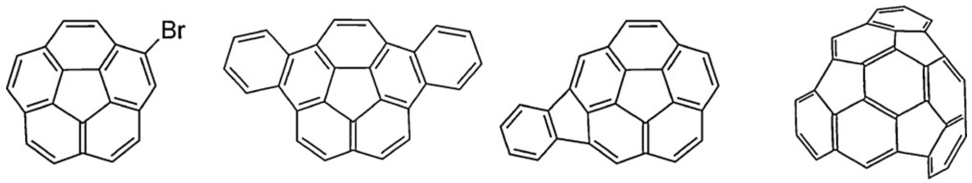


Fig. 12. The bis-corannulene adduct, $[Ru_2(O_2CCF_3)_2(CO)_4{\cdot}(C_{20}H_{10})_2]$.



$C_{20}H_9Br$ **monobromo-corannulene** $C_{28}H_{14}$ **dibenzo[*a*,*g*]-corannulene** $C_{26}H_{12}$ **monoindeno-corannulene** $C_{30}H_{12}$ ***C*$_3$-hemi-fullerene**

Scheme 2.

4.2.1. Monobromocorannulene

Rim substitution of hydrogen atoms by electron donating groups is known to enhance π-donation properties of buckybowls [11g]. In this regard, Siegel and co-workers [11g] have developed the efficient synthesis of monobromocorannulene, $C_{20}H_9Br$, by reacting corannulene with molecular bromine in the presence of iron trichloride as a catalyst. DFT calculations showed that the frontier molecular orbitals of $C_{20}H_{10}$ and $C_{20}H_9Br$ are very similar, although FMOs of monobromocorannulene are no longer degenerate [35]. The additional electron density provided by the bromine atom to the corannulene core is predominantly distributed over the rim carbon atoms without affecting the interior sites. Thus, monobromocorannulene, although being a stronger Lewis base, remains a very close electronic analogue of corannulene. Consequently, it was not surprising that deposition reactions afforded two products having the $[Rh_2]$:$C_{20}H_9Br$ ratios of 1:1 (1D polymer) and 3:2 (2D layer), similar to those with corannulene [35]. Both 1D coordination polymers with $C_{20}H_{10}$ and $C_{20}H_9Br$ have extended structures built on weak η^2-coordination with the identically positioned rim CC bonds of the corannulene core. However, there is some difference in the otherwise very similar 1D structures. In the corannulene complex, each dirhodium unit is coordinated to both convex (*exo*) and concave (*endo*) faces of $C_{20}H_{10}$ (Fig. 7), while there is an exclusive coordination of dimetal units to the convex or concave faces of $C_{20}H_9Br$ only (Fig. 13). There is also a noticeably greater flattening of the bowls in the bromocorannulene complex ($\Delta = 0.054$ Å) in comparison with the corannulene analogue ($\Delta = 0.036$ Å). The 2D networks with $C_{20}H_{10}$ and $C_{20}H_9Br$ also exhibit very similar solid-state structures (Fig. 8). The estimated diagonal pore size in the structure with bromocorannulene is slightly decreased compared with the corannulene case (17.2 *vs.* 17.7 Å).

4.2.2. Dibenzo[a,g]corannulene

To access buckybowls with larger surfaces, the benzoannulation synthetic procedures have been developed by Scott and co-workers [36] and Mehta and Sarma [37]. While dibenzo[*a*,*g*]corannulene (Scheme 2) can be prepared by flash vacuum pyrolysis [4g], it has been also obtained in relatively large quantities using standard solution methods with the aryl–aryl palladium-catalyzed coupling reaction as the culminating step [36]. Dibenzoannulation at *a* and *g* positions was found to flatten the bowl depth of the corannulene core by *ca.* 0.4 Å [38]. Despite the above progress in synthesis, no solution coordination studies of dibenzo[*a*,*g*]corannulene have yet been reported. The gas-phase reaction of this bowl with $[Rh_2(O_2CCF_3)_4]$ affords the product with the ratio of $[Rh_2]$ to $C_{28}H_{14}$ being equal to 3:2 [38]. Although the same ratio of components was also seen in the 2D corannulene-based network, the dibenzocorannulene complex assembles the reacting moieties in a complex 1D polymer (Fig. 14).

