

On the Road to a Termolecular Complex with Acetone: A Heterometallic Supramolecular Network

$\{[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4] \cdot \mu_2\text{-OCMe}_2 \cdot [\text{Cu}_4(\text{O}_2\text{CCF}_3)_4]\}$

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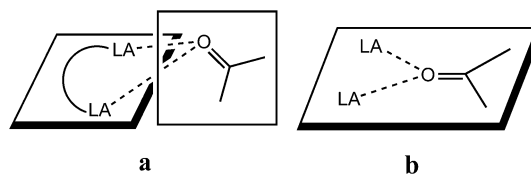
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A novel heterometallic supramolecular network $\{[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4] \cdot \mu_2\text{-OCMe}_2 \cdot [\text{Cu}_4(\text{O}_2\text{CCF}_3)_4]\}_\infty$ has been prepared by codeposition of the volatile mono(acetone) adduct $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4] \cdot \eta^1\text{-OCMe}_2$ and copper(I) trifluoroacetate, $[\text{Cu}_4(\text{O}_2\text{CCF}_3)_4]$. The product is of interest from the viewpoints of gas-phase supramolecular synthesis and a rare bridging coordination mode of acetone. It has been fully characterized by IR and NMR spectroscopy, elemental analysis, and X-ray diffraction. An X-ray structure revealed a layered 2D arrangement of the heterometallic $\{[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4] \cdot \mu_2\text{-OCMe}_2 \cdot [\text{Cu}_4(\text{O}_2\text{CCF}_3)_4]\}$ units built by axial intermolecular interactions of the open electrophilic Rh(II) and Cu(I) centers and O-atoms of neighboring carboxylate groups. The coordination of the acetone molecules within the $\{[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4] \cdot \mu_2\text{-OCMe}_2 \cdot [\text{Cu}_4(\text{O}_2\text{CCF}_3)_4]\}$ unit is asymmetric with the Rh–O and Cu–O distances being 2.2173(15) and 2.7197(17) Å, respectively. This work shows the potential of gas-phase deposition that may provide additional possibilities in supramolecular synthesis by utilizing intermolecular interactions and coordination bonds in a new way compared with conventional solution chemistry.

Introduction

The study of multidentate Lewis acids, which are complex reagents with multiple acceptor sites, is an increasingly active area of research¹ with valuable applications in the activation of various chemical bonds.² Great progress has recently been made³ in the preparation of bidentate complexes holding two sites of Lewis acidity in a well-defined orientation that permits them to interact simultaneously with a single basic atom in a guest molecule, i.e., a terminal carbonyl oxo

Chart 1



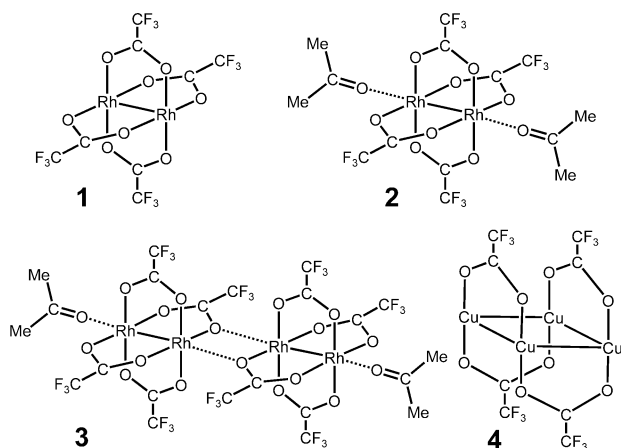
function.⁴ These bonds are, however, characteristically long, weak, and deformable resulting in nonplanar structures (Chart 1a). Therefore, current studies are directed to preparation of a termolecular doubly coordinated complex (Chart 1b) where two Lewis acids bind an oxygen atom along the directions of its sp^2 lone pairs and thus lie close to the carbonyl plane. Such adducts are expected to take better advantage of the electron density on an oxygen atom resulting in its additional electrophilic activation. Similar doubly coordinated com-

