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Paracyclophanes as Versatile π-Donor Ligands Directing Formation of Extended Organometallic Networks

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The coordination properties of multidentate nonplanar aromatic ligands containing two and three benzene rings, namely [2.2]- and [2.2.2]paracyclophanes, have been explored. A gas-phase deposition approach has been used to examine metal−π interactions in a solvent-free environment as well as to prepare organometallic π-complexes of paracyclophane ligands in crystalline form. To force bridging modes of paracyclophanes and to achieve the formation of extended organometallic assemblies, a dinuclear metal complex having two centers of Lewis acidity, namely $[Rh_2(O_2CCF_3)_4]$, has been used. As a result, a product with Rh_2:L^2 = 1:1 composition (**1**) has been obtained from the reaction of dirhodium(II,II) tetrakis(trifluoroacetate) with [2.2]paracyclophane ($L^2 = C_{16}H_{16}$). Complex **1** consists of alternating dimetal units and [2.2]paracyclophane bridges that form 1-D organometallic chains: $[Rh_2(O_2CCF_3)_4 \cdot (\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_{16}H_{16})]^1_\infty$. In the case of [2.2.2]paracyclophane ($L^3 = C_{24}H_{24}$), two new rhodium-based products of the stoichiometries Rh_2:L^3 = 1:2 (**2**) and 3:2 (**3**) have been prepared in crystalline form. Complex **2** is a discrete bis adduct with terminally bound aromatic ligands, $[Rh_2(O_2CCF_3)_4 \cdot (\eta^1\text{-}C_{24}H_{24})_2]$, while **3** exhibits a unique 2-D layered structure built on an unprecedented tridentate $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ coordination of [2.2.2]paracyclophane. Since the layers in **3** overlay to form [2.2.2]paracyclophane-based open channels running along the *c* direction, the gas sorption properties of the crystalline material, $\{[Rh_2(O_2CCF_3)_4]_3 \cdot (C_{24}H_{24})_2\}$, have been tested. In addition to mono- and tridentate coordination of $C_{24}H_{24}$ revealed in **2** and **3**, a rare bidentate bridging mode of [2.2.2]paracyclophane is found in its ruthenium(I) complex obtained by gas-phase reaction of hydrocarbon with the diruthenium(I,I) carbonyl trifluoroacetate unit, $[Ru_2(O_2CCF_3)_2(CO)_4]$. The resulting product of the Ru_2:L^3 = 1:1 composition exhibits a 1-D chain structure, namely $[Ru_2(O_2CCF_3)_2(CO)_4 \cdot (\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_{24}H_{24})]^1_\infty$ (**4**). Overall, three new coordination modes of [2.2.2]paracyclophane have been revealed to afford a discrete complex, as well as 1-D and 2-D extended organometallic networks. This versatility of [2.2.2]paracyclophane has been fully realized under gas-phase deposition conditions that allow one to utilize effectively the geometrical and electronic structures of aromatic ligands in the formation of new organometallic products.

Introduction

Utilization of directional metal−π-aromatic interactions in the formation of extended organometallic architectures is currently of increasing scientific interest[1] for potential applications in the areas of catalysis, macromolecular receptors, electrical conductors, and photoresponsive devices.[2] Importantly, the focus has been centered at the design of molecular systems that utilize unique properties of organic electron donors bearing two or more aromatic groups in cofacially oriented arrays, such as various cyclophanes.[3] Clearly, diversified topologies and unusual physical properties should be expected from the systematic incorporation of transition-metal ions and polynuclear clusters having interesting electronic and redox properties into such systems.[4] The general synthetic strategy to access hybrid supramolecular products is based on the solution coordination of the selected metal units by various organic spacers having

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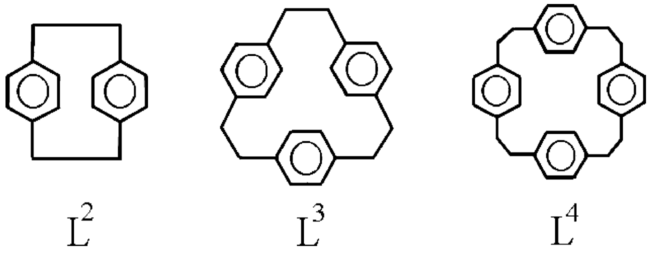
Chart 1



different geometries and properties.[5] However, the desired control over self-assembly in solutions is often limited, since weak intermolecular interactions can be affected by various metal−solvent interactions[6] or by unpredictable solvent-templating effects.[7] Further development of the supramolecular organometallic chemistry requires new methodologies with a high level of control over intermolecular interactions. This can be achieved under conditions of the gas-phase deposition approach that excludes interfering solvent effects in the process of synthesis and can be very effective in the controlled preparation of discrete complexes[8] and extended organometallic networks.[9] We have also demonstrated that a microscale deposition procedure[8,9] allows us to vary the stoichiometry of solid products and, therefore, offers a rational control over their composition. In addition, it provides a unique way to utilize intermolecular metal−π interactions for supramolecular assembling in a solvent-free environment. In this work we apply the deposition approach to study the reactivity of nonplanar aromatic ligands containing two or three benzene rings, [2.2]-paracyclophane and [2.2.2]paracyclophane.

A family of various $[2_n]$cyclophanes (Chart 1) has been of considerable interest for several decades[3,10] due to their structural versatility and their potential for efficient metal−ligand interactions in two or three dimensions. Furthermore, $[2_n]$cyclophane ligands exhibit unusual properties that stem from the overlap of their π molecular orbitals,[11] and that should provide unique possibilities for electronic communication between the connected units. This makes $[2_n]$cyclophanes very attractive ligands in supramolecular assembling reactions, especially when they serve as bridges between redox-active metal centers to form extended organometallic networks. Materials of this type are expected to exhibit a wide range of potentially interesting electrical and optical properties,[12] but controlled synthetic techniques to assemble hybrid solids with multidimensional structures are scarce.