Again, coordination is seen exclusively at the rim carbon atoms of a bowl, as in all dirhodium complexes described above. While the average Rh–C distances are similar to those in other dirhodium adducts, the Rh–C contact to the peripheral benzene ring of $C_{28}H_{14}$ is slightly longer than those to the central corannulene core. Binding of three $[Rh_2]$ units to one bowl results in the decrease of the bowl depth from 0.830 to 0.770 Å, with the overall effect ($\Delta = 0.06$ Å) being greater than that observed in the corannulene products [29]. Importantly, this complex features two transition metals on the concave surface of a geodesic polyarene, representing the only example of such complexation known so far. The large surface of dibenzo[*a*,*g*]corannulene is certainly a key for unlocking this possibility. Two dirhodium units are very tightly packed on the inside of $C_{28}H_{14}$ (Fig. 15), indicating that shrinking of the bowl surface area would most likely eliminate the ability of its concave face to accommodate multiple metal units.

4.2.3. Monoindenocorannulene

Indenoannulation [39], as opposed to benzoannulation, increases curvature of the corannulene core due to an additional five-membered ring in the polyarene framework [40]. Unlike

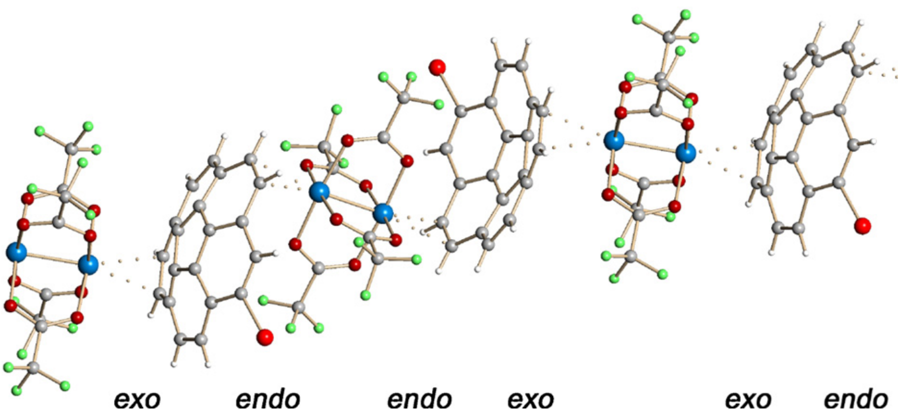


Fig. 13. A fragment of a 1D infinite chain in $[Rh_2(O_2CCF_3)_4{\cdot}(C_{20}H_9Br)]_\infty$.

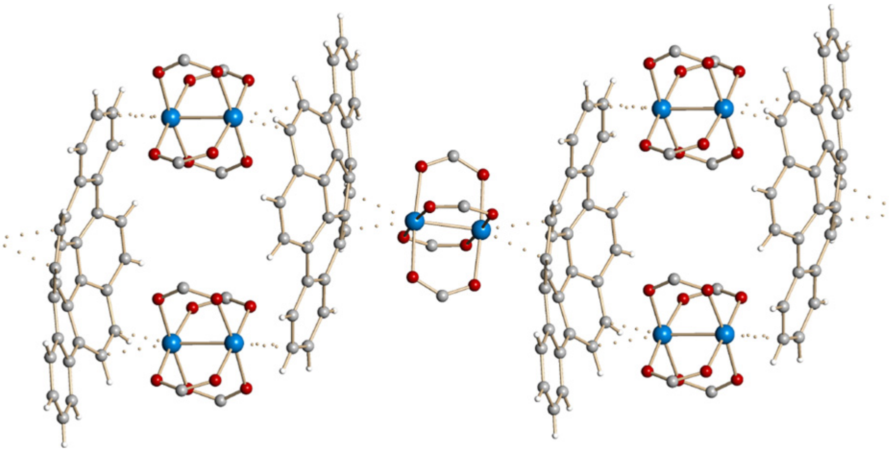


Fig. 14. A fragment of a 1D infinite chain in $[(Rh_2(O_2CCF_3)_4)_3\cdot(C_{28}H_{14})_2]_\infty$. The CF_3-groups are omitted.