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Chart 2

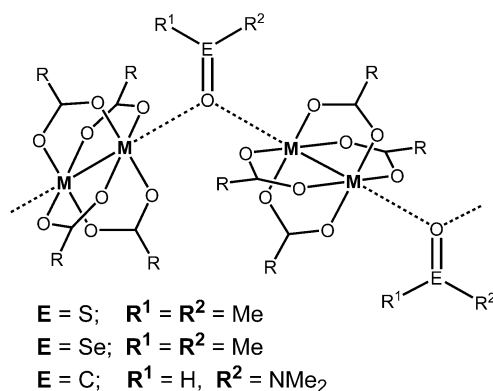


plexes have been postulated as activated intermediates or transition states upon addition of organometallic reagents to carbonyl compounds.⁵

Our approach to the assembling of termolecular adducts is based on the employment of an excess of polydentate transition metal complexes with strong Lewis acidic properties and a low concentration of donor molecules. These experimental conditions favor the formation of bidentate or polydentate bridges by the donor molecules.⁶ Such conditions are readily realized in the gas phase by simultaneous sublimation of donors and volatile Lewis acids which is then followed by deposition of crystalline donor–acceptor complexes. This approach allows control over the production of an excess of acceptor over donor molecules in vapor phase and thus results in uncommon coordination modes of the donor counterparts. In this way, the electrophilic dirhodium(II) tetrakis(trifluoroacetate) complex, $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]$ (**1**, Chart 2), has been reacted with donor molecules having terminal $\text{E}=\text{O}$ functions ($\text{E} = \text{S}, \text{Se}, \text{C}$), such as DMSO,^{7a} DMSeO,^{7b} and DMF.^{7c} When an excess of the dirhodium complex was used, the adducts obtained from the vapor phase showed the bridging modes for the O-containing molecules (Chart 3). According to the Gutmann scale,⁸ acetone exhibits significantly lower donor ability than do DMF and DMSO. However, acetone is practically more interesting with a promise of the $\text{C}=\text{O}$ bond activation, which makes its study worthwhile. Furthermore, only few examples of the bridging coordination of acetone by metal centers (alkali-metal ions,⁹ mercury(II),^{4d,10} and a copper(I) complex¹¹) have been reported so far.

In this work we have tested deposition reactions in a system having high concentration of the dimetal complex

Chart 3



$[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]$ and limited amounts of acetone. Instead of the known bis(acetone) adduct (**2**), these reactions have afforded a mono(acetone) adduct $\{\text{Me}_2\text{CO} \cdot [\text{Rh}_2(\text{O}_2\text{CCF}_3)_4] \cdot \text{OCMe}_2\}$ (**3**) having a “dimer of dimers” structure with terminally bound acetone (Chart 2). This behavior contrasts with that of DMSO, DMSeO, and DMF, which under similar deposition conditions serve as O-bridges (Chart 3). However, an addition of the volatile and polydentate Lewis acid $[\text{Cu}_4(\text{O}_2\text{CCF}_3)_4]$ (**4**, Chart 2)¹² to **3** afforded a unique heterometallic product, $\{[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4] \cdot \mu_2\text{-OCMe}_2 \cdot [\text{Cu}_4(\text{O}_2\text{CCF}_3)_4]\}$ (**5**), that is built on a rare bridging coordination of acetone. In this paper, we report details on the preparation, spectroscopic characterization, and X-ray diffraction study of the title compound.

Results and Discussion

We began this study by testing deposition reactions of the bidentate electrophilic complex $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]$ (**1**) in the presence of very low concentrations of acetone in gas phase that should favor the bridging mode of Me_2CO . It is worth mentioning that the only product known prior to our work was a benzene solvate of the bis(adduct) $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4] \cdot 2(\eta^1\text{-OCMe}_2) \cdot \text{C}_6\text{H}_6$ (**2a**),¹³ which crystallized from a solution containing **1** and an excess of acetone. We have isolated another polymorph devoid of interstitial solvent molecules, $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4] \cdot 2(\eta^1\text{-OCMe}_2)$ (**2b**).¹⁴ The latter has been used as a controlled source of acetone in deposition reactions with **1**.

