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Supramolecular Assemblies of Dimetal Complexes with Polydentate N-Donor Ligands: From a Discrete Pyramid to a 3D Channel Network

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Reactions of a dinuclear metal complex in the form of dirhodium(II) tetra(trifluoroacetate), $[Rh_2(O_2CCF_3)_4]$ (**1**), with a number of strong N-donor ligands having functional groups rigidly oriented at different directing angles have been found to yield supramolecular architectures of differing complexity. All structures have been established by X-ray crystallography. From reaction of **1** with neutral tris(4′-pyridyl)methylsilane ligand, $CH_3Si(C_5H_4N)_3$ (**L1**), a discrete pyramid-shaped hexanuclear complex $\{[Rh_2(O_2CCF_3)_4]_3CH_3Si(C_5H_4N)_3(\eta^1\text{-}C_6H_6)_3\}\cdot C_6H_6$ (**2**$\cdot C_6H_6$) has been isolated from benzene. In **2** three molecules of **1** are strongly coordinated to one **L1** ligand at only one axial position of each dirhodium unit at the Rh–N distances of 2.152(6) Å. The second rhodium atom of each dimetal complex in **2** weakly coordinates a benzene molecule with an Rh–C distance of 2.69(2) Å. A supramolecular complex of the composition $\{[Rh_2(O_2CCF_3)_4]_2(C_6H_5)_2Si(C_5H_4N)_2\}$ (**3**) has been prepared by reacting the dinuclear units **1** with a potentially bidentate ligand, bis(4′-pyridyl)diphenylsilane, $(C_6H_5)_2Si(C_5H_4N)_2$ (**L2**), having two pyridyl groups rigidly oriented at 109°. In **3**, one **L2** ligand coordinates two dirhodium molecules **1** through their axial positions with the Rh–N distance of 2.150(5) Å. An interesting extended 2D layered motif is formed by additional contacts of open axial positions of dirhodium units with phenyl groups of the neighboring ligands at Rh–C distances which average to 2.88(1) Å. A supramolecular compound of the composition $\{[Rh_2(O_2CCF_3)_4]_3(HO)C(C_5H_4N)_3(\eta^1\text{-}C_6H_6)\}\cdot{}^1/_2C_6H_6$ (**4**$\cdot{}^1/_2C_6H_6$) has been formed when linear dirhodium units **1** were reacted with tris(4′-pyridyl)methanol (**L3**) having tetrahedral directing angles that average to 110°. A building block in the solid structure of **4** is a hexanuclear molecule in which one **L3** ligand binds three dimetal units of **1** through N atoms of pyridyl groups at the average Rh–N distance of 2.143(7) Å. A unique extended pseudo-3D structure in **4** is created by additional Rh–O coordination bonds as well as by weak metal–arene interactions.

Introduction

Transition metal complexes are versatile building blocks in supramolecular chemistry.[1] In many cases their employment has been limited to the use of mononuclear metal complexes. Recently, however, molecular assemblies incorporating dinuclear metal species as rigid or semirigid corner units have become an intensely active research area.[2]

Our experience in the chemistry of dirhodium(II) tetra(trifluoroacetate), $[Rh_2(O_2CCF_3)_4]$ (**1**), led us to use its avid ability for axial coordination in the design of various

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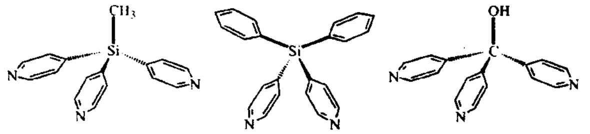
Chart 1



L1 **L2** **L3**

supramolecular architectures.[3] Previous results showed that **1** is a strong dinuclear Lewis acid toward a variety of donor molecules. The $[Rh_2(O_2CCF_3)_4]$ units serve as strictly linear components, while the Lewis bases serve as appropriate linear or angular building blocks.[3−8] In this work we attempted the synthesis of supramolecular species using this acceptor dirhodium complex **1** and several strong polydentate N-donor ligands, namely, $CH_3Si(C_5H_4N)_3$ (**L1**), $(C_6H_5)_2Si(C_5H_4N)_2$ (**L2**), and $(HO)C(C_5H_4N)_3$ (**L3**). Ligands **L1**−**L3** have pyridyl groups rigidly oriented at different well-defined angles and were perceived to have the potential to serve as perfect linkers for possible formation of discrete oligomeric polyhedra.[9] Although this specific goal has not yet been achieved, the architectures of various compositions and complexity that have been found are interesting on their own. The syntheses and crystal structures of three new supramolecular assemblies **2**−**4** are reported here.