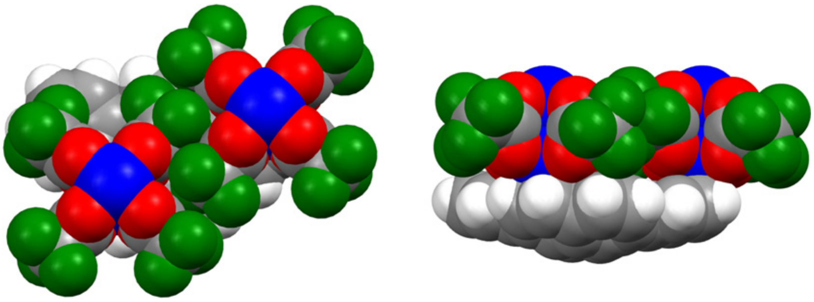


Fig. 15. Space-filling top (left) and side (right) views of the two dirhodium units on the concave face of $C_{28}H_{14}$.

corannulene and dibenzocorannulene, where the bowl-to-bowl interconversion is fast at room temperature [8g,11c,41], monoindenocorannulene (Scheme 2, [40b]) exists as a static bowl [39d] with both planar (indeno-site) and non-planar (corannulene core) parts. Two general procedures have been developed for the indenoannulation of polycyclic π-systems: a Suzuki–Heck-type coupling cascade introduced by Scott and de Meijere [39a–c, e] and a formal [(2 + 2) + 2] cycloaddition to *peri*-diethynyl corannulene derivatives developed by Siegel [39d]. The first transition metal complex of monoindenocorannulene, $[(Rh_2(O_2CCF_3)_4)_2\cdot(C_{26}H_{12})]$, has been recently prepared by gas-phase deposition [42]. The X-ray diffraction analysis reveals the formation of a 2D organometallic network based on a rare tetra-bridged coordination of a π-bowl (Fig. 16). The 2:1 stoichiometry of $[Rh_2]$ to the polyarene is unique among structurally characterized complexes of buckybowls, including corannulene, monobromocorannulene, and dibenzo[*a*,*g*]corannulene, where products with $[Rh_2]$:L = 1:1 and/or 3:2 were obtained

Importantly, in addition to η^2-rim binding, one Rh(II) center interacts exclusively with interior carbon atoms on the convex bowl surface, exhibiting an η^2-coordination type to the spoke bond previously observed only in closed all-carbon buckyballs. The lat-