Several $[2_n]$cyclophane ligands such as [2.2]paracyclophane (L^2),[13] [2.2.2]paracyclophane (L^3),[14] and tetramesitylene (L^4)[15] are currently available. The first member of this family, namely $C_{16}H_{16}$, shows extensive coordination chemistry with a number of main-group and transition-metal centers.[16] In particular, metal carbonyl clusters with various nuclearities have been studied in complexation reactions with $C_{16}H_{16}$ to afford a diverse range of organometallic products which display metal−π-arene bonding modes ranging from η^6 to η^3:η^3 and η^2:η^2:η^2.[10b,17] However, while extended organometallic architectures with $C_{16}H_{16}$ are known for silver(I),[1b,5b] such solid networks with paracyclophane bridges are very rare for the redox or magnetically interesting transition-metal centers. Several silver-containing 1-D chains, such as $[Ag(GaCl_4)\cdot(\mu_2\text{-}\eta^2{:}\eta^3\text{-}C_{16}H_{16})]_\infty$ and $[Ag(ClO_4)\cdot(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_{16}H_{16})]_\infty$, have been isolated from solutions.[18] Very recent

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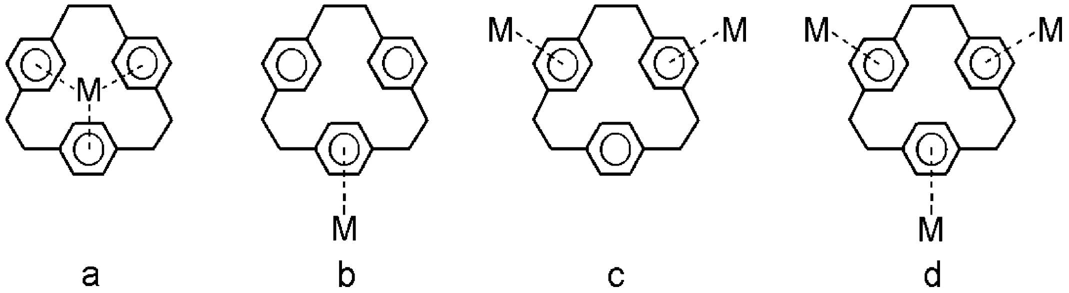
Chart 2



examples from the work of Munakata et al. included two- and three-dimensional layered networks based on $Ag^+-\pi$ interactions, in which [2.2]paracyclophane exhibits a variety of bridging modes, including a unique μ-tetra-η^2 coordination.[2f,19] We expanded this research to transition metals[20] and showed the propensity of electrophilic diruthenium complexes having two centers of Lewis acidity, such as $[Ru_2(O_2CCF_3)_2(CO)_4]$[20a] and $[Ru_2(O_2CCF_3)_4]$,[20b] to form extended organometallic networks with the [2.2]paracyclophane bridges under deposition conditions.

The coordination chemistry of the second member of this family, [2.2.2]paracyclophane ($C_{24}H_{24}$), is even more interesting, as both external[21] and internal[14,22] metal complexes (Chart 2) have been isolated from solutions and structurally characterized.[23] There have been a few reports concerning coordination of more than one transition-metal center to [2.2.2]paracyclophane (Chart 2c,d), but all products had discrete molecular structures.[21a−d] Herein we explore the interactions of [2.2]- and [2.2.2]paracyclophanes with dinuclear transition-metal complexes having Rh_2^{4+} and Ru_2^{2+} cores that have been selected as linear building blocks[20,24] for the construction of extended architectures based on ligand bridging modes.

Results and Discussion

To prepare new organometallic complexes of paracyclophanes, we rely on gas-phase co-deposition of complementary building units, which is a very effective tool for utilizing directional metal π-arene interactions without interfering solvent effects.[8,9,20] The experimental technique is based on the sublimation of the volatile electrophilic dimetal complexes $[Rh_2(O_2CCF_3)_4]$[25] and $[Ru_2(O_2CCF_3)_2(CO)_4]$[20a] in the presence of aromatic ligands followed by deposition of the corresponding donor−acceptor adducts in crystalline form.

From the system containing $[Rh_2(O_2CCF_3)_4]$ and [2.2]paracyclophane, we have isolated the new product **1** in the form of air-stable but slightly moisture sensitive crystals. The composition of this product was confirmed by elemental analysis to be $[Rh_2(O_2CCF_3)_4]:(C_{16}H_{16}) = 1:1$. The IR spectra showed the presence of aromatic and carboxylate functions, and the molecular structure of **1** has been determined by X-ray diffraction.

Complex **1** consists of alternating dimetal units and [2.2]paracyclophane ligands (Figure 1) that form 1-D polymeric chains: $[Rh_2(O_2CCF_3)_4\cdot(\mu_2\text{-}C_{16}H_{16})]^1_\infty$. The organometallic network is built on interactions between the rhodium(II) centers and the aromatic rings of [2.2]paracyclophane. Each rhodium atom has two bonding Rh−C contacts at 2.571(3) and 2.636(3) Å (Table 1). The latter values are much shorter than the rest of the metal−carbon distances. Therefore, coordination of [2.2]paracyclophane in **1** is of a η^2 type with respect to each Rh^{II} center. Complex **1** is isostructural with the recently isolated diruthenium(II,II) analogue $[Ru_2(O_2CCF_3)_4\cdot(\mu_2\text{-}C_{16}H_{16})]^1_\infty$.[20b] In the latter, the two bonding Ru−C distances are 2.670(3) and 2.757(3) Å, which are noticeably longer than those contacts in **1**.

Our previous study of planar polycyclic aromatic hydrocarbons (PAHs)[26] has revealed an interesting trend: the η^2-metal coordination of $[Rh_2(O_2CCF_3)_4]$ is site-selective and is well correlated with a π-bond order character of C−C bonds in various PAHs, as confirmed by Hückel calculations. The dirhodium(II,II) tetrakis(trifluoroacetate) complex works as a very sensitive electrophilic probe to find the most nucleophilic sites of the polyaromatic systems. Consistently, coordination of only "external" carbon atoms (those having hydrogen atoms attached) has been observed so far for the large family of planar PAHs.[26] The only exception where an "internal" carbon atom was involved in rhodium(II) binding was the fluoranthene-based complex. The product **1** and its ruthenium(II) analogue[20b] having μ_2-η^2:η^2-[2.2]paracyclophane bridges are other rare examples where internal (or bridgehead) carbon atoms are involved in metal binding.

