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Coordination Chemistry Reviews 251 (2007) 1690–1698
COORDINATION CHEMISTRY REVIEWS
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Review

Designed solvent-free approach toward organometallic networks built on directional metal–π-arene interactions[☆]

Marina A. Petrukhina[*]

Department of Chemistry, University at Albany, State University of New York, 1400 Washington Avenue, Albany, NY 12222, USA

Received 3 October 2006; accepted 18 November 2006
Available online 24 November 2006

Contents

Abstract

This work overviews our recent results on application of the gas phase deposition approach toward controlled formation of novel solid organometallic networks. Volatile electrophilic dimetal complexes of Rh(II), Ru(II), and Ru(I) and various organic π-donors have been used as complementary building blocks in co-deposition reactions. The selected ligands range from hydrocarbons having isolated π-bonds and aromatic rings to conjugated polyarenes with planar or curved unsaturated carbon surfaces. The selected dimetal core complexes have a strong avidity for axial coordination and function as linear spacers in organometallic assembling reactions. Co-deposition of the above blocks in a solvent-free environment results in the controlled assembling of crystalline organometallic products. The technique is very effective in differentiation of π-bonding sites of multifunctional ligands and in utilization of directional metal–π-arene interactions for the construction of extended frameworks.

Keywords: Solvent-free synthesis; Organometallic; Transition metals; Polyarenes; Buckybowls

1. Introduction

Designed engineering of organometallic networks is currently less developed compared to the construction of supramolecular architectures built on various metal–ligand coordination bonds [1]. Generally, the expectations for organometallic assemblies are the same; the geometry of building blocks should predetermine the structural organization of a supramolecular system, while the properties of individual units should define the properties of a hybrid product.

However, an efficient use of intermolecular metal–π-arene interactions for self-assembling in solutions may be thwarted by the lability of complexes, by solvent- and ion-templating effects, or by solvent competition for coordination [2]. To avoid complications listed above, the use of new crystal engineering tools that exclude solvents [3] is very important in order to control assembling processes. Therefore, in contrast to solution self-assembling methods, we introduced and tested a micro-scale technique that excludes solvents from chemical reactions and relies on the co-deposition of volatile complementary building

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[☆] Based on a keynote lecture presented at the 37th International Conference on Coordination Chemistry, 13–18 August 2006, Cape Town, South Africa.

[*] Tel.: +1 518 442 4406; fax: +1 518 442 3462.
E-mail address: marina@albany.edu.

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doi:10.1016/j.ccr.2006.11.004

units from the gas phase. This technique can utilize a variety of volatile organic donors ranging from hydrocarbons with isolated π carbon–carbon bonds to conjugated polyarenes with planar or curved unsaturated carbon surfaces. For this work we initially selected dimetal core complexes that function as linear spacers and allow ligands to impose a specific network topology. The degree of structural control in this case depends on the nature and dimensions of a ligand, the controlled positioning of binding sites along the ligand backbone, or the change of coordination mode. At the same time, rich redox chemistry, interesting optical and magnetic properties associated with multiply bonded dimetal complexes coupled with their high affinity for axial coordination render them ideal building blocks for the construction of new types of molecular architectures [4]. In this account we demonstrate how various π-donor ligands function as building blocks in the solvent-free co-deposition reactions with dimetal spacers to afford new crystalline organometallic products in a controlled fashion.

2. Solvent-free synthetic methods

The solvent-free preparation of coordination polymers and metal-organic frameworks has attracted special interest in recent years. Solvent-free methods address a major environmental concern, namely the demand from both economic and ecological standpoints for increasingly clean and efficient new synthetic techniques that keep costs and waste production low. In this regard, an exclusion of hazardous, expensive, and often toxic organic solvents from chemical processes should be a very viable approach to the above issues. Then, the development of new laboratory scale solvent-free preparative techniques should eventually lead to a broad use of large scale 'green' industrial production methods. Moreover, the exclusion of solvents can provide access to new products and materials that are not readily accessible by conventional solution methods. In this respect, a comparison of solution and solvent-free techniques for related systems provides insights into the role of solvents as structural templates in self-assembling processes [5].

A common solvent-free synthetic approach that is currently under development in several research groups is based on the use of mechanochemical methods. Grinding together metal salts and bridging organic ligands has been shown as an effective and convenient preparative method to produce discrete metal complexes [6] and 1D coordination polymers [7]. The first quantitative mechanochemical preparation of a robust 3D microporous framework has been reported this year [8]. It should be noted here that mechanochemical synthesis yields products in the form of polycrystalline powders, and this leaves X-ray powder diffraction as the only tool for their structural characterization. Powder diffraction data are usually supported by calculations and compared with diffraction patterns of the structures characterized by single crystal X-ray crystallography. When there is no match with the known frameworks, the polycrystalline products obtained by mechanochemical methods lack structural identification.