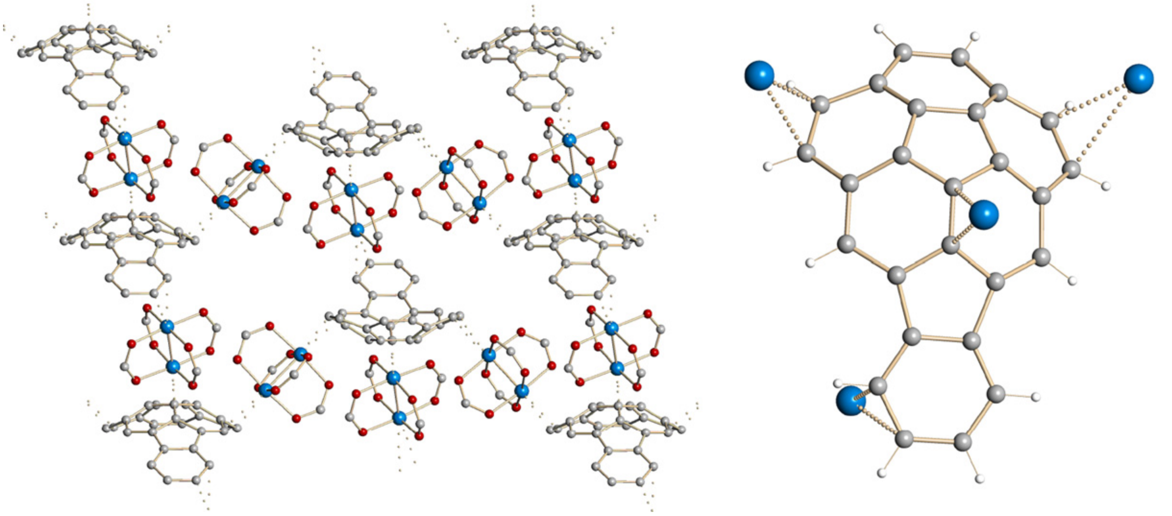


Fig. 16. A fragment of a 2D network in $[(Rh_2(O_2CCF_3)_4)_2\cdot(C_{26}H_{12})]_\infty$. The CF_3-groups and H-atoms are omitted (left). A tetradentate μ_4-η^2:η^2:η^2:η^2-coordination of $C_{26}H_{12}$ depicting only one metal atom of each dimetal unit (right).

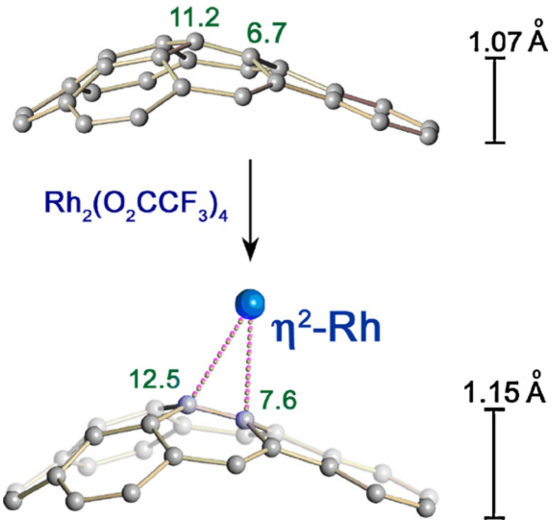


Fig. 17. Increasing the bowl depth and POAV angles of the spoke C-atoms of $C_{26}H_{12}$ upon coordination.

ter unique coordination of Rh(II) accentuates the pyramidalization of the C-atoms of monoindenocorannulene. Pyramidalization of the complexed hub-C-atom is increased to 12.5°, surpassing the curvature of C_{60} and reaching that of the highly curved pentaindenocorannulene (averaged for all hub C-atoms is 12.6° [40a]) having four more five-membered rings than $C_{26}H_{12}$. As a consequence, the bowl depth of $C_{26}H_{12}$ is significantly increased in comparison with its free form ($\Delta = 0.08$ Å), setting the record on how metal coordination may enhance the buckybowl curvature (Fig. 17). The effect can be compared with that provided by annulation of one additional pentagon to a bowl [40b].

DFT calculations showed that indenoannulation at the corannulene core results in a significant perturbation of the electronic structure of $C_{26}H_{12}$ in comparison with that of $C_{20}H_{10}$. The $\Delta E_{\text{HOMO–LUMO}}$ gap of $C_{26}H_{12}$ is significantly reduced compared to $C_{20}H_{10}$ (3.86 *vs.* 4.73 eV), rendering it to be a softer ligand. The bond order calculations revealed that the preferred coordination sites of $C_{26}H_{12}$ are the rim of the corannulene core (non-planar part), followed by the interior spoke, and then the rim of the indeno-site (planar part). This calculated trend is nicely followed by the average experimental Rh–C bond distances in the solid-state structure of $[(Rh_2(O_2CCF_3)_4)_2\cdot(C_{26}H_{12})]$: 2.567 (rim) < 2.687 (spoke) < 2.715 Å (indeno-site). A similar trend was observed for the rim and spoke $[Rh_2]$-adducts with corannulene [8z]. Both L → M and M → L interaction energies follow the same trend as the total bonding energies, with the former contribution being *ca.* 5 times greater than the latter. Theoretical analysis of the spoke *mono*-adduct with $C_{26}H_{12}$ revealed an increase of the POAV angle of the hub C-atom from 11.1 to 12.5° [42], while the pyramidalization of the second atom of the spoke bond remained unchanged showing the asymmetry in coordination. In contrast, when the *tris*-adduct better describing the experimental structure is considered as a model system, the pyramidalization of both C-atoms of the spoke bond involved in η^2-binding is increased. The bowl depth of $C_{26}H_{12}$ is significantly affected in this calculated *tris*-adduct, remaining almost unchanged in the rim-coordinated adducts. Thus, as it was seen in the case of corannulene, η^2-coordination to the interior part of the polyarene surface provides greater deformation of the bowl than η^2-rim binding.