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. Three nitrogen-containing donor ligands, namely, $CH_3Si(C_5H_4N)_3$ (**L1**), $(C_6H_5)_2Si(C_5H_4N)_2$ (**L2**), and $(HO)C(C_5H_4N)_3$ (**L3**) (Chart 1), have been synthesized by published methods.[9,10] The anhydrous form of $[Rh_2(O_2CCF_3)_4]$ was prepared using a literature procedure.[11] Elemental analyses were performed by Canadian Microanalytical Service, Delta, British Columbia. The IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrophotometer using KBr pellets.

Syntheses. Preparation of $\{[Rh_2(O_2CCF_3)_4]_3CH_3Si(C_5H_4N)_3(C_6H_6)_3\}\cdot C_6H_6$ ($2\cdot C_6H_6$). The dirhodium complex, $Rh_2(O_2CCF_3)_4$ (0.050 g, 0.075 mmol), was dissolved in 10 mL of dichloromethane to give a green solution. A colorless solution of $CH_3Si(C_5H_4N)_3$ (0.014 g, 0.05 mmol) in 20 mL of benzene was carefully layered on a top of the CH_2Cl_2 solution. After 2 weeks the layers had mixed to give a pink solution and a purple, still unidentified, polycrystalline solid at the bottom of the tube. The solution was separated from the solid by filtration through Celite and then reduced to half its volume. Hexanes (20 mL) were carefully placed on the top of the dichloromethane−benzene mixture. The system was kept at about 10 °C. Dark purple crystals of $2\cdot C_6H_6$ came out over a period of 2 months. Yield: ca. 15%. Anal. Calcd: C, 29.99; H, 1.53; N, 1.64. Found: C, 28.17; H, 1.37; N, 1.66. The C and H values are slightly low due to loss of some benzene of solvation. IR (KBr, cm^{-1}): 1670s, 1664s, 1262s, 1194s, 1164s, 1199s, 1021s, 860m, 804s, 739s, 700w, 690w, 663w, 642w, 628w, 587w, 550w, 534w, 526w, 510w, 476w, 458w, 454w, 450w, 444m, 410m.

Preparation of $\{[Rh_2(O_2CCF_3)_4]_2(C_6H_5)_2Si(C_5H_4N)_2\}$ (3). Complex **1** (0.056 g, 0.085 mmol) was dissolved in 25 mL of CH_2Cl_2 to give a green solution. On top of this dichloromethane solution was added 15 mL of benzene as a buffer layer, followed by careful layering of a solution containing the $(C_6H_5)_2Si(C_5H_4N)_2$ ligand, (0.030 g, 0.08 mmol) in 10 mL of benzene. After 2 weeks the layers had mixed to give a pink-purple solution. The volume of this solution was reduced by $^2/_3$, and 15 mL of hexanes was then layered on top. Small pink crystals of **3** appeared on the bottom of the tube in a month. Yield: 50%. Anal. Calcd: C, 27.59; H, 1.10. Found: C, 27.55; H, 1.08. IR (KBr, cm^{-1}): 1667s, 1655m, 1233s, 1194s, 1168s, 1122m, 1071w, 996w, 857m, 814w, 786m, 737s, 710w, 700w, 525m, 513m.