Solvent-free high-temperature reactions in melts are also utilized as a fruitful alternative to solution coordination [9]. This includes the recently developed melt synthetic routes toward the rare earth amides, for which solvent molecules are known to be competitive ligands when reactions are performed in solutions. Crystallization under melt reaction conditions often affords single crystalline products. Additionally, several metal activation procedures such as the formation of amalgams or microwave assistance can be used to facilitate melt reactions. Importantly, it has been shown that the crystal structures and hence the properties of the products of melt reactions differ from those isolated from analogous reactions carried out in classical solvents.

In contrast to mechanochemical methods or melt reactions, we develop an original solvent-free technique that is based on the gas phase sublimation–deposition procedures of complementary volatile donor and acceptor building blocks [10]. Reactions are performed in small glass ampoules in the temperature range of 40–350 °C to reproducibly afford crystalline products in good yields. The composition of products is controlled by varying the ratio of starting materials and by rational control of reaction conditions (reaction temperature, temperature gradient, and time).

The use of the gas phase deposition conditions that exclude solvents from coordination reactions and chemical transformations has allowed us to isolate products inaccessible from conventional solution methods. Since no solvent molecules compete for metal coordination sites, very weak donors can be examined and weak donor–acceptor intermolecular interactions can be utilized in the construction of supramolecular products. Reactions are performed on a micro-scale and require only milligrams of starting materials, which is important for testing new reagents that are not available in macro-scale quantities. The products are deposited in the form of single crystals, and such an ease of crystallization from the gas phase has allowed us to fully utilize X-ray crystallography for structural characterization of the products. The availability of the structural data greatly facilitates the elucidation of the structure–property relationships for the newly prepared materials. We proved this technique to be very effective for the preparation of new inorganic and organometallic metal complexes, for investigation of ligating properties of various donors [11], for entrapment of reactive intermediates formed in the gas phase [12], and for preparation of termolecular complexes with the potential of terminal oxo-function activation [13].

Herein we demonstrate the effectiveness of the method for utilizing weak intermolecular metal–π-aromatic interactions in supramolecular organometallic assembling. We also show how this technique is used for testing the reactivity of various π-donors, including a novel class of bowl-shaped polyaromatic hydrocarbons (buckybowls). Importantly, multiple metal coordination to a ligand can be readily achieved under gas phase reaction conditions to force extreme and rare coordination modes of polyarenes.

3. π-Donor systems in gas-phase deposition reactions

3.1. Isolated π-bonds and aromatic rings

A number of electrophilic and volatile metal complexes can be used in deposition reactions, including a very strong

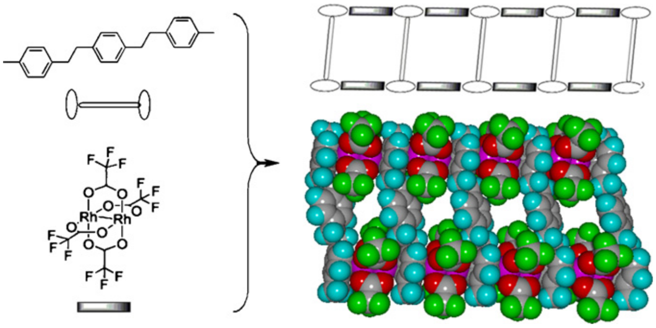


Fig. 1. Gas phase reaction of $[Rh_2(O_2CCF_3)_4]$ and 1,4-bis(*p*-tolylethyl)benzene to afford a ladder-like network, $[(Rh_2(O_2CCF_3)_4)_2\cdot(C_{24}H_{26})]_\infty$.

Lewis acidic unit having two open coordination sites, namely dirhodium(II,II) tetrakis(trifluoroacetate) [14]. The $[Rh_2(O_2CCF_3)_4]$ unit has a great ability to bond axially to a variety of donor ligands [15], including unsaturated hydrocarbons with isolated C=C and C≡C bonds [16a,b]. The early study on diphenylacetylene is a good example of how the gas-phase reactions allowed us to effectively control product stoichiometries and thus to illustrate an ambidentate behaviour of the Ph_2C_2 ligand in metal binding [16a]. Two complexes of the compositions $[Rh_2]:Ph_2C_2 = 1:2$ and 1:1 have been selectively prepared under different sublimation–deposition conditions. While the former has a bis-adduct type of structure with two alkyne groups coordinated to axial positions of the dirhodium unit, in the latter diphenylacetylene acts as a bifunctional ligand using its both alkyne and arene functions to form an extended 1D polymer.