4.2.4. Hemifullerene

The largest and deepest buckybowl studied in metal binding reactions so far is the C_3-symmetric hemifullerene, $C_{30}H_{12}$ (Scheme 2, [43]). First attempts to prepare the hemifullerene transition metal complex by treating it with $[Pt(C_2H_4)(PPh_3)]$ resulted in the insertion of platinum into the peripheral CC bond of one of the five-membered rings [44]. The feasibility of such an unusual aryl-aryl bond breaking has been attributed to the relief of strain at the edge of this highly curved polyaromatic hydrocarbon. The only structurally characterized π-complex of the $C_{30}H_{12}$-hemifullerene has been obtained using co-deposition reaction [45]. Under gas-phase conditions, dirhodium tetratrifluoroacetate binds to hemifullerene giving a product with the ratio of $[Rh_2]$ to $C_{30}H_{12}$ being equal to 3:1. Its X-ray diffraction analysis revealed a formation of a 3D network in the solid state (Fig. 18). Similar to the complex with monoindenocorannulene, four metal centers are bound to each $C_{30}H_{12}$-bowl resulting in its tetra-bridged coordination. While three Rh-atoms approach the hemifullerene ligand from the convex side (η^2-mode), one is bound to its concave side in an η^1-fashion. Despite the large available surface area of the ligand, only rim carbon atoms of $C_{30}H_{12}$ are involved in metal coordination. In this complex, only one of the three dirhodium units has the $C_{30}H_{12}$-molecules coordinated to both of its open axial positions. The other two form "dimers of dimers" core structures via Rh···O intermolecular interactions. The formation of such dimers is not surprising due to the very limited volatility of the $C_{30}H_{12}$-hemifullerene and was previously documented in the gas-phase reactions when excess of dimetal complexes was used [46]. It is