Thus, sublimation–deposition reactions in the system containing two complexes, $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]$ (**1**) and its bis-

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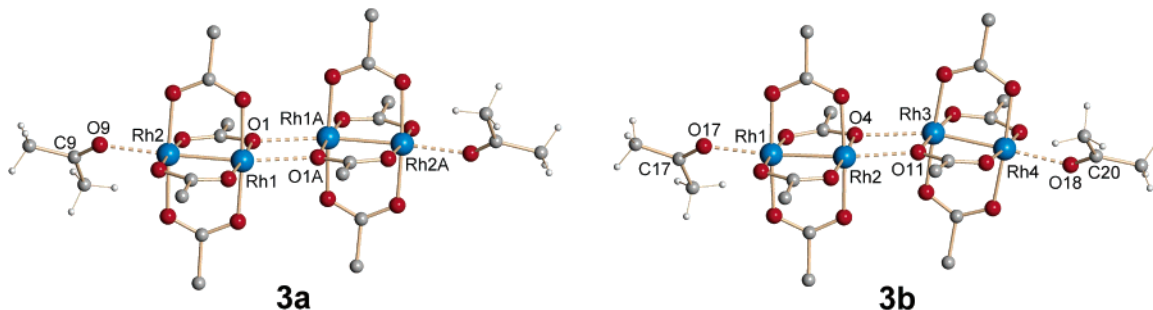


Figure 1. Mono(acetone) adduct $\{\text{Me}_2\text{CO} \cdot [\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]_2 \cdot \text{OCMe}_2\}$ (**3**) having a “dimer of dimers” structure: **3a** is centrosymmetric, and in **3b** the two Rh_2^{4+} units are crystallographically independent. Intermolecular $\text{Rh} \cdots \text{O}$ interactions between two dirhodium molecules as well as coordination of acetone by the rhodium centers are shown by dashed lines. Fluorine atoms of the CF_3 groups are omitted for clarity.

(acetone) adduct, $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot 2(\eta^1\text{-OCMe}_2)]$ (**2b**), resulted in the isolation of a new product **3** in the form of green air-stable crystals. The composition of **3** is $[\text{Rh}_2]:\text{Me}_2\text{-CO} = 1:1$ as determined by elemental analysis. IR data for the mono(acetone) adduct **3** and the bis(acetone) adduct **2b** show similar carbonyl stretching frequencies of 1684 and 1686 cm^{-1} , respectively. This is consistent with the presence of terminally coordinated acetone molecules. These carbonyl stretching frequencies are ca. 30 cm^{-1} less than that of neat acetone ($\nu(\text{C}=\text{O})$ 1716 cm^{-1}).

Complex **3** seems to be the only stable product that crystallized from the vapor phase mixtures containing the volatile dirhodium complex **1** in the presence of the controlled amount of acetone. In gas-phase reactions we have observed the formation of **3** on numerous occasions, at different temperatures and in various systems, and it was often isolated as a byproduct. In this work, the yield of pure **3** was optimized at 55–65% after 3 days of deposition at 160 °C. Two polymorphs of **3** have been isolated and structurally characterized. The X-ray diffraction studies reveal a “dimer of dimers” type of structure for **3**, $\{\text{Me}_2\text{-CO} \cdot [\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]_2 \cdot \text{OCMe}_2\}$, in which the central tetra-rhodium core is terminated by an acetone molecule at each end (Figure 1). The central core consists of two $[\text{Rh}_2(\text{O}_2\text{-CCF}_3)_4]$ units held together by axial $\text{Rh} \cdots \text{O}$ contacts: this unit is centrosymmetric in **3a** but has no center of symmetry in **3b**.

All major geometrical characteristics of **3a,b** are similar. The $\text{Rh}-\text{Rh}$ distances of 2.3959(13) and 2.3976(6) Å in **3a,b** are comparable with that of 2.4064(8) Å in the bis(acetone) adduct **2b**. The $\text{Rh}(1) \cdots \text{O}(1)$ axial contact between two dirhodium units is 2.410(7) Å in the centrosymmetric complex **3a**. The corresponding distances in **3b** are 2.374(4) for $\text{Rh}(3) \cdots \text{O}(4)$ and 2.525(4) Å for $\text{Rh}(2) \cdots \text{O}(11)$. The $\text{Rh}-\text{O}_{\text{acetone}}$ distances of 2.208(7) in **3a** and of 2.196(4) Å in **3b** (average of two) are slightly shorter than that in the bis(acetone) adduct **2b** (2.252(4) Å).¹⁴ The $\text{C}=\text{O}$ bond lengths of the η^1 -coordinated acetone are 1.208(15) in **3a** and 1.234(7) in **3b** (average of two), whereas that in **2b** is

1.219(7) Å. The observed difference between such distances in **3a,b** along with the fact that the standard deviations for these bonds are too large makes it difficult to discuss subtle effects of metal coordination on the η^1 -bound carbonyl group of acetone.