Recently, a hydrocarbon having three separate aromatic rings, namely 1,4-bis(*p*-tolylethyl)benzene ($C_{24}H_{26}$), has been tested as an elongated π-donor in gas phase assembling reactions with the $[Rh_2(O_2CCF_3)_4]$ unit [16c]. As a result, a novel organometallic ladder built on directional rhodium(II)–π-arene interactions was formed in good yield (Fig. 1). In the framework, each $C_{24}H_{26}$ ligand exhibits a tetradentate bridging coordination having four metal centers attached to the opposite sides of the two peripheral benzene groups. Such coordination was supported by orbital interaction computational analysis of the reacting partners, thus showing that the solvent-free conditions provide a unique environment for a metal to differentiate π-bonding sites of the multifunctional π-donating ligand.

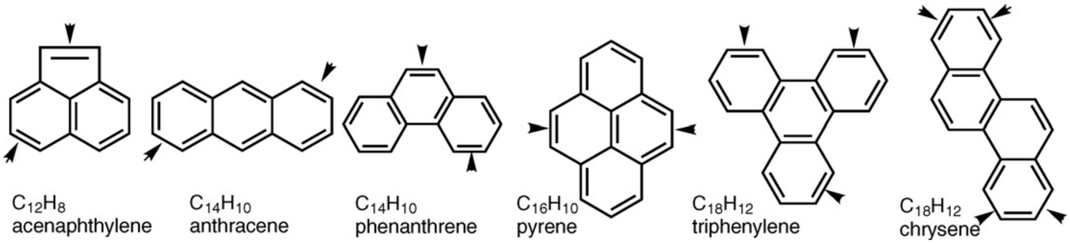
3.2. *Planar polycyclic aromatic hydrocarbons*

The co-deposition approach has been proven successful for the coordination of planar polycyclic aromatic hydrocarbons (PAHs) [17]. A set of various PAHs (Scheme 1) has been tested in reactions with dirhodium(II,II) tetrakis(trifluoroacetate) to afford crystalline products with various stoichiometries $[Rh_2]:PAH = 1:2$, 1:1, 3:2, and 3:1.

Single-crystal X-ray diffraction revealed a variety of structural motifs ranging from discrete bis-adduct molecules to extended 1D chains and 2D networks, all based on the directional rhodium–η^2-arene interactions. The structural control of product topologies in such reactions is readily achieved by selection of the geometry and dimensions of PAHs. Thus, several three-ring PAHs (including compact four-ring pyrene) have formed 1D polymers with the linear dirhodium unit, while triphenylene in its unique tridentate bridging mode (μ_3-η^2:η^2:η^2) has directed the formation of a ribbon-like network (Fig. 2). The elongated chrysene functioned as a tetradentate bridge (μ_4-η^2:η^2:η^2:η^2) to afford an extended 2D layer [17]. It should be pointed out here that no significant distortions of the aromatic systems of PAHs have been observed upon their coordination to rhodium compared to the structures of uncoordinated ligands.

Importantly, these studies with planar PAHs have revealed an interesting trend that rhodium(II) coordination is site-selective and is correlated with the π-bond order of the C=C bonds, as determined by Hückel calculations [17]. Complexation of planar PAHs by $[Rh_2(O_2CCF_3)_4]$ has been seen invariably at the rim C=C sites with the highest π-bond order. This makes the dirhodium complex a very sensitive electrophilic probe to test reactivity and to identify binding sites of more interesting and less explored non-planar, curved, and branched polyaromatic hydrocarbons. The latter ligands should provide a wider range of possibilities for connecting dinuclear (and, prospectively, polynuclear) metal building blocks together to construct new 3D extended frameworks.

Before moving to such systems, a unique example of the site controlled arene coordination should be mentioned. Recent preparation of the first bismuth-rhodium tetracarboxylates [18] has provided access to a remarkable class of heterobimetallic molecules that are expected to show different reactivity at two open axial sites. Utilizing solvent-free reaction conditions, we have tested the coordination ability of the heterometallic $[BiRh(O_2CCF_3)_4]$ complex toward pyrene ($C_{16}H_{10}$) and isolated a new adduct $[BiRh(O_2CCF_3)_4\cdot(C_{16}H_{10})]$ [19]. Importantly, coordination of pyrene is different at two ends of the heterobimetallic core (Fig. 3). One pyrene η^6-coordinates two bismuth centers from the two neighboring heterobimetallic units, while the other pyrene η^2-binds two different rhodium centers. Thus, the pyrene ligand functions either as an η^6:η^6 bridge toward bismuth or as an η^2:η^2 bridge toward rhodium.



Scheme 1.