Preparation of $[Rh_2(O_2CCF_3)_4]_3(HO)C(C_5H_4N)_3(C_6H_6)\}\cdot {^1/_2}C_6H_6$ ($4\cdot {^1/_2}C_6H_6$). The ligand $(HO)C(C_5H_4N)_3$ (0.015 g, 0.05 mmol) was dissolved in 20 mL of CH_2Cl_2. A solution of the dimetal complex **1** (0.053 g, 0.08 mmol) in 10 mL of benzene was then carefully layered over the dichloromethane solution of the ligand. Over 2 days at room temperature the layers mixed to give a pink solution and a polycrystalline purple solid. The solution was filtered through Celite, and the filtrate was reduced in volume by $^1/_2$ and then maintained at 10 °C. Crystals of $4\cdot {^1/_2}C_6H_6$ came out in 3 weeks. Yield: 40%. IR (KBr, cm^{-1}): 2960w, 2925w, 2856w, 1669m, 1664m, 1660m, 1231m, 1193s, 1168m, 1070w, 1105w, 1018w, 859m, 828w, 786w, 738m, 538w.

X-ray Structure Determinations. Single crystals of compounds **2**−**4** were obtained as described above. X-ray diffraction experiments were carried out on a Nonius FAST diffractometer with an area detector using Mo Kα radiation. Details concerning data collection have been fully described elsewhere.[12] Fifty 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.[13] Reflection profiles were fitted and values of F^2 and $\sigma(F^2)$ for each reflection were obtained by the program PROCOR.[14] All calculations were done on a DEC Alpha computer running VMS. The coordinates of the rhodium atoms in each structure were found in direct method E maps using the structure solution program SHELXTL.[15] The remaining atoms

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Table 1. Crystallographic Data for **2**−**4**

	2·C_6H_6	**3**	**4**·$^1/_2C_6H_6$
formula	$Rh_6SiO_{24}N_3F_{36}C_{64}H_{39}$	$Rh_4SiO_{16}N_2F_{24}C_{38}H_{18}$	$Rh_6O_{25}N_3F_{36}C_{49}H_{22}$
fw	2563.53	1654.27	2354.16
cryst syst	trigonal	monoclinic	monoclinic
space group	$R\bar{3}$	$C2/c$	$P2_1/c$
a (Å)	25.160(2)	21.726(6)	23.175(2)
b (Å)	25.160(2)	16.795(1)	16.1746(7)
c (Å)	23.382(5)	17.798(3)	23.782(4)
α (deg)	90.00	90.00	90.00
β (deg)	90.00	90.14(2)	93.101(7)
γ (deg)	120.00	90.00	90.00
V (Å^3)	12819(3)	6494(2)	8902(2)
Z	1	4	4
ρ_{calcd} (g·cm^{-3})	1.992	1.692	1.757
μ (mm^{-1})	1.297	1.140	1.224
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
temp (K)	213(2)	213(2)	213(2)
no. of unique data	3700	5749	15590
no. of obsd data [$I > 2\sigma(I)$]	3286	4948	12839
no. of params refined	383	408	972
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.0475, 0.1132	0.0677, 0.1854	0.0800, 0.2093
R1,[a] wR2[b] (all data)	0.0551, 0.1240	0.0784, 0.2047	0.0980, 0.2309
quality-of-fit[c]	1.051	1.088	1.048

[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 $= [\sum[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{params})]^{1/2}$, based on all data.

were located after an alternating series of least-squares cycles and difference Fourier maps.[16] The fluorine atoms of all CF_3 groups were disordered over two or three different rotational orientations. All the benzene molecules (coordinated to the Rh and not) in **2** and **4** are disordered. This disorder was modeled individually in each case. Disorder of the coordinated benzene molecules does not affect the coordination mode in both cases; therefore it was not addressed specifically in the text. All details on distances, occupancies, etc. were included in the CIFs provided as Supporting Information. Anisotropic displacement parameters were assigned to all atoms, except the disordered fluorine atoms and disordered carbon atoms of solvent molecules. Relevant crystallographic data for complexes **2**·C_6H_6, **3**, and **4**·$^1/_2C_6H_6$ are summarized in Table 1.