It is informative to compare the geometrical characteristics of [2.2]paracyclophane in complex **1** with data for the uncoordinated parent ligand. The crystal structure of [2.2]paracyclophane was reported in 1949,[13] and it was later reexamined.[27]

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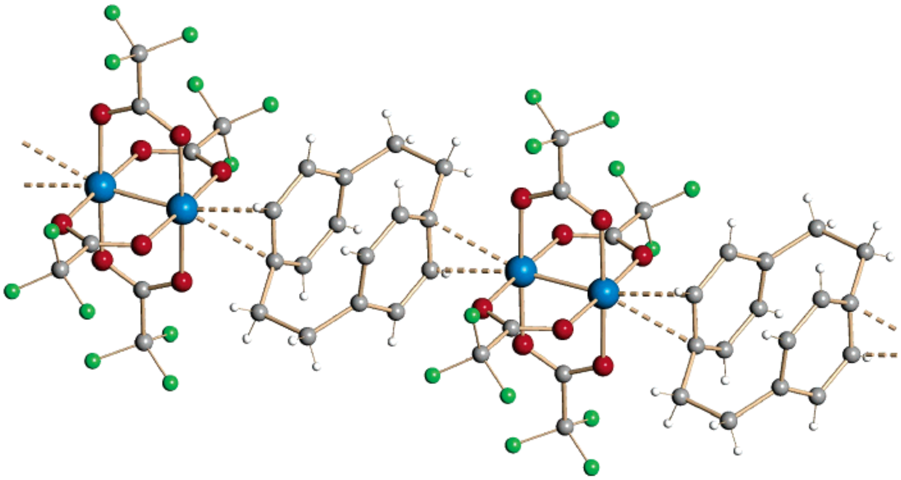

Figure 1. Fragment of a 1-D chain in **1**, $[Rh_2(O_2CCF_3)_4 \cdot (\mu_2\text{-}C_{16}H_{16})]^1_\infty$: (blue) Rh; (red) O; (green) F; (dark gray) C; (light gray) H (this color scheme is used for all other rhodium complexes).

Table 1. Selected Distances (Å) and Angles (deg) in the Complexes $[Rh_2(O_2CCF_3)_4 \cdot (C_{16}H_{16})]$ (1) and $[Ru_2(O_2CCF_3)_4 \cdot (C_{16}H_{16})]^{20b}$

	M = Rh (**1**)	M = Ru[20b]
M−M	2.4306(4)	2.2993(5)
$M-O_{av}$	2.039(2)	2.064(3)
M···C(1)	2.571(3)	2.670(3)
M···C(2)	2.636(3)	2.757(3)
M−M···C(1)	164.11(7)	164.93(8)
M−M···C(2)	164.85(7)	165.16(8)
$C(1)-C(2)_{coord}$	1.392(4)	1.385(5)
$C(1)-C(2)_{free}$	1.404(4)	1.393(5)

The dimensions of the $C_{16}H_{16}$ molecule are interesting: the three C−C aliphatic bond lengths are 1.54, 1.55, and 1.54 Å, while the C−C bond lengths in the benzene rings are all 1.40 Å, but these benzene rings are not flat. The two bridgehead carbon atoms in each benzene ring are displaced from the plane of the other four atoms by 0.13 Å to relieve the strain in the system. The coordination of metal centers to the bridgehead carbon atoms in $[M_2(O_2CCF_3)_4 \cdot (C_{16}H_{16})]$ (M = Rh, Ru) is most likely related to this unusual nonplanar character of the aromatic rings in [2.2]paracyclophane. In contrast, the rhodium(II) centers of $[Rh_2(O_2CCF_3)_4]$ coordinate to the external carbon atoms of *p*-xylene in the polymeric organometallic product isolated.[26b]

The two analogues $[M_2(O_2CCF_3)_4 \cdot (\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_{16}H_{16})]$ (M = Rh, Ru) provide an interesting data set to compare electrophilic properties of the dirhodium(II,II) and diruthenium(II,II) tetrakis(trifluoroacetates) in binding to the same aromatic substrate. This comparison reveals an interesting trend: the shorter M−M bonding within the dimetal core (2.2993(5) Å in the ruthenium complex versus 2.4306(4) Å in **1**) results in a noticeable weakening of metal−π-arene bonding in the ruthenium complex (Table 1). The average metal−carbon bonding distance is 2.604 Å in the rhodium complex **1** versus 2.714 Å in the ruthenium analogue. A comparison of geometrical parameters of the π-bonded [2.2]paracyclophane with the structure of the uncomplexed $C_{16}H_{16}$ molecule[13,27] confirms that coordination is weak in both complexes. Even the distances between the two planes drawn through four carbon atoms of the benzene rings of [2.2]paracyclophane (3.060 Å in **1** and 3.067 Å in the ruthenium product) are not significantly affected by coordination (compared with 3.09 Å for a free ligand). However, the calculated displacement of two bridgehead carbon atoms from the plane of the other four atoms in [2.2]paracyclophane becomes slightly greater in its metal complexes: 0.144 Å in **1** and 0.153 Å in the ruthenium analogue.

Along with the recently reported ruthenium complexes $[Ru_2(O_2CCF_3)_2(CO)_4 \cdot (\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_{16}H_{16})]^{20a}$ and $[Ru_2(O_2CCF_3)_4 \cdot (\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_{16}H_{16})]$,[20b] compound **1** constitutes a rare transition-metal complex having both aromatic rings of [2.2]paracyclophane involved in coordination. Prior to this, there were attempts to explain the preferences of $C_{16}H_{16}$ for the formation of discrete complexes by the through-space resonance effect within the ligand that results in deactivation of the second uncoordinated ring toward further interaction, when an electron-withdrawing metal complex is attached to one of the rings.[10b,28] The selection of dimetal Rh_2^{4+}, Ru_2^{4+}, and Ru_2^{2+} units having two open centers of Lewis acidity has been crucial for forcing [2.2]paracyclophane to function in the bridging bidentate fashion that resulted in the formation of 1-D extended organometallic polymers.