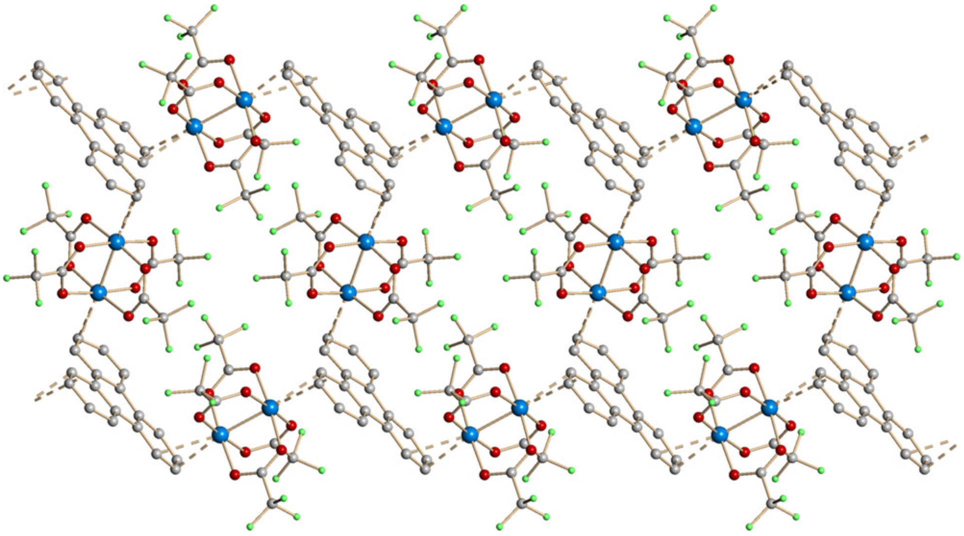


Fig. 2. A fragment of a pseudo-2D ribbon in $[(Rh_2(O_2CCF_3)_4)_3\cdot(C_{18}H_{12})_2]_\infty$. Rh blue, O red, F green, C gray, H light gray.

3.3. Non-planar polyaromatic ligands

Recently, we have tested the coordination properties of multidentate non-planar aromatic ligands containing two or three benzene rings, [2.2]paracyclophane ($C_{16}H_{16}$) and [2.2.2]paracyclophane ($C_{24}H_{24}$), respectively [20]. The use of the $[Rh_2(O_2CCF_3)_4]$ complex having two centers of Lewis acidity has forced rare and novel bridging modes of paracyclophanes that have not been observed in solution reactions. The gas phase deposition technique effectively utilized the geometrical and electronic structures of these ligands for the controlled formation of crystalline organometallic products having the desired topologies. This was clearly seen from a direct comparison of two different paracyclophanes in the coordination to the same linear dimetal unit. The isolated complex of [2.2]paracyclophane is based on the bidentate bridging mode of $C_{16}H_{16}$ and exhibits a chain polymeric structure, $[Rh_2(O_2CCF_3)_4\cdot(\mu_2\text{-}C_{16}H_{16})]_\infty$. Such complexes, in which $C_{16}H_{16}$ acts as the μ_2-η^2:η^2-bridge, have been previously known only in the case of silver(I) compounds isolated from solution [21]. We have also reported that linear complexes of ruthenium, namely diruthenium(I,I) bis(trifluoroacetate) tetracarbonyl $[Ru_2(O_2CCF_3)_2(CO)_4]$ and diruthenium(II,II) tetrakis(trifluoroacetate) $[Ru_2(O_2CCF_3)_4]$ react with [2.2]paracyclophane under deposition conditions to form similar 1D organometallic polymers built on the same rare coordination of $C_{16}H_{16}$ [22,23].

For more versatile [2.2.2]paracyclophane we have found several coordination modes (Fig. 4) [20], including a novel tridentate η^2:η^2:η^2 bridging coordination that directed formation of a unique organometallic layer, $[(Rh_2(O_2CCF_3)_4)_3\cdot(\mu_3\text{-}C_{24}H_{24})_2]_\infty$.

The latter has infinite open channels with aromatically functionalized 'walls' that are comprised of the benzene rings of [2.2.2]paracyclophane. Its interesting porous structure prompted us to test this crystalline material for potential gas recognition and sorption, since [2.2.2]paracyclophane is a well-known receptor for the Ag(I), Sn(II), and Ge(II) cations in solution [24,25]. The gas sorption measurements were carried out with H_2, N_2, and CO_2 gases that could fit the small gate entrance of the [2.2.2]paracyclophane channels. No sorption was detected for N_2 and H_2 gases at 77 K, and only a small amount of CO_2 was reversibly absorbed by the product [20].