Results and Discussion

Much attention has been directed toward the use of multidentate linear and angular nitrogen donors in supramolecular design.[17] In principle, for a selected metal complex, the topology of the supramolecular network is governed by the geometry of the ligand. In practice, the supramolecular assembling may be complicated by additional factors, which may play a very important but unpredictable role. The main limitation we have found so far when using **1** as a dimetal complex is that different solubility of polymers and oligomers often favors the formation of the former. In addition, some weak interactions or solvent involvement may drive the reaction in unanticipated directions. Therefore, the problem of controlling the shape of supramolecular networks toward a desired product is not simple and provides challenges for synthetic chemists. We report here our findings on systems containing a linear two-coordinated rigid structure element in the form of a very strong Lewis acceptor **1** and three different nitrogen-containing Lewis bases **L1**−**L3** (Chart 1). Pyridyl-containing ligands **L1** and **L3** are tritopic linkers for possible dodecahedra (although **L3** has an additional coordination site, the OH group), while **L2** is expected to be a 109° linker for a pentagon.[9] Although none of the desired polyhedra have been obtained, three remarkable supramolecular architectures **2**−**4** with angular ligands **L1**−**L3** and dinuclear metal complex **1** have been isolated. Their synthesis and crystal structures are presented here.

The compound $\{[Rh_2(O_2CCF_3)_4]_3CH_3Si(C_5H_4N)_3(C_6H_6)_3\}\cdot C_6H_6$ (**2**·C_6H_6) with a stoichiometry of $[Rh_2]$:L = 3:1 has been isolated from benzene in low yield from reaction of dirhodium tetra(trifluoroacetate) with $CH_3Si(C_5H_4N)_3$ (**L1**) after the major insoluble and so far unidentifiable polymeric product (which might be a mixture of various polymers and oligomers) crashed out of solution. The pink-purple crystalline compound **2** is very soluble in both CH_2Cl_2 and benzene and stable in air, but slowly loses solvent molecules at room temperature.

An X-ray structural analysis of **2**·C_6H_6 shows a highly symmetrical molecule in the solid state, crystallizing in trigonal space group $R\bar{3}$. As depicted in Figure 1, complex **2** consists of three $[Rh_2(O_2CCF_3)_4]$ units bound at axial positions to three N-donor atoms of pyridyl groups of the ligand, $CH_3Si(C_5H_4N)_3$, at the Rh−N distance of 2.152 Å. Thus the shape of the supramolecule is that of a pyramid. The bond angles about the central Si(1) atom deviate from an idealized tetrahedral geometry, ranging from 105.7(2)° to 113.0(2)°. The Rh−Rh distances, 2.4197(8) Å, are typical of singly bonded Rh_2^{4+} units having axially coordinated ligands, and other metrical characteristics of the dirhodium units are normal.[18] Selected distances and angles for **2** are listed in Table 2 and compared with those for **3** and **4**.

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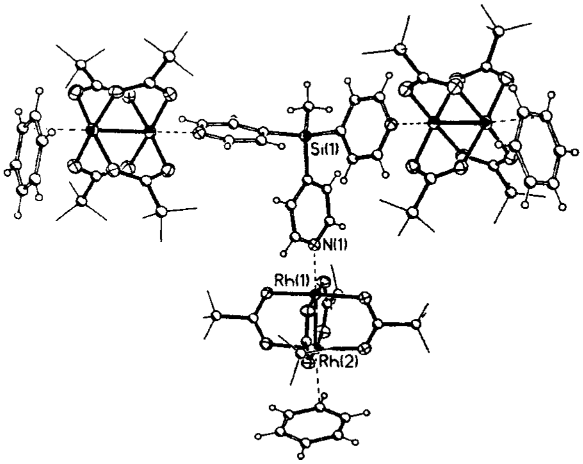

Figure 1. A perspective drawing of the pyramidal complex $\{[Rh_2(O_2CCF_3)_4]_3CH_3Si(C_5H_4N)_3(\eta^1\text{-}C_6H_6)_3\}$ (**2**). Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon and hydrogen atoms are shown as spheres of arbitrary radii. Fluorine atoms of CF_3 groups are omitted. Dashed lines indicate axial coordination to rhodium atoms.