Complex **3** has a discrete “dimer of dimers” structure for a 1:1 composition. It is structurally similar to that recently reported for the mixed carboxylate rhodium(II) complex $\{\text{Me}_2\text{CO} \cdot [\text{Rh}_2(\text{O}_2\text{CC}_6\text{H}_2\text{Pr}_3)_2(\text{O}_2\text{CCF}_3)_2]_2 \cdot \text{OCMe}_2\}$, which was isolated from solution.¹⁵ Contrarily, when **1** and strong oxo-containing donors Me_2SO and Me_2SeO react, the products have axial ligands with a μ_2 -O-bridging mode so that one-dimensional zigzag chains $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot \mu_2\text{-O-DMS}(\text{Se})\text{O}]_n$ form (Chart 3).^{7a,b} A similar extended structural motif has recently been observed in an analogous dirhodium complex with DMF ligands.^{7c} It was previously found that THF affords products with a 1D chain and a “dimer of dimers” structure.¹⁶

This volatile preorganized tetranuclear rhodium building block **3** capped by acetone molecules appears highly desirable for utilization in gas-phase coordination reactions. We have recently confirmed^{6b} that **3** produces the mono(acetone) fragments $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot \eta^1\text{-OCMe}_2]$ in gas phase. Their high volatility and an “one-end” Lewis acidity have been used to synthesize a complex with the thermally unstable 1,4-diiodobutadiyne.^{6b} In this work, to force the bridging coordination of acetone, we have codeposited **3** with a tetradentate Lewis acid, namely copper(I) trifluoroacetate, $[\text{Cu}_4(\text{O}_2\text{CCF}_3)_4]$ (**4**), that has four open Lewis acidic sites (Chart 2).¹² The latter is known to show a great avidity for additional coordination in solution and to form adducts with unsaturated species containing carbon–carbon bonds, such as $[\text{Cu}_4(\text{O}_2\text{CCF}_3)_4 \cdot 2\text{C}_6\text{H}_6]$ ^{12b} and $[\text{Cu}_4(\text{O}_2\text{CCF}_3)_4 \cdot 2\text{EtC}\equiv\text{CEt}]$.^{12c} Although we had isolated the crystalline product $[\text{Cu}_4(\text{O}_2\text{CCF}_3)_4]$ without exogenous ligands by deposition,^{12a} we had not utilized its avid acidity and multidentate coordination ability in gas-phase coordination reactions.

The rhodium(II) adduct **3** was codeposited with the copper(I) complex **4** at 120 °C giving a product $\{[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4] \cdot \text{OCMe}_2 \cdot [\text{Cu}_4(\text{O}_2\text{CCF}_3)_4]\}$ (**5**) in the form of green needle-shaped crystals which are air stable but slightly moisture

(14) X-ray data for $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot (\text{OCMe}_2)_2]$ (**2b**): $\text{Rh}_2\text{O}_{10}\text{C}_{14}\text{F}_{12}\text{H}_{12}$, $f_w = 774.06$; monoclinic, $P2_1/n$; $a = 8.7596(5)$, $b = 8.988(3)$, $c = 15.1591(9)$ Å; $\beta = 96.820(9)^\circ$; $V = 1185.1(4)$ Å³, $Z = 2$; $D_{\text{calcd}} = 2.169$ g/cm³; $T = 213(2)$ K. The final R_1 (on F_o) was 0.0380, and wR_2 (on F_o^2) = 0.0931 for 192 parameters and 36 restraints, 1547 unique data (1441 reflections with $I > 2\sigma(I)$). All CF_3 groups were disordered. See Supporting Information for structural details.