3.4. Bowl-shaped polyaromatic hydrocarbons

From a coordination viewpoint, bowl-shaped polyaromatic hydrocarbons or buckybowls [26] are unique ligands

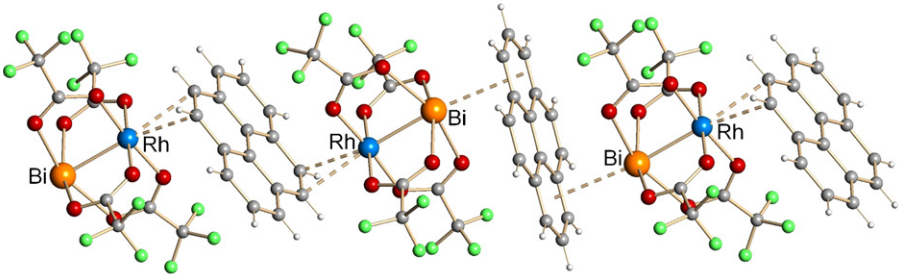


Fig. 3. A fragment of a 1D polymer in $[BiRh(O_2CCF_3)_4\cdot(C_{16}H_{10})]_\infty$.

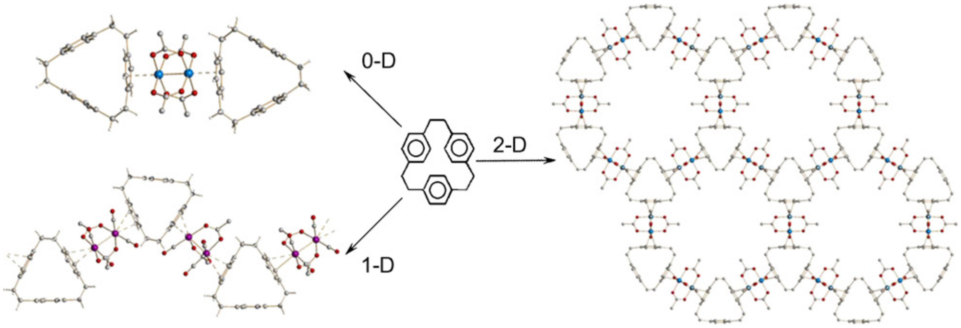


Fig. 4. The [2.2.2]paracyclophane-based complexes: $[Rh_2(O_2CCF_3)_4\cdot(C_{24}H_{24})_2]$ (0D), $[Ru_2(O_2CCF_3)_2(CO)_4\cdot(C_{24}H_{24})]_\infty$ (1D), and $[(Rh_2(O_2CCF_3)_4)_3\cdot(C_{24}H_{24})_2]_\infty$ (2D). F-atoms are removed for clarity.

that have multi-site coordination possibilities, namely, convex and concave polyaromatic faces, edge or rim carbon atoms capped by hydrogen atoms. They share with fullerenes the convex three-dimensional surface of unsaturated carbon atoms but in contrast have a concave carbon surface that is open and readily accessible. These hydrocarbons constitute a new family of polyarenes that is expected to exhibit system-dependent preferences for metal binding. Substantial efforts have recently been directed toward studying the reactivity and ligating properties of buckybowls using various computational techniques [27,28]. However, control of their reactivity in coordination reactions presents a challenge, and experimental evidences regarding preferences for metal binding are still rather scarce and mainly limited to the smallest bowl, corannulene ($C_{20}H_{10}$; Scheme 2) [29].

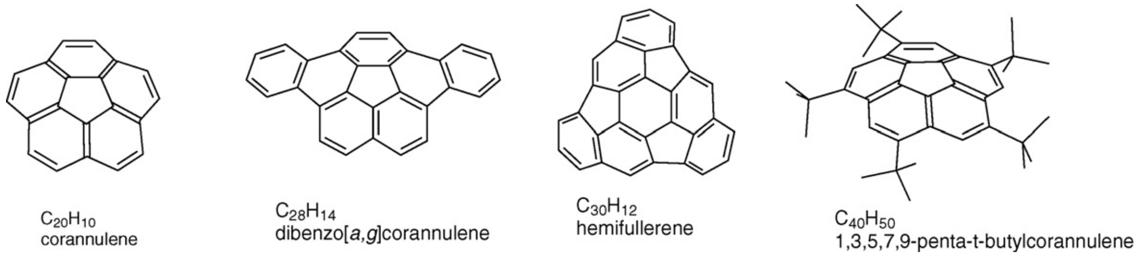
The first metal complex of corannulene, $[(\eta^6\text{-}C_{20}H_{10})Ru(C_5Me_5)]^+$ was isolated and spectroscopically characterized back in 1997 [28a]. NMR evidence for η^6-complexation of corannulene by $[Ir(C_5Me_5)]^{2+}$ was reported in 2003 [30], but structural X-ray characterization of the first η^6-corannulene complex was not achieved until 2004 [31]. Three new silver(I)-based networks built on η^2- and η^1-binding of Ag^+ ions to the rim sites of corannulene have been reported in 2005 [32]. An attempt to prepare a transition metal complex of $C_{30}H_{12}$ (Scheme 2) by reacting it with $[Pt(C_2H_4)(PPh_3)_2]$ resulted in the insertion of platinum into the peripheral C–C bond of one of the five-membered rings [33]. The ligating properties of buckybowls other than $C_{20}H_{10}$ and $C_{30}H_{12}$ remained unexplored, although more than two-dozen members of this family are known to date.