Reaction of $[Rh_2(O_2CCF_3)_4]$ with [2.2.2]paracyclophane (L^3) originally afforded a mixture of two new products having different compositions, Rh_2:L^3 = 1:2 (**2**), 3:2 (**3**), which were deposited in different parts of the same ampule. As they were well-separated in the reaction tube, both products were collected in pure form. The procedure to optimize the yield of **3** was later developed. Compounds **2** and **3** are air stable but show some sensitivity to moisture. They have similar IR spectra but exhibit distinctly different solubilities. While **2** is soluble in chloroform and can be characterized by ^1H NMR, complex **3** can be dissolved only in coordinating solvents that substitute the [2.2.2]paracyclophane ligand, releasing it in a free form. X-ray diffraction studies performed on crystals of **2** and **3** revealed their crystal structures, which explained this difference.

Complex **2** exhibits a discrete bis-adduct type of structure (Figure 2) with a central dirhodium molecule having two [2.2.2]paracyclophane ligands attached to its axial positions, $[Rh_2(O_2CCF_3)_4 \cdot (C_{24}H_{24})_2]$. The shortest bonding contact of 2.566(7) Å is between the rhodium atom and the C(1) atom of the aromatic ring (Table 2). The Rh−C distances to the adjacent carbon atoms are much longer: 2.944(7) and 2.956(7) Å. Therefore, the terminal [2.2.2]paracyclophane coordination in **2** can be regarded as an η^1 or η^3 type. Previously, only η^6 external coordination has been seen in metal complexes of $C_{24}H_{24}$.[21]

Complex **3** exhibits a different structure that has several interesting and novel features. It is built on the tridentate

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[28] (a) Papoyan, G. A.; Butin, K. P.; Hoffmann, R.; Rozenberg, V. I. *Russ. Chem. Bull.* **1998**, *47*, 153−159. (b) Bond, A. M.; Dyson, P. J.; Humphrey, D. G.; Lazarev, G.; Suman, P. *J. Chem. Soc., Dalton Trans.* **1999**, 443−448.

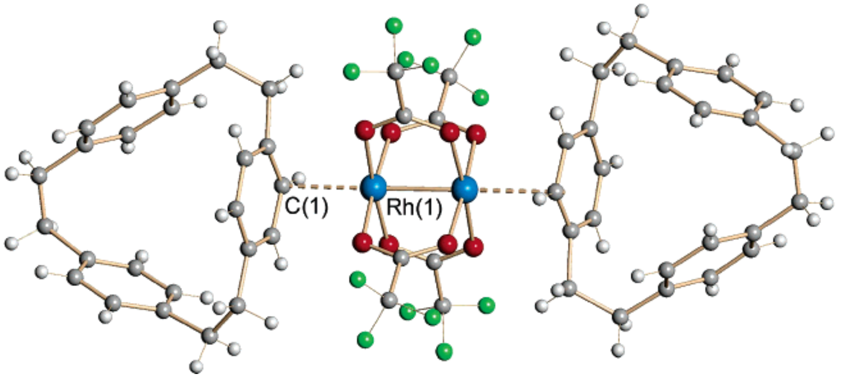

Figure 2. The bis-adduct complex [$Rh_2(O_2CCF_3)_4$·$(C_{24}H_{24})_2$] (**2**).

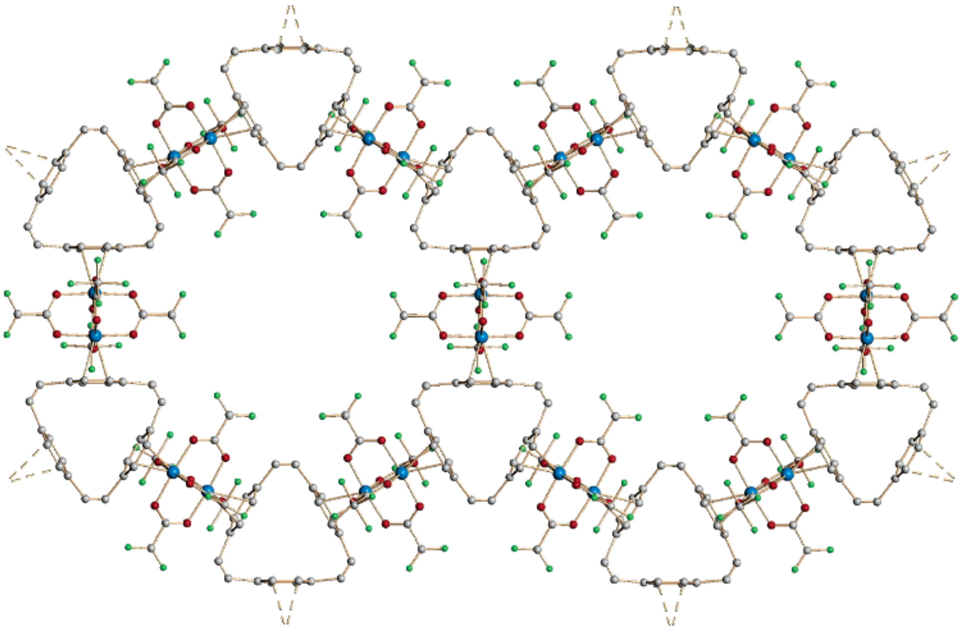

Figure 3. Fragment of a 2-D layer in **3**, {[$Rh_2(O_2CCF_3)_4$]$_3$·(μ_3-$C_{24}H_{24}$)$_2$}$^2_\infty$.