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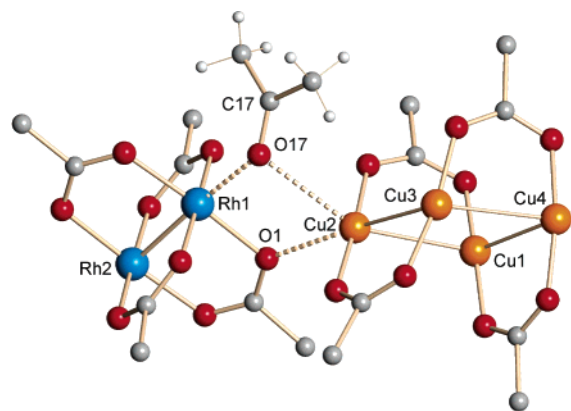


Figure 2. A crystallographically independent heterometallic unit $\{[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4] \cdot \mu_2\text{-OCMe}_2 \cdot [\text{Cu}_4(\text{O}_2\text{CCF}_3)_4]\}$ in **5**. Fluorine atoms of the CF_3 groups are omitted.

sensitive. The IR spectrum of **5** is dominated by strong absorptions of trifluoroacetate functions of both copper(I) and rhodium(II) complexes ranging from 1680 to 1600 cm^{-1} obscuring the region where one would expect the $\text{C}=\text{O}$ stretching frequency of the bridged acetone.

A single-crystal X-ray diffraction study of **5** has revealed that an asymmetric unit contains one dirhodium complex, one tetracopper block, and one acetone molecule that connects two metal units together (Figure 2). An additional axial contact of the Cu(2) atom with the O(2) atom of the trifluoroacetate group of dirhodium complex at $2.511(2)\text{ \AA}$ is also important.

The acetone molecule bridges the dirhodium and tetracopper units in an asymmetric fashion: the $\text{Rh}(1)\text{-O}(17)$ is $2.2173(15)$, and the $\text{Cu}(2)\text{-O}(17)$ is $2.7197(17)\text{ \AA}$. The former is comparable with the $\text{Rh}\text{-O}_{\text{acetone}}$ distances in **3** which has a terminally bound acetone, while the latter is much longer than the $\text{Cu}\text{-O}_{\text{acetone}}$ distance of $2.423(9)\text{ \AA}$ in the copper(I) complex having $\mu_2\text{-OCMe}_2$.¹¹ The sum of bond angles at the O(17) atom in **5** is $344.0(1)^\circ$, showing that the resulting coordination geometry of the acetone oxygen atom is distorted from trigonal planar. The $\text{C}(17)=\text{O}(17)$ bond distance in the μ_2 -acetone molecule of $1.229(3)\text{ \AA}$ in **5** is comparable with that in **3** having η^1 -bound OCMe_2 . The planar configuration of the acetone molecule is preserved in complex **5** as the sum of the bond angles at the C(17) is $360.0(2)^\circ$. It appears that the acetone molecule is not affected significantly by complexation.

Two neighboring dirhodium units in **5** are further linked at the open rhodium ends through the $\text{Rh}\cdots\text{O}$ axial contacts at $2.3918(15)\text{ \AA}$ in the same fashion as in the “dimer of dimers” complex **3** (Figure 3).

In addition, tetranuclear copper units are also engaged in intermolecular interactions through all three open electrophilic copper ends that bind to the O atoms of trifluoroacetate groups of the neighboring copper units (Figure 4). Two copper atoms, Cu(1) and Cu(3), exhibit only one contact each with the O(16) and the O(12) atoms, respectively, at $2.774(2)$ and $2.674(2)\text{ \AA}$. The Cu(4) atom has two intermolecular contacts with the O(9) and O(13) atoms at $2.563(2)$ and $2.725(2)\text{ \AA}$. All these intermolecular $\text{Cu}\cdots\text{O}$ distances are

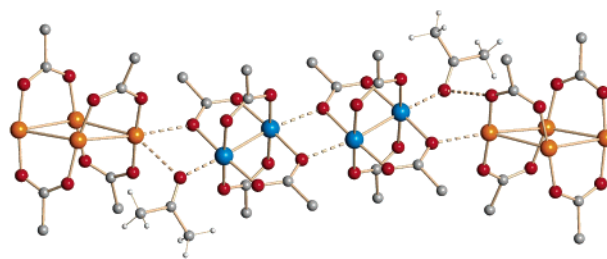


Figure 3. Fragment of a supramolecular structure **5** showing aggregation of two units $\{[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4] \cdot \mu_2\text{-OCMe}_2 \cdot [\text{Cu}_4(\text{O}_2\text{CCF}_3)_4]\}$ through additional axial $\text{Rh}\cdots\text{O}$ interactions. Fluorine atoms are omitted.