To test the reactivity of buckybowls and to identify their preferred binding sites, we rely on the solvent-free approach that has been proven successful for the coordination of planar PAHs [17]. The first crystalline complexes of corannulene have been successfully prepared in our laboratory in 2003 [34]. We then tested other bowls having different geometry and curvature, namely, dibenzo[*a,g*]corannulene and the C_3-symmetric hemifullerene, as well as the rim-substituted 1,3,5,7,9-penta-*tert*-butylcorannulene (Scheme 2) [35]. Initially, we examined their reactivity using the $[Rh_2(O_2CCF_3)_4]$ unit that was proven to be an excellent electrophilic probe for planar polyarenes.

For corannulene, two products having compositions $[Rh_2]:(C_{20}H_{10}) = 1:1$ and 3:2 have been prepared to exhibit extended 1D and 2D structural motifs, respectively (Fig. 5).

Interestingly, the product composition of the only dibenzo [*a,g*]corannulene complex isolated, $[Rh_2]:(C_{28}H_{14}) = 3:2$ [36], was the same as that of the 2D corannulene-based network. However, a complex 1D structural motif was found to feature the unprecedented complexation of two transition metals to the concave surface of a geodesic polyarene (Fig. 6). In the case of the hemifullerene, $C_{30}H_{12}$ [37], a single complex of the composition $[Rh_2]:(C_{30}H_{12}) = 3:1$ has been isolated and found to exhibit a doubly interpenetrated 3D network (Fig. 7).

In all of the above complexes, rhodium(II) centers approach the bowls from both the *exo* and the *endo* sides, but they interact exclusively with the rim C=C bonds of the polyarenes. The mode of coordination is η^2 for all Rh-atoms except for one metal center that is bound to a bowl in the η^1-fashion in the hemifullerene complex (Fig. 8). The latter metal atom most probably has steric problems in approaching the deep $C_{30}H_{12}$ bowl from its concave side. Importantly, multiple metal coor-



Scheme 2.

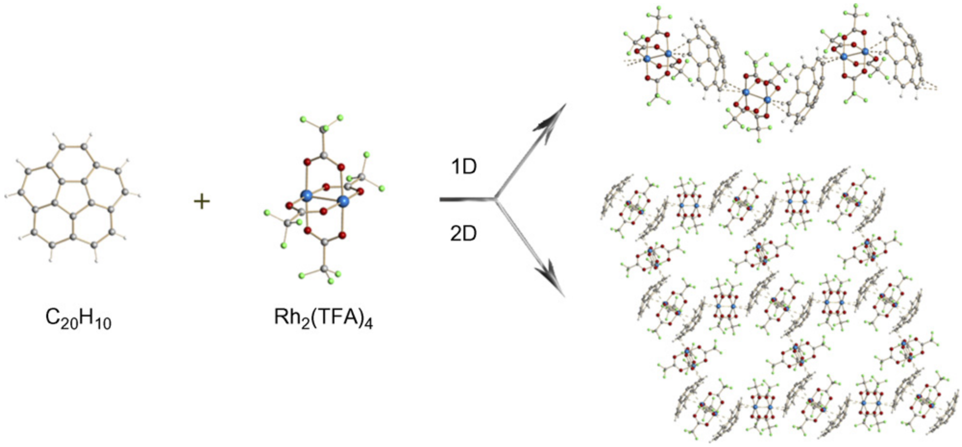


Fig. 5. Fragments of a polymeric chain in $[Rh_2(O_2CCF_3)_4{\cdot}(C_{20}H_{10})]_\infty$ and of a layer in $[(Rh_2(O_2CCF_3)_4)_3{\cdot}(C_{20}H_{10})_2]_\infty$.