Table 2. Selected Distances (Å) and Angles (deg) in the Complexes [$Rh_2(O_2CCF_3)_4$·$(C_{24}H_{24})_2$] (2), {[$Rh_2(O_2CCF_3)_4$]$_3$·$(C_{24}H_{24})_2$} (3), and [$Ru_2(O_2CCF_3)_2(CO)_4$·$(C_{24}H_{24})$] (4)

	M = Rh (**2**)	M = Rh (**3**)	M = Ru (**4**)
M−M	2.4239(5)	2.4205(11)	2.6688(4)
M−O$_{av}$	2.035(3)	2.032(4)	2.138(2)
M···C(1)	2.566(7)	2.662(5)	2.563(3)[a]
M···C(2)		2.662(5)	2.836(3)[a]
M−M···C(1)	170.62(19)	163.47(12)	159.8(1)[a]
M−M···C(2)		163.47(12)	156.0(1)[a]
C(1)−C(2)$_{coord}$	1.376(11)	1.386(11)	1.394(5)[a]
C(1)−C(2)$_{free}$	1.378(11)	1.393(17)	1.394(5)[a]

[a] Distances and angles are averaged for two independent units.

coordination of [2.2.2]paracyclophane that serves as a triangular building node directing the coordination of three dimetal complexes. The dirhodium [$Rh_2(O_2CCF_3)_4$] unit uses both axial positions for the arene binding and functions as a linear spacer in the structure of **3**. As a result, the two complementary donor and acceptor building blocks in **3** form an extended 2-D hybrid layer, {[$Rh_2(O_2CCF_3)_4$]$_3$·(μ_3-$C_{24}H_{24}$)$_2$}$^2_\infty$ (Figure 3).

Two bonding Rh−C distances in **3** are symmetry related; they are 2.662(5) Å for each rhodium(II) center. Having three metals coordinated to one ligand, [2.2.2]paracyclophane shows a unique μ_3-η^2:η^2:η^2 bridging coordination in the structure of **3**. It is worth mentioning here that the tridentate η^6:η^6:η^6 external coordination of [2.2.2]paracyclophane has been seen in a chromium carbonyl complex[21a] and it was later crystallographically confirmed in a bismuth(III) chloride complex.[21b] An internal tridentate η^2 (3 × η^2) Ag−C coordination has been observed in a [2.2.2]-paracyclophane silver(I) complex.[29]

Interestingly, in the structure of **3** the layers overlap in such a way that the [2.2.2]paracyclophane ligands form straight channels running along the *c* axis of the unit cell (Figure 4). These open channels are aligned parallel to each other and have aromatically functionalized "walls" comprised of the benzene rings of [2.2.2]paracyclophanes. The projection of the channel onto the *ab* plane gives a hexagon with the diameter of the inscribed circle being ca. 2.5 Å when the van der Waals radii of carbon atoms are taken into account.

The 2-D layer in **3** can also be considered as constructed of the zigzag 1-D chains of the 1:1 composition brought together by additional dimetal units (Figure 3). Although our attempts to isolate the 1-D polymer from the system containing dirhodium(II,II) tetrakis(trifluoroacetate) and [2.2.2]paracyclophane by varying the ratio of reagents and temperature regimes during sublimation reactions were not successful, we have prepared such a product from a similar system using an isoelectronic dimetal complex. By codeposition of $C_{24}H_{24}$ with the linear

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(29) (a) Kang, H. C.; Hanson, A. W.; Eaton, B.; Boekelheide, V. *J. Am. Chem. Soc.* **1985**, *107*, 1979−1885. (b) Saarenketo, P.; Suontamo, R.; Jödicke, T.; Rissanen, K. *Organometallics* **2000**, *19*, 2346−2353.

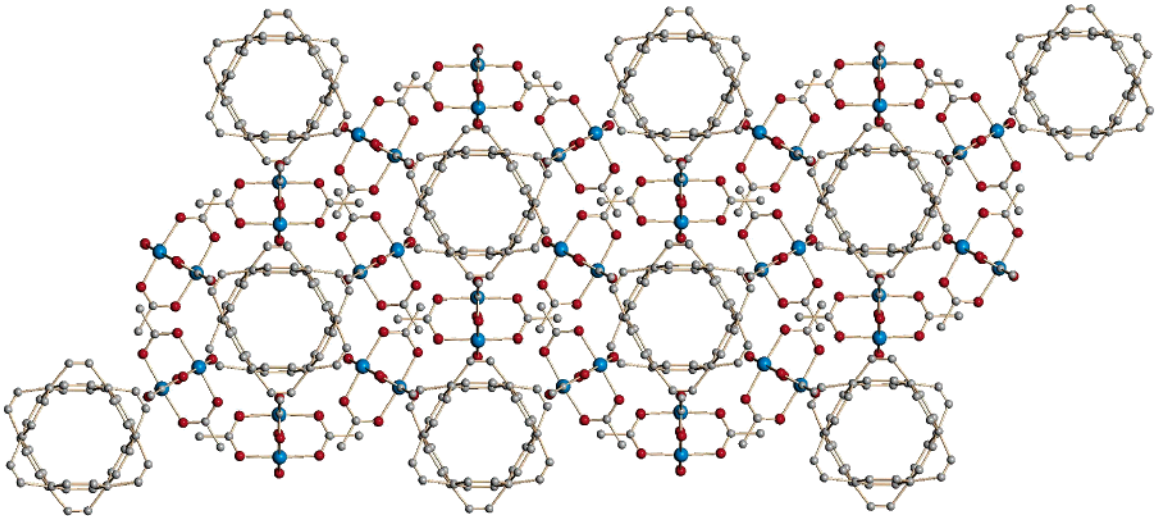

Figure 4. Superposition of two layers in the structure of **3** shown as a projection onto the *ab* plane. Fluorine and hydrogen atoms are omitted for clarity.