Table 2. Selected Distances (Å) and Angles (deg) in Supramolecular Assemblies **2**−**4**

	2	3	4
Rh−Rh	2.4197(8)	2.4151(9)	2.4105(9) 2.4130(10) 2.4126(10)
Rh−O_{TFA} (av)	2.036(5)	2.029(6)	2.033(7)
Rh−N	2.152(6)	2.150(5)	2.125(7) 2.166(7) 2.137(7)
Rh−$O_{(OH)}$			2.470(5)
Rh−$C_{(Ph,Pyr)}$		2.776(8) 2.988(13)	2.781(8)
Rh−C_{benz}	2.69(2)		2.66(3)
Rh−Rh−N	178.1(2)	179.1(2)	176.8(2) 177.8(2) 179.7(2)
Rh−Rh−C	174.9(5)	165.4(2)	179.2(2) 157.8(2) 171.1(5)
Rh−Rh−O			171.4(1)

An interesting feature of molecule **2** is the presence of a benzene molecule at the open axial end of each dirhodium unit at the Rh−C distance of 2.69(2) Å. This terminal coordination of benzene by the rhodium(II) centers is best designated as an η^1 mode because the other two Rh−C distances, to the adjacent carbon atoms of benzene, are much longer (ca. 3.1 Å). So far the preferred coordination of the aromatic rings by the rhodium centers of dirhodium tetra(trifluoroacetate) has been found to be a bridging η^2:η^2 mode with a small inequality of the Rh−C linkages.[3d,19] For comparison, in the 1D polymeric chain $[Rh_2(O_2CCF_3)_4\cdot(C_6H_6)]_\infty$ the benzene molecules are axially coordinated to the Rh(II) atoms in a $\mu_2,\eta^2:\eta^2$ mode with two Rh−C distances of 2.646(6) and 2.678(6) Å.[19a] For a number of supramolecular adducts of **1** with polycyclic aromatic hydrocarbons as bridges reported recently, these Rh−C contacts fall into the range of 2.51−2.73 Å.[3d] Therefore, this weak η^1-terminal solvation of dirhodium complexes by benzene is quite rare; only one example of η^1-coordination of fluoranthene by complex **1** has been observed so far.[3d]

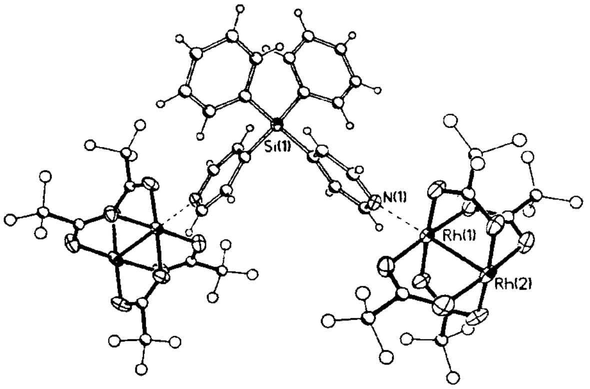

Figure 2. The basic building block in the crystal structure of $\{[Rh_2(O_2CCF_3)_4]_2(C_6H_5)_2Si(C_5H_4N)_2\}$ (**3**). Atoms are represented by thermal ellipsoids at the 40% probability level. Fluorine, carbon, and hydrogen atoms are shown as spheres of arbitrary radii. Only one orientation of each disordered CF_3 group is depicted.

Hexametallic transition metal complexes exhibit a fascinating variety of structural patterns,[2d,20,21] and the structure of the pyramid (**2**) is unique among them. We believe it is a very soluble species which, when present in solution, is a building block for larger and more complex supramolecular networks, such as we observed with the formation of extended structures **3** and **4**.

Complex **3** has been obtained from reaction of **1** with a potentially bidentate ligand, $(C_6H_5)_2Si(C_5H_4N)_2$ (**L2**), in moderate yield as the only product. It is soluble in benzene and dichloromethane and is very stable in the solid state. Chemical analysis data are consistent with the composition of Rh_2:L = 2:1. The latter was confirmed by X-ray crystal structure determination of $[Rh_2(O_2CCF_3)_4]_2(C_6H_5)_2Si(C_5H_4N)_2$ (**3**), which crystallizes in monoclinic space group *C*2/*c*.