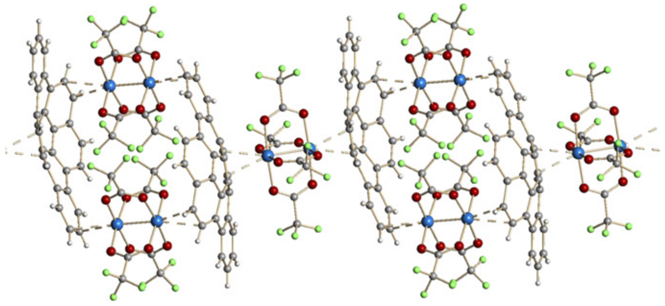


Fig. 6. A fragment of a 1D chain in $[(Rh_2(O_2CCF_3)_4)_3{\cdot}(C_{28}H_{14})_2]_\infty$.

dination to a bowl has been readily achieved under gas phase reaction conditions. For example, two and three metal centers are bound to corannulene in the isolated rhodium(II) complexes to make the bowl 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 in contrast to corannulene, the large concave surface area of $C_{28}H_{14}$ allows coordination of two dirhodium units at the *endo* site of the bowl. Four metal centers coordinate to a single hemifullerene ligand in its rhodium(II) complex, resulting in a unique tetradentate μ_4-η^2:η^2:η^2:η^1 bridging coordination of the $C_{30}H_{12}$ bowl. When the rim sites of the corannulene core were blocked by five bulky *tert*-butyl groups in $C_{40}H_{50}$, no metal complexation was observed upon co-deposition with the dirhodium complex [38].

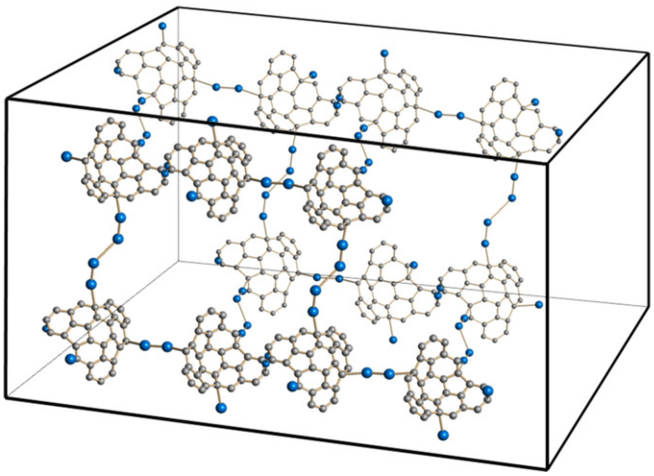


Fig. 7. A fragment of a 3D network in $[(Rh_2(O_2CCF_3)_4)_3{\cdot}(C_{30}H_{12})]_\infty$. Only Rh- and C-atoms are shown.

The revealed preference of buckybowls for rim coordination by strongly Lewis acidic rhodium(II) centers was recently extended to isoelectronic ruthenium(I). The first discrete bis-corannulene ruthenium(I) complex $[Ru_2(O_2CCF_3)_2(CO)_4{\cdot}(C_{20}H_{10})_2]$ has been crystallized from the gas phase co-deposition reaction of the corresponding building blocks. The central diruthenium core has two terminally η^2-rim bound $C_{20}H_{10}$ molecules with metals bound to the *exo* face of the bowl [39]. Such coordination, along with the previously reported $[Ru(C_5Me_5)]^+$- and Ag^+-corannulene complexes [31,32], demonstrates the preference of the convex (*exo*) carbon surface of corannulene for binding. Our experimental results were supported by DFT calculations that predicted the η^2-*exo*-rim corannulene complex to be slightly favored over the η^2-*endo*-rim-bound ruthenium complex.

We reasoned at this point that further softening the Lewis acidity of metal complexes should decrease the preference for rim binding to the corannulene bowl and we turned to a one-end ruthenium(I) unit, namely $[Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_5]$. According to our DFT charge distribution analysis, it was expected to behave as a much softer Lewis acid than the dimetal trifluoroacetate complexes of Rh(II) and Ru(I). Our experimental results on co-deposition of corannulene with the above diruthenium(I,I) molecule confirmed our expectations [40]. A unique corannulene complex $[Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_5{\cdot}(C_{20}H_{10})]$ having two crystallographically independent units cocrystallized together was isolated. One is an η^2-rim bound complex, while the other is a η^1-hub corannulene-based complex (Fig. 9). These discrete complexes of ruthenium(I) also show the preference of the convex corannulene surface for metal binding. More importantly, the hub-corannulene complex represents the first example of metal coordination to the interior region on the surface of a bowl-shaped polyarene and also demonstrates for the first time a degree of similarity between the convex carbon surfaces of corannulene and of the C_{60}-fullerene in metal binding reactions.