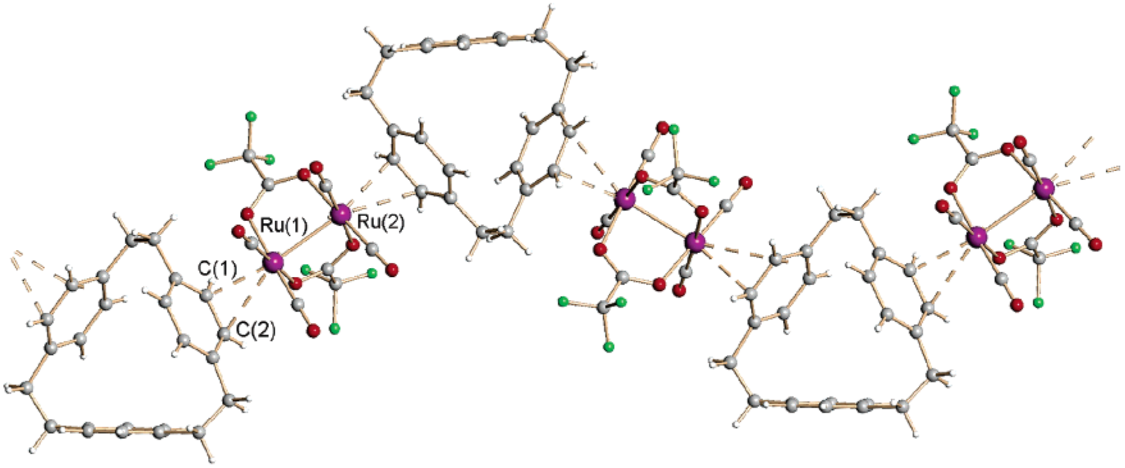

Figure 5. Fragment of a 1-D chain in **4**, $[Ru_2(O_2CCF_3)_2(CO)_4{\cdot}(C_{24}H_{24})]^1{}_\infty$: (purple) Ru; (red) O; (green) F; (dark gray) C; (light gray) H.

diruthenium(I,I) unit having two open metal coordination sites, $[Ru_2(O_2CCF_3)_2(CO)_4]$, a new organometallic product of the 1:1 composition has been crystallized. This new complex in the solid state consists of the alternating diruthenium units and aromatic ligands that form an extended chain structure, $[Ru_2(O_2CCF_3)_2(CO)_4{\cdot}(C_{24}H_{24})]^1{}_\infty$ (**4**), as determined by an X-ray structural study (Figure 5). Only two benzene rings of [2.2.2]paracyclophane are involved in metal binding in **4**, while the third ring remains uncoordinated. Regarding ruthenium(I) coordination, the two shortest Ru−C distances are inequivalent, being 2.579(3) and 2.823(3) Å for Ru(1) and 2.546(3) and 2.848(3) Å for Ru(2). The rest of the Ru−C distances are greater than 3.19 Å. Therefore, the coordination of [2.2.2]paracyclophane in the structure of **4** can be regarded as the bidentate η^2:η^2 bridge having rather inequivalent Rh−C intermolecular contacts with respect to each ruthenium center. Previously, two complexes of $C_{24}H_{24}$ having two benzene rings involved in metal binding have been crystallographically characterized, and both have [2.2.2]paracyclophane acting as an η^6:η^6 bridge.[21c,d]

In contrast to [2.2]paracyclophane, only external carbon atoms of $C_{24}H_{24}$ are involved in metal coordination in complexes **2**−**4**. The C−C bond distances and angles of the coordinated [2.2.2]paracyclophane are very similar to those found in the free parent ligand,[14] thus confirming weak intermolecular metal−π interactions in **2**−**4**.

The interesting solid porous structure of **3** prompted us to test this crystalline material for potential gas recognition and sorption. In this context, it is worth stressing that [2.2.2]paracyclophane is a well-known and efficient receptor for the silver cations in solution.[30] It is also known to form internal complexes with Sn(II) and Ge(II) in solution, due to the ability of the hydrocarbon cage of [2.2.2]paracyclophane to stabilize low oxidation states of the incorporated metals.[31] Since the estimated gate entrance to the [2.2.2]paracyclophane channels in **3** appeared to be quite small, the gas adsorption measurements were carried out with H_2, N_2, and CO_2 gases, which are regarded as linear multinuclear molecules having van der Waals diameters of ca. 2.4 for H_2 and ca. 3.4 Å for N_2 and CO_2. No gas adsorption could be detected for N_2 and H_2 gases at 77 K, and only a small amount of CO_2 was reversibly adsorbed by **3** (see the Supporting Information).

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[30] (a) Pierre, J. L.; Baret, P.; Chautemps, P.; Armand, M. *J. Am. Chem. Soc.* **1981**, *103*, 2986−2988. (b) Pierre, G.; Baret, P.; Chautemps, P.; Pierre, J. L. *Electrochim. Acta* **1983**, *28*, 1269−1271. (c) Heirtzler, F. R.; Hopf, H.; Jones, P. G.; Bubenitschek, P. *Tetrahedron Lett*. **1995**, *36*, 1239−1242. (d) Chartroux, C.; Rambusch, T.; Gloe, K.; Horn, M.; Vögtle, F. *J. Prakt. Chem*. **1999**, *341*, 778−784.

[31] (a) Scholz, G.; Schaefer, C.; Rominger, F.; Gleiter, R. *Org. Lett*. **2002**, *4*, 2889−2892. (b) Mireles, N.; Sansores, L. E.; Martinez, A.; Salcedo, R. *Int. J. Quantum Chem*. **2003**, *94*, 51−56. (c) Schaefer, C.; Scholz, G.; Gleiter, R.; Oeser, T.; Rominger, F. *Eur. J. Inorg. Chem*. **2005**, 1274−1281.