In the molecule of $[Rh_2(O_2CCF_3)_4]_2(C_6H_5)_2Si(C_5H_4N)_2$ (**3**), one ligand binds two dirhodium units in a fashion similar to that in **2** at one axial end of **1** with the Rh−N distance of 2.150(5) Å (Figure 2). The bond angles about the central Si(1) atom span the range from 107.1(4)° to 112.2(5)°. The Rh−Rh distance of 2.4151(9) Å within the dinuclear unit, as well as the Rh−O distances, which average to 2.021(6) Å, is typical for the dirhodium(II) tetra(trifluoroacetate) complexes having axially coordinated ligands.[18] An interesting 2D architecture (Figure 3) is achieved in the solid state upon packing of the $[Rh_2(O_2CCF_3)_4]_2(C_6H_5)_2Si(C_5H_4N)_2$ building blocks through the interactions of open dirhodium ends with phenyl groups of the neighboring ligands. The metal−π interaction is of an η^2 type, which means that the Rh center exhibits two contacts with the 3,4-carbon atoms of the phenyl group. The Rh−C distances are long and

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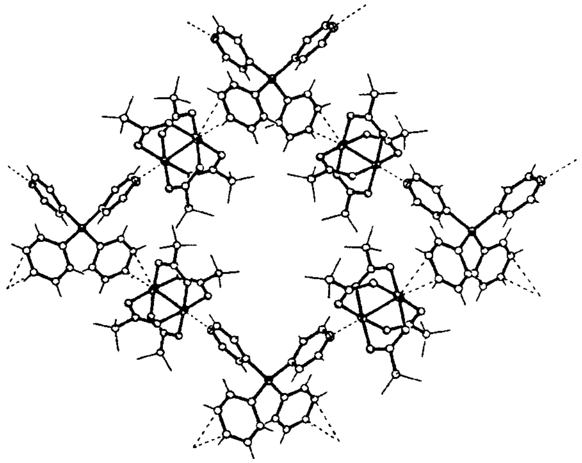

Figure 3. A fragment of the 2D layered structure of **3**. The fluorine and hydrogen atoms are omitted for clarity. Dashed lines show axial coordination to rhodium atoms.

dissimilar, namely, 2.776(8) and 2.988(13) Å. The latter are significantly longer than the Rh−C contact in **2** with benzene molecules terminating open axial positions of dirhodium units. It is interesting that the use of a very powerful Lewis acid in the form of dirhodium tetra(trifluoroacetate) forces a bidentate **L2** ligand to act in a bifunctional tetradentate fashion in **3**, through two N-donor atoms and two phenyl groups. Supramolecular quadrangles consisting of four ligands and four dinuclear complexes **1** (Figure 3) create a 2D layered motif, which has no close interlayer contacts. Attempts to force the formation of a polygonal (possibly pentagonal) product by using a higher ratio of **L2** to **1** led only to the formation of unidentifiable, noncrystalline solids.

In our attempts to generate new supramolecules, we have also employed a multidentate ligand **L3**, which was previously shown to form large oligomeric species in solutions.[9] For example, by reacting tris(4′-pyridyl)methanol (**L3**) with a rodlike bidentate diplatinum complex, a supramolecular dodecahedron was built in a single step. In that assembly only the N-donor centers were involved in coordination[9a] although this ligand has four potential donor sites: three N atoms of the pyridyl groups and one O atom of the hydroxyl group. A homochiral, helical polymer has recently been prepared when reacting **L3** with a chiral linear zinc linker.[22]

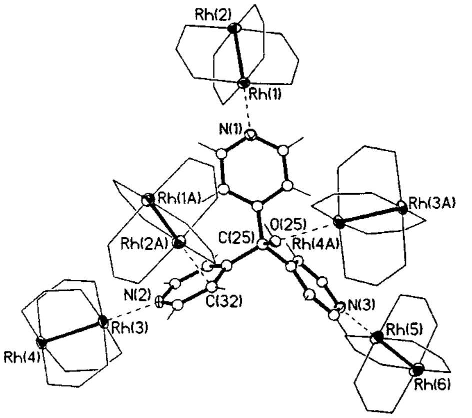

Figure 4. Pentadentate coordination of tris(4′-pyridyl)methanol, (HO)-$C(C_5H_4N)_3$ (**L3**), by the $[Rh_2(O_2CCF_3)_4]$ complexes in the crystal structure of **4**. The CF_3 groups are omitted for clarity.