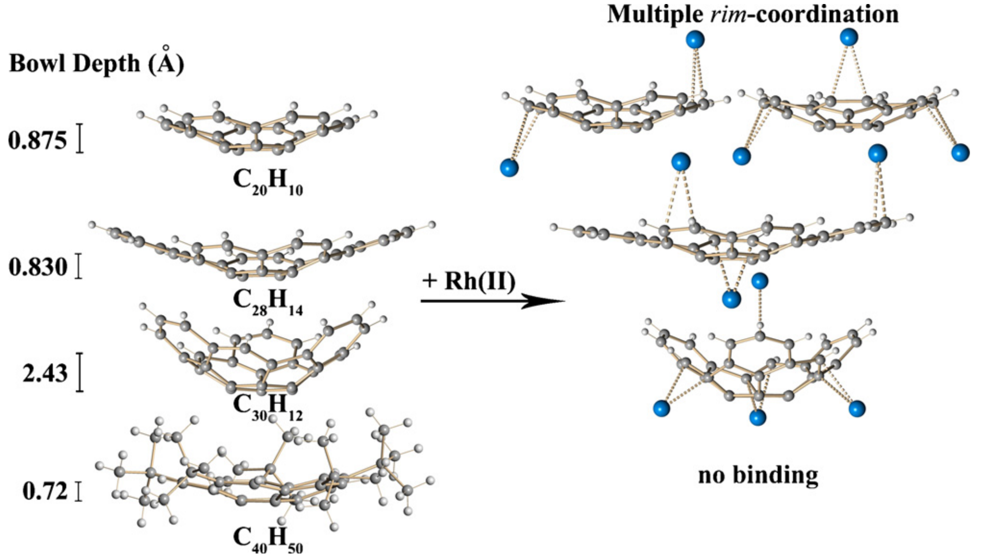


Fig. 8. Selected bowls with their bowl depths (left) and coordination modes (right) in the isolated rhodium(II) complexes. Only one Rh-atom of each dimetal unit is shown.

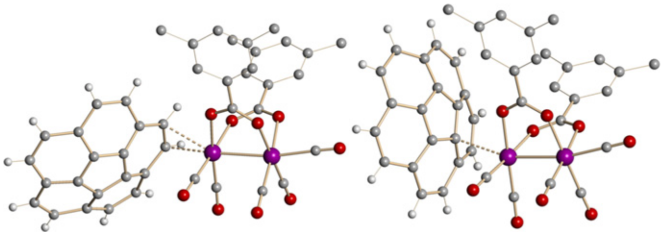


Fig. 9. The η^2-rim- and η^1-hub-corannulene coordinated complexes in $[Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_5\cdot(C_{20}H_{10})]$.

4. Concluding remarks

In summary, in this work we have shown that co-deposition of volatile metal complexes with π-donating ligands in a solvent-free environment allows one to effectively utilize directional metal–π-arene interactions in the formation of novel crystalline organometallic products, especially in the construction of extended networks. The gas phase co-deposition reactions provide unique conditions for the controlled assembling of desired topologies, and that should be beneficial for accessing the targeted properties of hybrid materials. Volatile electrophilic dimetal complexes of Rh(II), Ru(II), and Ru(I) and various organic π-donors have been used as building blocks in such gas phase reactions to show the effect of the ligand structure on the product topology.

Several novel organometallic buckybowl-based complexes have been isolated to reveal ligating preferences of this new class of polyarenes. Importantly, by creating an excess of metal units in the gas phase, buckybowls were forced to function as multidentate ligands and exhibited rare bi-, tri-, and tetradentate bridging modes. A direct comparison of several bowl-shaped molecules in binding of the same linear dimetal unit clearly showed the role of the geometry and curvature of a bowl in directing the formation of extended networks ranging from 1D to 3D systems. The preference of bowls for rim coordination of the electrophilic rhodium(II) and ruthenium(I) centers has been clearly observed. However, when a soft Lewis acid complex was selected, a coordination switch to the hub-site of corannulene has been seen for the first time. Thus, we have also demonstrated that the gas phase deposition technique is very efficient in studying the reactivity of a new class of bowl-shaped polyarenes.

It is worth stressing here that the extended metal-organic frameworks obtained by gas phase deposition have no solvent incorporated, and that provides a clear advantage over traditional solution preparative techniques. Therefore, this original synthetic method can be a powerful tool for various research applications. The resultant family of solid hybrid materials can be expected to acquire a unique importance in the development of new research areas. The potential applications may include novel reagents for metal and gas storage and transport, as well as for cage confined catalysis.

Acknowledgements

The contribution to this work of all students, postdoctoral associates, and collaborators listed in the references cited is gratefully acknowledged. This work is supported by the Donors of the American Chemical Society Petroleum Research Fund (PRF #42910-AC3) and the National Science Foundation Career Award (NSF-0546945). The author especially thanks Alexander S. Filatov and Yulia Sevryugina for preparation of colour figures.

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