Table 3. Crystallographic Data for $[Rh_2(O_2CCF_3)_4{\cdot}(C_{16}H_{16})]^1_\infty$ (1), $[Rh_2(O_2CCF_3)_4{\cdot}(C_{24}H_{24})_2]$ (2), $\{[Rh_2(O_2CCF_3)_4]_3{\cdot}(C_{24}H_{24})_2\}^2_\infty$ (3), and $[Ru_2(O_2CCF_3)_2(CO)_4{\cdot}(C_{24}H_{24})]^1_\infty$ (4)

	1	2	3	4
formula	$Rh_2O_8F_{12}C_{24}H_{16}$	$Rh_2O_8F_{12}C_{56}H_{48}$	$Rh_6O_{24}F_{36}C_{72}H_{48}$	$Ru_2O_8F_6C_{32}H_{24}$
fw	866.19	1282.76	2598.56	852.65
cryst syst	triclinic	orthorhombic	hexagonal	monoclinic
space group	$P\bar{1}$	$Pbca$	$R\bar{3}m$	$P2_1/c$
a (Å)	8.8646(6)	16.2821(10)	20.5186(5)	9.7452(6)
b (Å)	9.0912(6)	12.3917(8)	20.5186(5)	22.7415(14)
c (Å)	10.8615(7)	27.1720(17)	17.7415(9)	14.6650(9)
α (deg)	114.4310(10)	90.00	90.00	90.00
β (deg)	104.5180(10)	90.00	90.00	100.4900(10)
γ (deg)	99.7510(10)	90.00	120.00	90.00
V (Å^3)	733.55(8)	5482.3(6)	6468.7(4)	3195.7(3)
Z	1	4	3	4
D_{calcd} (g cm^{-3})	1.961	1.554	2.001	1.772
μ (mm^{-1})	1.247	0.695	1.272	1.030
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
transm factors	0.7138−0.9636	0.7829−0.8909	0.8941−0.9509	0.8692−0.9408
temp (K)	173(2)	173(2)	173(2)	173(2)
no. of data/obsd/params	3314/3210/226	6591/5415/346	1389/1234/118	7550/6367/492
R1,[a] wR2[b] ($I > 2\sigma(I)$)	0.0326, 0.0839	0.0503, 0.1316	0.0442, 0.1109	0.0358, 0.0876
R1,[a] wR2[b] (all data)	0.0334, 0.0848	0.0601, 0.1413	0.0500, 0.1162	0.0449, 0.0922
quality of fit[c]	1.054	1.030	1.038	1.027

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. [c] Quality of fit $= [\Sigma[w(F_o^2 - F_c^2)^2]/(N_{observns} - N_{params})]^{1/2}$, based on all data.

Conclusions

In the course of this work several novel [2.2]paracyclophane- and [2.2.2]paracyclophane-based organometallic complexes have been isolated as thermally stable solids with molecular structures based on weak but directional metal−π-arene interactions. A one-step deposition procedure in a solvent-free environment was used for the preparation and isolation of organometallic products in the form of single crystals. This technique was shown to be very effective in utilizing the geometrical and electronic structures of the aromatic ligands for the controlled formation of organometallic networks having the desired topologies. This is clearly seen from the comparison of two different paracyclophanes in the coordination of linear dimetal units. The only isolated rhodium(II) complex of [2.2]paracyclophane is based on the bidentate bridging mode of $C_{16}H_{16}$ and has a chain polymeric structure, namely $[Rh_2(O_2CCF_3)_4{\cdot}(\mu_2\text{-}C_{16}H_{16})]^1_\infty$. For the more versatile [2.2.2]paracyclophane several coordination modes have been found, including a terminal mode in the bis adduct $[Rh_2(O_2CCF_3)_4{\cdot}(\eta^1\text{-}C_{24}H_{24})_2]$ and a bidentate η^2:η^2 bridge in the 1-D polymeric ruthenium(I) product $[Ru_2(O_2CCF_3)_2(CO)_4{\cdot}(\mu_2\text{-}C_{24}H_{24})]^1_\infty$. A novel tridentate η^2:η^2:η^2 bridging coordination of [2.2.2]paracyclophane was found to direct the formation of a unique extended organometallic layer, $\{[Rh_2(O_2CCF_3)_4]_3{\cdot}(\mu_3\text{-}C_{24}H_{24})_2\}^2_\infty$.

Experimental Section

Materials and Methods. All reactions involving the preparation of unligated dimetal complexes, $[Rh_2(O_2CCF_3)_4]$[25] and $[Ru_2(O_2CCF_3)_2(CO)_4]$,[20a] were carried out under a dinitrogen atmosphere using standard Schlenk techniques. Paracyclophane ligands were purchased from Aldrich and resublimed before use. IR spectra were recorded on a Nicolet Magna 550 FTIR spectrometer in the range 4000−400 cm^{-1} using KBr pellets. NMR spectra were recorded on a Varian Gemini spectrometer at 300 MHz for proton and at 282 MHz for fluorine. Chemical shifts for ^{1}H are reported relative to the residual solvent peaks or TMS and for ^{19}F relative to the internal standard $CFCl_3$ (δ 0.0 ppm). Elemental analyses were performed by Canadian Microanalytical Services, Ltd.

$[Rh_2(O_2CCF_3)_4{\cdot}(C_{16}H_{16})]$ (1). A mixture of $[Rh_2(O_2CCF_3)_4]$ (0.045 g, 0.068 mmol) with [2.2]paracyclophane (0.012 g, 0.058 mmol) was sealed under vacuum in a small glass ampule. The ampule was placed in an electric furnace having a small temperature gradient along the length of the tube. The temperature was set at 145 °C. The next day green platelike single crystals were deposited in the "cold" end of the ampule, where the temperature was a few degrees below 145 °C. Yield: 35−40%. When the reaction temperature was increased to 150−155 °C and the reaction time was changed to 3 days, the total yield of the single crystalline product was increased to 50−55%. Anal. Calcd for $Rh_2C_{24}F_{12}O_8H_{16}$: C, 33.28; H, 1.86. Found: C, 33.37; H, 1.93. IR (KBr, cm^{-1}): 2933 w, 2864 w, 2363 w, 2344 w, 1669 s, 1461 w, 1326 w, 1197 s, 1167 s, 1088 w, 859 w, 808 w, 786 w, 739 m. ^{1}H NMR (22 °C, acetone-d_6): δ 3.02 (s, 8H, CH_2), 6.45 (s, 8H, CH).