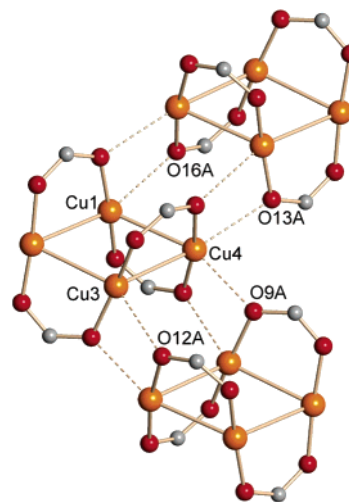


Figure 4. Fragment of a supramolecular structure **5** showing intermolecular $\text{Cu}\cdots\text{O}$ interactions. The CF_3 groups of trifluoroacetate ligands are omitted.

shorter than the sum of the van der Waals radii (2.95 \AA)¹⁷ and are indicative of weak copper–oxygen interactions.

All intermolecular metal–oxygen interactions result in the introduction of additional links in two dimensions affording a complex layered 2D $\{[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4] \cdot \mu_2\text{-OCMe}_2 \cdot [\text{Cu}_4(\text{O}_2\text{CCF}_3)_4]\}_\infty$ network (Figure 5).

In summary, using a deposition approach from the rigid preorganized and volatile building blocks **3** and **4**, we have prepared a unique heterometallic assembly, $\{[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4] \cdot \mu_2\text{-OCMe}_2 \cdot [\text{Cu}_4(\text{O}_2\text{CCF}_3)_4]\}$ (**5**). In complex **5** two different Lewis acids interact concomitantly with the oxygen atom of a weakly basic carbonyl function of acetone. Although this interaction is weak and the geometry of acetone is not affected by complexation, **5** is of interest as one of the rare examples of the bridging $\mu_2\text{-O}$ coordination of acetone.^{4d,9–11} To our knowledge, this is only the second crystallographically reported example of a $\mu_2\text{-OCMe}_2$ molecule bridged by the two transition metal centers.¹¹ These results demonstrate the potential of using polydentate Lewis acids in the concomitant $\text{C}=\text{O}$ bond coordination and give new routes to the synthesis of mixed-metal hybrid materials. Gas-phase assembling may provide additional possibilities for controlled supramolecular synthesis by utilizing intermolecular interactions and coordination bonds in a way that may be difficult or simply impossible to use in solution self-assembling procedures.

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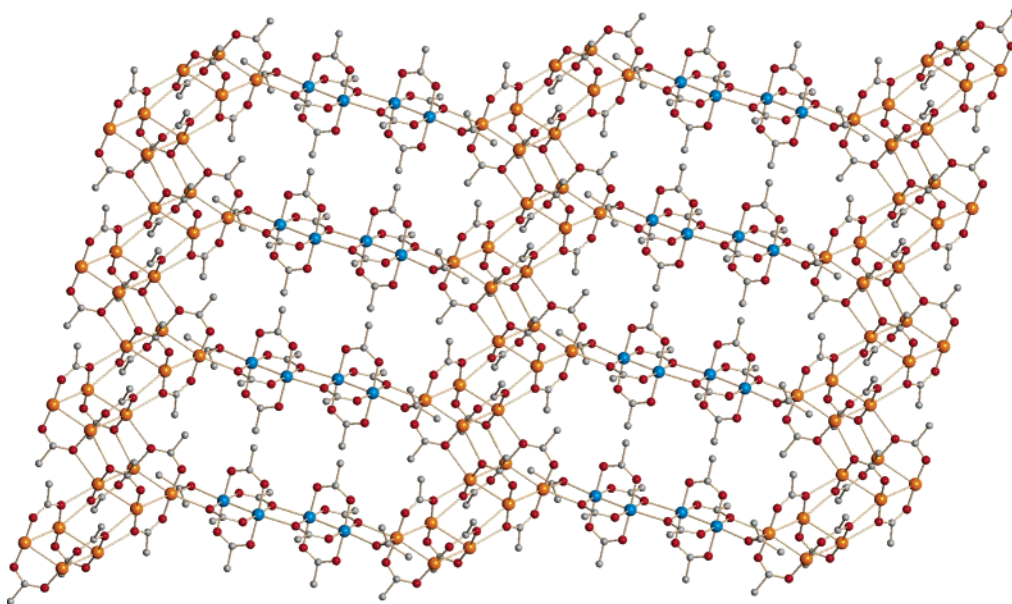