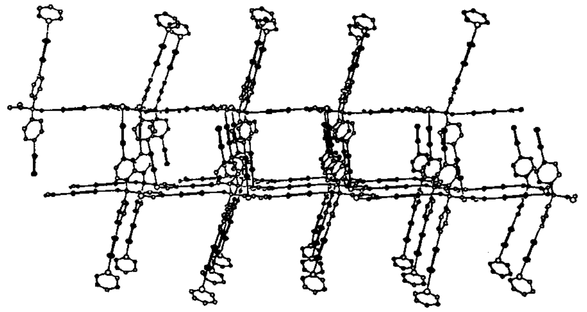

Figure 5. The supramolecular hybrid core $\{[Rh_2(O_2CCF_3)_4]_3{\cdot}(HO)C(C_5H_4N)_3\}$wrapped by benzene molecules in the crystal structure of **4**. The bare Rh_2 units are used to represent dimetal complexes. Hydrogen atoms of the ligand are omitted.

By reaction of tris(4′-pyridyl)methanol with linear dirhodium units **1** a novel supramolecular complex has been formed in moderate yield. This compound $\{[Rh_2(O_2CCF_3)_4]_3(HO)C(C_5H_4N)_3(C_6H_6)\}{\cdot}{}^1/_2C_6H_6$ ($\mathbf{4}{\cdot}{}^1/_2C_6H_6$) is stable in air. However, it loses solvent at room temperature, which prevented obtaining accurate chemical analysis data. It has been characterized by X-ray crystallography. In the crystal structure of **4**, each **L3** ligand coordinates three crystallographically independent dirhodium units, namely, Rh(1)−Rh(2), Rh(3)−Rh(4), and Rh(5)−Rh(6) (Figure 4). Coordination occurs through the N atoms of the pyridyl groups and involves the Rh(1), Rh(3), and Rh(5) atoms. The three Rh−N bond distances are only slightly different and average to 2.143(7) Å. The three Rh−Rh distances within the dimetal units are about the same and average to 2.412(1) Å. The bond angles around the central C(25) atom deviate from ideal tetrahedral geometry and range from 106.7(6)° to 114.2(7)°. In contrast to **2,** an extended motif is formed in **4** by additional contacts of the supramolecular units, $\{[Rh_2(O_2CCF_3)_4]_3(HO)C(C_5H_4N)_3\}$, via the atoms Rh(2) and Rh(4) with the O atoms and C atoms of pyridyl groups of the neighboring complexes (Figure 5). The Rh(4) atom has a strong interaction with the oxygen atom of the OH group at the Rh−O distance of 2.470(5) Å. The Rh(2) atom has a contact with the carbon atom of the pyridyl ring at the Rh−C(32) distance of 2.781(8) Å. In addition, the Rh(6) atom binds a benzene molecule with one Rh−C contact at 2.66(3) Å. Interestingly, all benzene molecules are located on the outer surface of the supramolecular layers, enveloping the $\{[Rh_2(O_2CCF_3)_4]_3(HO)C(C_5H_4N)_3\}$ core. It is interesting that in the previous work[9a] the **L3** ligand used only N-donor sites for coordination of the bidentate diplatinum complex that served as the edge unit. However, in its reaction with the coordinatively unsaturated bidentate dirhodium complex, we observe an unusual coordination mode of tris(4′-pyridyl)methanol. In supramolecular assembling of **4** this ligand utilizes not only four potential donor sites, three N and one O, but unexpectedly becomes pentadentate, as the aromatic functionality of the pyridyl group is also involved in binding to a rhodium center.

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Conclusion. Three new supramolecular complexes, **2**−**4**, have been obtained by combining angular trifunctional or difunctional N-donor ligands with the linear bidentate Lewis acid [$Rh_2(O_2CCF_3)_4$]. The structures of **2**−**4** are not the ones that were envisioned before the work was begun because of the of the ability of [$Rh_2(O_2CCF_3)_4$] to interact with the π-electrons of aromatic rings. We had not expected this, but in fact these latter interactions come into play to such an extent that they are structure-determining. We believe that by using other, less (Lewis) acidic, [$Rh_2(O_2CR)_4$] molecules with the same bi- and tridentate angular donors, it may be possible to obtain discrete supramolecular polygons and polyhedra.

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Supporting Information Available: Three 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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