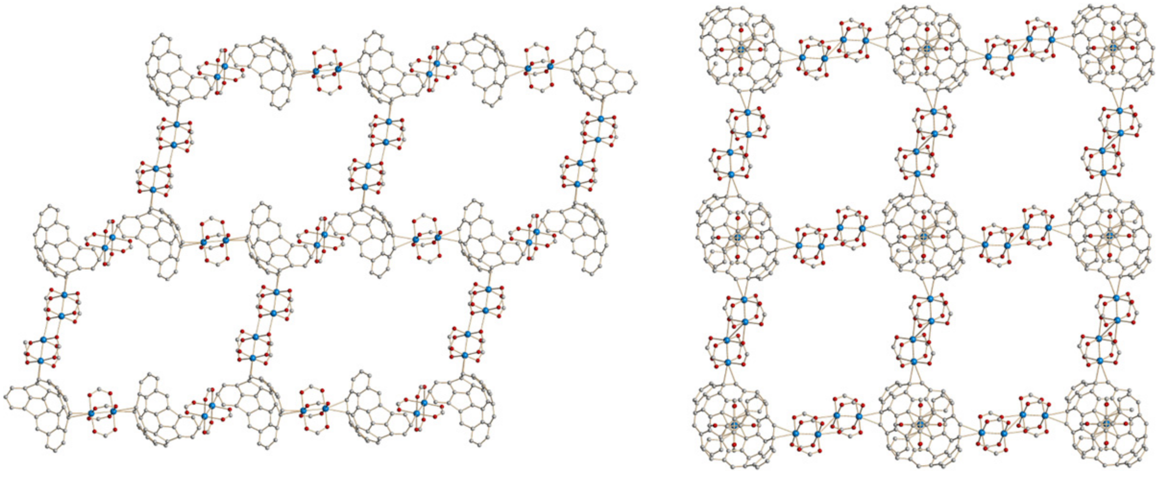
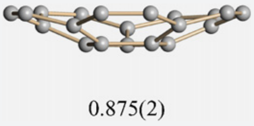
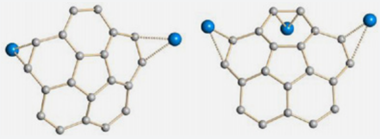
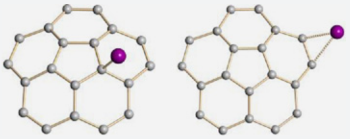
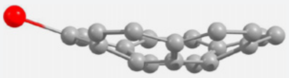
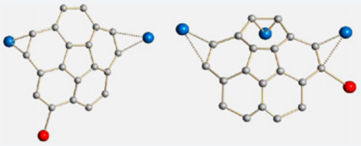
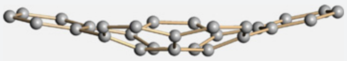
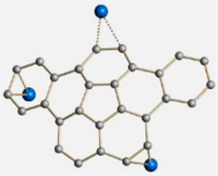
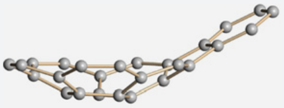
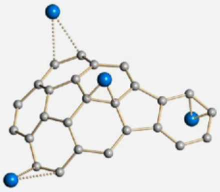
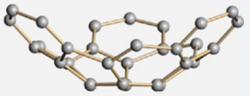
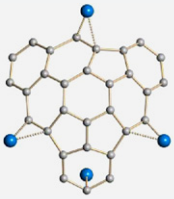


Fig. 18. Two views of the 3D structure in $[(Rh_2(O_2CCF_3)_4)_3\cdot(C_{30}H_{12})]_\infty$ perpendicular (left) and along (right) the direction of the 1D coordination polymer based on alternating $[Rh_2]$ and $C_{30}H_{12}$ units. "Dimers of dimers" extend the structure in the other two dimensions. The CF_3-groups and H-atoms are omitted.

Table 1
Coordination of π-bowls in the structurally characterized Rh(II) and Ru(I) complexes.

Formula	Side view,[a] Bowl depth in a free form (Å)	Coordination modes,[b]	Bowl depth in a complexed form (Å)
$C_{20}H_{10}$	 0.875(2)		μ_2-η^2:η^2 0.839(3) μ_3-η^2:η^2:η^2 0.861(3)
			η^1 0.940(4) η^2 0.860(1)
$C_{20}H_9Br$	 [c] 0.862 (calc)[c]		μ_2-η^2:η^2 0.808(2) μ_3-η^2:η^2:η^2 –
$C_{28}H_{14}$	 0.830(3)		μ_3-η^2:η^2:η^2 0.770(3)
$C_{26}H_{12}$	 1.065(4)		μ_4-η^2:η^2:η^2:η^2 1.148(6)
$C_{30}H_{12}$	 [c] 2.41(4)[c]		μ_4-η^2:η^2:η^2:η^1 –
$C_{40}H_{50}$	 0.72(5)	No binding	–

[a] H-atoms are removed.
[b] Only one metal atom of each dimetal unit is shown.
[c] Severe disorder of $C_{20}H_9Br$ and $C_{30}H_{12}$ precludes obtaining accurate bowl depth values in the X-ray structures of their complexes.

noteworthy that the calculated bonding energies for the η^2-rim mono-adducts of $C_{30}H_{12}$ and $C_{20}H_{10}$ are almost the same (18.3 *vs.* 18.8 kcal/mol) and only slightly lower than those for the acenaphthylene and pyrene analogues [8z]. Hence, a significant increase in curvature of a π-bowl on going from $C_{20}H_{10}$ to $C_{30}H_{12}$ showed no effect on the stability of the rim-adducts of $[Rh_2(O_2CCF_3)_4]$.