Figure 5. Fragment of a 2D layer in the structure of **5**. Fluorine and hydrogen atoms are omitted.

Experimental Section

General Procedures. All the syntheses and purifications were carried out under an atmosphere of N_2 in standard Schlenkware. All solvents were freshly distilled under N_2 from suitable drying agents. Anhydrous $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]$ (**1**) was prepared by a carboxylate exchange procedure from $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4]$.¹⁸ The bis(adduct) **2b** was made by the modified literature procedure.¹³ Copper(I) trifluoroacetate was synthesized by reacting Cu_2O with trifluoroacetic anhydride in refluxing benzene.¹²

Elemental analyses were performed by Canadian Microanalytical Service, Delta, BC, Canada. IR spectra were recorded on a Nicolet Magna 550 FTIR spectrometer using KBr pellets. ^1H and ^{19}F NMR spectra were obtained using a Bruker XL-300 spectrometer.

Syntheses. $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot 2\text{OCMe}_2]$ (**2b**). To 0.1 g of $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]$ (**1**) was added 3 mL of acetone to form a clear blue solution. This was followed by addition of 12 mL of hexanes. After 3 days blue blocks of the bis(adduct) $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot 2\text{OCMe}_2]$ (**2b**) crystallized in almost quantitative yield. Yield: 94%. IR (KBr, cm^{-1}): 2964 w, 2934 w, 2921 w, 2850 w, 1686 s, 1663 s, 1462 w, 1321 w, 1378 w, 1363 w, 1195 s, 1162 s, 1100 w, 1023 w, 858 m, 807 w, 789 m, 738 s, 719 w. ^1H NMR (CDCl_3 , 22 °C): δ 2.57.

$[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot \text{OCMe}_2]_2$ (**3**). $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]$ (**1**) (0.070 g, 0.110 mmol) was mixed with the bis(adduct) $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot 2\text{OCMe}_2]$ (**2b**) (0.012 g, 0.016 mmol) in a glass ampule, and the mixture was flame-sealed under vacuum. The ampule was placed in a tube furnace at 160 °C. Large green block-shaped crystals of **3** were collected in 3 days. Yield: 65% (based on **1**). Anal. Calcd: C, 18.45; H, 0.84. Found: C, 18.80; H, 0.74. IR (KBr, cm^{-1}): 3129 w, 3046 w, 2927 w, 2856 w, 1684 s, 1656 s, 1463 m, 1423 w, 1373 w, 1224 s, 1196 s, 864 s, 789 m, 742 s. ^1H NMR (CDCl_3 , 22 °C): δ 2.72.

$[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot \text{OCMe}_2 \cdot \text{Cu}_4(\text{O}_2\text{CCF}_3)_4]$ (**5**). The complexes $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot \text{OCMe}_2]_2$ (**3**) and $[\text{Cu}_4(\text{O}_2\text{CCF}_3)_4]$ (**4**) were mixed in a 1:1 ratio (0.06:0.06 mmol), and the mixture was sealed under vacuum in a glass ampule. The ampule was placed in an electric furnace at 120 °C. The deposition and crystal growth were stopped

after 3 days to afford green block-shaped crystals of **5** that collected in the cold section of the ampule where the temperature was set at ca. 110 °C. Yield: 45% (based on **3**). Anal. Calcd: C, 16.05; H, 0.43. Found: C, 15.89; H, 0.37. IR (KBr, cm^{-1}): 2922 w, 2853 w, 1671 s, 1648 s, 1621 m, 1475 m, 1199 s, 865 m, 840 w, 810 w, 788 m, 742 m, 559 w, 531 w. ^1H NMR (CDCl_3 , 22 °C): δ 2.71. ^{19}F NMR (CDCl_3 , 22 °C): δ -75.0, -74.1.