$[Rh_2(O_2CCF_3)_4{\cdot}(C_{24}H_{24})_2]$ (2) and $[Rh_2(O_2CCF_3)_4]_3{\cdot}(C_{24}H_{24})_2$ (3). A mixture of $[Rh_2(O_2CCF_3)_4]$ (0.050 g, 0.075 mmol) with [2.2.2]paracyclophane (0.024 g, 0.075 mmol) was sealed under vacuum in a small glass ampule. The ampule was kept in an electric tube furnace at 144 °C for 3 days. The product **2** was deposited in the coldest end of the ampule in the form of blue-green crystals. Yield of **2**: 45%. Anal. Calcd for $Rh_2C_{56}F_{12}O_8H_{48}$: C, 52.44; H, 3.77. Found: C, 52.38; H, 3.81. IR (KBr, cm^{-1}): 3094 w, 3048 w, 3017 w, 2930 m, 2868 w, 2859 w, 1169 s, 1516 m, 1459 w, 1445 w, 1416 w, 1224 s, 1195 s, 1169 s, 1097 w, 1023 w, 920 w, 864 m, 808 m, 790 m, 742 m. ^{1}H NMR (22 °C, $CDCl_3$): δ 2.93 (broad, 12H, CH_2), 6.70 (broad, 12H, CH).

Very small green crystals of **3** were grown in the hot end of the same ampule; they were well separated from **2** and manually collected for X-ray characterization. Yield of **3**: 15−20%. IR (KBr, cm^{-1}): 3048 w, 3029 w, 2930 w, 2867 w, 1669 s, 1517 w, 1466 w, 1446 w, 1415 w, 1221 sh, 1198 s, 1169 sh, 926 w, 862 m, 809 w, 788 m, 742 m, 535 w, 543 w, 531 w. Complex **3** was also prepared in a pure form by the improved method described below.

$[Rh_2(O_2CCF_3)_4]_3{\cdot}(C_{24}H_{24})_2$ (3). $[Rh_2(O_2CCF_3)_4]$ (0.045 g, 0.068 mmol) was loaded in a glass ampule of 9 mm diameter and 70 mm length, while $C_{24}H_{24}$ (0.005 g, 0.016 mmol) was placed in an ampule of a smaller diameter and length (4 × 20 mm). The latter ampule was carefully inserted inside the larger one to prevent direct contact of the two reagents in the solid state. The outer ampule was sealed under vacuum and placed in an electric tube furnace at 155 °C for 3 days. During this time period green blocks grew inside the small ampule. Yield: 70%. Anal. Calcd for $Rh_6C_{72}F_{36}O_{24}H_{48}$: C, 33.28; H, 1.86. Found: C, 33.62; H, 1.99. IR (KBr, cm^{-1}): 3047 w, 3026 w, 2958 w, 2918 m, 2849 w, 1665 s, 1561 w, 1509 m, 1459 w, 1442 w, 1343 w, 1237 m, 1218 m, 1194 s, 1168 m, 1151 s, 1022 w, 920 w, 861 m, 807 m, 785 m, 739 m, 595 w, 540 w, 473 w. ^{1}H NMR (22 °C, acetone-d_6): δ 2.93 (s, 12H, CH_2), 6.69 (s, 12H, C*H*).

[$Ru_2(O_2CCF_3)_2(CO)_4 \cdot (C_{24}H_{24})$] (4). A mixture of [$Ru_2(O_2CCF_3)_2(CO)_4$] (0.035 g, 0.065 mmol) and [2.2.2]paracyclophane (0.010 g, 0.032 mmol) was sealed under vacuum in a small glass ampule. The ampule was then placed in an electric tube furnace at 160 °C. Brown blocks appeared after 3 h in the hot end of the ampule. Yield: 70%. Anal. Calcd for $Ru_2C_{32}F_6O_8H_{24}$: C, 45.07; H, 2.82. Found: C, 45.45; H, 2.84. IR (KBr, cm^{-1}): 3025 w, 2924 w, 2918 w, 2894 w, 2866 w, 2051 s, 2010 s, 1983 s, 1978 s, 1927 sh, 1663 s, 1516 w, 1509 w, 1502 w, 1469 w, 1443 w, 1341 w, 1215 s, 1155 s, 1090 w, 971 w, 949 w, 922 w, 863 m, 807 m, 789 m, 737 m, 661 w, 592 m, 569 m, 535 w, 518 w. ^{1}H NMR (22 °C, CDCl$_3$): δ 2.92 (s, 12H, CH_2), 6.68 (s, 12H, C*H*). ^{19}F NMR (22 °C, CDCl$_3$): δ −74.76.

X-ray Diffraction Studies. Single crystals of compounds **1**−**4** were obtained as described above. X-ray diffraction experiments were carried out on a Bruker SMART APEX CCD diffractometer equipped with a Mo target X-ray tube ($\lambda = 0.710\ 73$ Å) operating at 1800 W power. The frames were integrated with the Bruker SAINT software package[32] using a narrow-frame integration algorithm. The data were corrected for absorption effects using the empirical method (SADABS).[33] The structures were solved by direct methods and refined using the Bruker SHELXTL (version 6.1) software package.[34] Full-matrix least-squares refinement was carried out on F^2. All non-hydrogen atoms were refined anisotropically, except for the disordered carbon and fluorine atoms. The fluorine atoms of the CF$_3$ groups in **1**−**4** were disordered over two or three rotational orientations, and this disorder was modeled individually in each case. In compound **3** in addition to rotational disorder, some CF$_3$ groups of carboxylates exhibit a symmetry-related reflectional disorder. Moreover, the CH$_2$ bridges of [2.2.2]paracyclophane in **3** were disordered over two orientations. The same types of disorder of CH$_2$ bridges were found in **2** and **4** and modeled individually. This disorder does not affect the coordination mode of [2.2.2]-paracyclophane. All hydrogen atoms of [2.2]paracyclophane in **1** were found in the difference Fourier map and refined independently. The refinement of hydrogen atoms of [2.2.2]paracyclophane in the structures **2**−**4** was mixed. Relevant crystallographic data for complexes **1**−**4** are summarized in Table 3.

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Supporting Information Available: Four CIF files giving X-ray crystallographic data and text and a figure giving results of gas sorption studies. This material is available free of charge via the Internet at http://pubs.asc.org.

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