5. General trends

The isolated π-complexes of several buckybowls, including the only known transition metal complexes of dibenzo[*a*,*g*]corannulene, monoindenocorannulene, and hemifullerene, illustrate the advantage of the gas-phase deposition method in accessing the single crystalline products in one step. Their X-ray crystallographic analyses revealed the preferential coordination sites for a number of unique non-planar polyaromatic ligands, expanding the coordination studies of buckybowls beyond the smallest corannulene broadly examined in solution. Several different coordination modes of π-bowls have now been experimentally identified (Table 1), showing a general preference of electrophilic Rh(II) and Ru(I) centers for rim coordination. However, a careful selection of metal units and bowls has resulted in the involvement of the interior polyarene surface in coordination, as illustrated by the isolated η^1-hub and η^2-spoke coordinated products. Importantly, multiple metal binding to a bowl has been readily achieved under gas-phase reaction conditions revealing the coordination limits of the selected buckybowls. For example, two and three metal centers are bound to $C_{20}H_{10}$ and $C_{20}H_9Br$ in the Rh(II) complexes to make the bowls function in the μ_2-η^2:η^2- and μ_3-η^2:η^2:η^2-bridging modes, respectively. The latter tridentate mode is also realized in the dibenzo[*a*,*g*]corannulene complex, but the large concave surface area of $C_{28}H_{14}$ allows coordination of two dirhodium units to the *endo* face of the bowl. Four metal centers coordinate to $C_{26}H_{12}$ and $C_{30}H_{12}$ in their Rh(II) complexes resulting in the rare tetradentate μ_4-η^2:η^2:η^2:$\eta^{2(1)}$-bridging coordination of π-bowls. It is noteworthy that when the rim sites of the corannulene core are blocked by five bulky *tert*-butyl groups in $C_{40}H_{50}$, no metal complexation is observed upon co-deposition with the same dirhodium complex [47].

Furthermore, these structurally characterized complexes provide a good set for evaluation of metal binding effects on geometries of π-bowls having different depth, strain, and surface areas. A comparison of the bowl depths in the free and coordinated forms shows that the effect depends on the coordination site. In general, the η^2-rim binding slightly flattens a bowl and mostly affects the geometry of the 6-membered ring involved in coordination. In contrast, the η^1- or η^2-metal binding to the interior part of the bowl surface leads to its curvature increase, with the effect being the greatest for the latter coordination mode. For example, the pyramidalization angle of the hub-C-atom involved in the above coordination is increased from 8.3 to 10.8° in corannulene, and it even surpasses the curvature of C_{60} in the indenocorannulene spoke complex [42]. Overall, the effects of metal complexation on the bowl geometry in the η^2-coordinated complexes are not as pronounced as in some η^6-complexes, where almost complete flattening of the corannulene molecule has been observed [8s]. Rather than being a brute force affecting the bowl as a whole, these effects are more delicate and site-specific, thus likely causing the subtle modification of a particular area on the polyaromatic surface.

6. Concluding remarks

Buckybowls are now shown to exhibit system-dependent coordination properties. By selecting a proper metal unit and by tuning the structure and electronics of a π-bowl, one can modulate the overall binding mode and direct the coordination to surface exterior or interior, to the convex or concave, or both faces of bowl-shaped polyarenes. The formation of several discrete Ru(I) η^2-complexes [33,34], showing the exclusive metal coordination to the *exo* face of corannulene, along with η^6-complexes of Rh [8q], Ir [8q], Ru [8s] and η^2-bound Ag [19] products, experimentally reveals the general preference of the convex carbon surface of $C_{20}H_{10}$ for metal binding. However, the newly added sumanene complexes [20–22] prove that the concave bowl surface can also be engaged in metal coordination. Thus, an expansion of these studies to larger and more strained π-bowls should most likely reveal novel aspects of their coordination chemistry, as well as new and unusual reactivity patterns in metal binding reactions, and that should greatly stimulate their applications in materials chemistry.

Acknowledgments

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