X-ray Crystallographic Procedures. The X-ray diffraction experiments for **2b** and **3a** were collected on a Nonius FAST diffractometer with an area detector at -60 °C using $\text{Mo K}\alpha$ radiation. A total of 50 reflections were used in cell indexing, and about 250 reflections, in cell refinement. Axial images were used to confirm the Laue group and all dimensions. The data were corrected for Lorentz and polarization effects by the MADNES program.¹⁹ Reflection profiles were fitted, and values of F^2 and $\sigma(F^2)$ for each reflection were obtained by the program PROCOR.²⁰

The X-ray intensity data for **3b** (-175 °C) and **5** (-100 °C) were measured on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (λ ($\text{K}\alpha$) = 0.710 73 Å) operated at 1800 W power. The crystals were mounted on a goniometer head with silicone grease. The detector was placed at a distance of 6.14 cm from the crystal. For each experiment a total of 1850 frames were collected with a scan width of 0.3° in ω and an exposure time of 20 s/frame. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm to a maximum 2θ angle of 56.56° (0.75 Å resolution). The final cell constants are based upon the refinement of the XYZ-centroids of several thousands reflections above 20σ (I). Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the empirical method (SADABS).

The structures were solved and refined by full-matrix least-squares procedures on $|F^2|$ with the software package SHELXTL-

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Table 1. Crystallographic Data for $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot \eta^1\text{-OCMe}_2]_2$ (**3a,b**) and $\{[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4] \cdot \mu_2\text{-OCMe}_2 \cdot [\text{Cu}_4(\text{O}_2\text{CCF}_3)_4]\}^{2\infty}$ (**5**)

	3a	3b	5
formula	$\text{Rh}_2\text{O}_9\text{F}_{12}\text{C}_{11}\text{H}_6$	$\text{Rh}_4\text{O}_{18}\text{F}_{24}\text{C}_{22}\text{H}_{12}$	$\text{Rh}_2\text{Cu}_4\text{O}_{17}\text{F}_{24}\text{C}_{19}\text{H}_6$
fw	715.98	1431.96	1422.22
cryst system	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a (Å)	9.1670(10)	17.7890(7)	8.5009(5)
b (Å)	8.7782(5)	8.6834(4)	11.1068(6)
c (Å)	25.642(4)	26.3947(11)	20.8409(12)
α (deg)			92.3950(10)
β (deg)	95.090(10)	104.5460(10)	94.6990(10)
γ (deg)			107.5290(10)
V (Å ³)	2055.3(4)	3946.5(3)	1865.49
Z	4	4	2
D_{calcd} (g·cm ⁻³)	2.314	2.410	2.532
μ (mm ⁻¹)	1.756	1.829	3.293
λ (Å)	Mo K α (0.710 73)	Mo K α (0.710 73)	Mo K α (0.710 73)
transm factors		0.6100–0.8675	0.3318–0.7786
T (K)	213(2)	98(2)	173(2)
data/obsd/params	2683/2193/321	9823/7809/617	8347/7773/606
$R1,^a$ $wR2^b$ [$I > 2\sigma(I)$]	0.0646, 0.1517	0.0514, 0.1117	0.0246, 0.0634
$R1,^a$ $wR2^b$ (all data)	0.0815, 0.1647	0.0692, 0.1196	0.0264, 0.0645
quality-of-fit ^c	1.091	1.066	1.032

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

97, version 6.12.²¹ The coordinates of metal atoms for the structures were found in direct method E maps. The remaining atoms were located after an alternating series of least-squares cycles and difference Fourier maps. The hydrogen atoms for all structures were included at idealized positions for structure factor calculations. The fluorine atoms of some CF_3 groups were disordered over two or three different rotational orientations. Anisotropic displacement parameters were assigned to all non-hydrogen atoms, except the disordered fluorine atoms. Relevant crystallographic data for all compounds are summarized in Table 1.

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Supporting Information Available: X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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