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Dicarboxylate-Bridged Ruthenium Complexes as Building Blocks for Molecular Nanostructures

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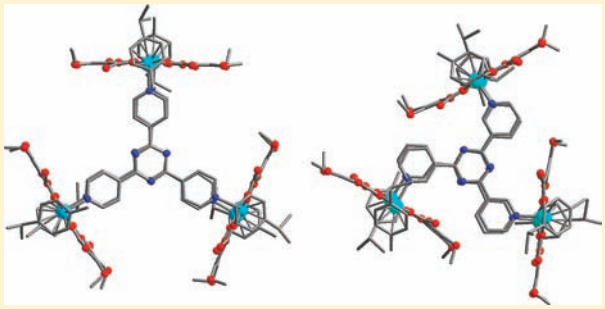
Supporting Information

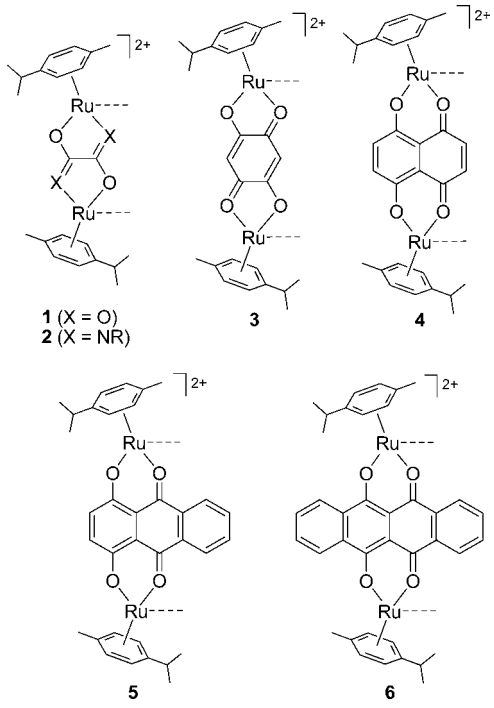
ABSTRACT: Ruthenium complexes with bridging dicarboxylate ligands were combined with 1,2-di-4-pyridylethylene (dpe), 2,4,6-tri-4-pyridyltriazine (4-tpt), or 2,4,6-tri-3-pyridyltriazine (3-tpt) to give a tetranuclear rectangle or hexanuclear coordination cages. The cages display a trigonal-prismatic geometry, as evidenced by single-crystal X-ray crystallography. The 4-tpt-based cages are able to encapsulate polyaromatic molecules such as pyrene, triphenylene, or coronene, whereas the 3-tpt-based cages were found to be incompetent hosts for these guests.



INTRODUCTION

In the area of supramolecular coordination chemistry, the reaction of polyfunctional ligands with transition-metal complexes having two available coordination sites has been used extensively for the construction of macrocycles and cages.[1] Instead of mononuclear complexes, it is possible to use dinuclear complexes with one available coordination site at each metal center. For example, it has been shown that dinuclear platinum(II) complexes with two weakly coordinated ligands (e.g., triflate or nitrate) are versatile building blocks for the construction of supramolecular assemblies.[2] In a similar fashion, dinuclear palladium(II),[3] rhenium(I),[4] and zinc(II)[5] complexes with available coordination sites on each metal center have been combined with polyfunctional N- or O-donor ligands. Organometallic half-sandwich complexes of ruthenium can also be used in this context. (Arene)ruthenium(II) complexes were connected by oxalato (**1**),[6] oxamidato (**2**),[7] dihydroxybenzoquinonato (**3**),[8] dihydroxynaphtoquinonato(**4**),[9] dihydroxyanthracenedionato (**5**),[10] and dihydroxynaphthacenedionato (**6**) ligands.[11] The dimers were then mixed with N-donor ligands to give polycationic assemblies.[12,13] Complexes of this kind have been discussed for applications as sensors for ions[14,15] and for nitroaromatics,[16] as antitumor agents,[17] as binders to telomeric DNA,[18] and as transport vehicles for antitumor drugs[19] and for photosensitizers.[20]

In the examples cited above, the Ru centers of the dinuclear building block are connected by di- or tritopic ligands to give macrocycles and cages. To access more complex molecular architectures, we have started to explore the utilization of dinuclear ruthenium complexes, in which the two metal centers themselves are part of a macrocyclic framework.[21−23] Below we report the synthesis of a molecular rectangle and novel coordination cages based on carboxylate-bridged ruthenium macrocycles.



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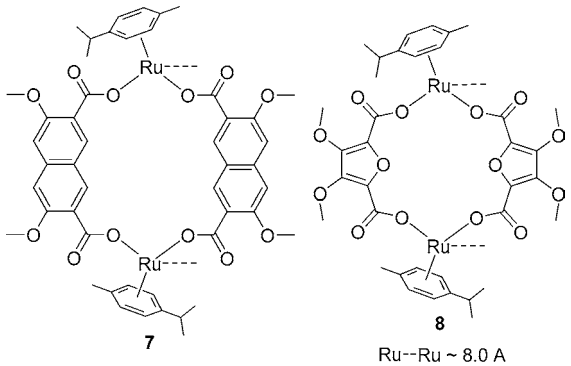
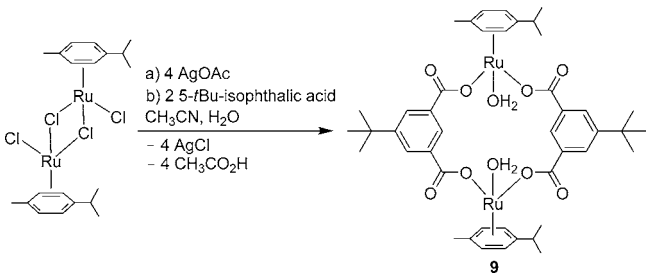
RESULTS AND DISCUSSION

Recently, we have shown that the dinuclear ruthenium fragment **7** containing two bridging 3,6-dimethoxynaphthalene-2,7-dicarboxylate ligands can be linked with the tritopic N-donor ligand 2,4,6-tri-4-pyridyltriazine (4-tpt) to give a hexanuclear coordination cage.[21] In a related fashion, fragment **8** was combined with the tetratopic ligand tetrakis(4-pyridylphenyl)-ethylene to give an octanuclear cage.[22] Both cages featured remarkably adaptable structures: upon the addition of suited guest molecules, we observed pronounced conformational[21] or constitutional changes.[22] This plasticity was attributed to the presence of carboxylate ligands, which are kinetically labile and display a flexible coordination geometry. These first results prompted us to explore the supramolecular coordination chemistry of dinuclear, carboxylate-bridged (cymene)ruthenium complexes in more detail.



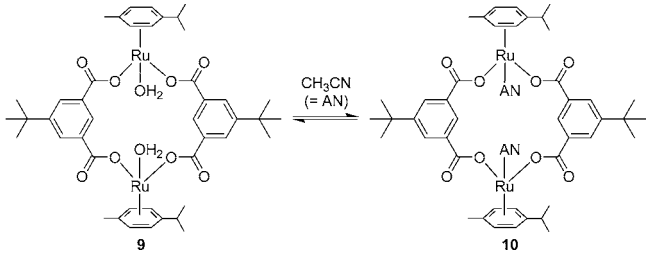
Our investigations started with the synthesis of the new ruthenium dimer **9** containing bridging 5-*tert*-butylisophthalate ligands. Complex **9** was obtained in a stepwise fashion: the dimeric complex $[(\text{cymene})\text{RuCl}(\mu\text{-Cl})]_2$ was first mixed with AgOAc in acetonitrile to produce the carboxylate complex $[(\text{cymene})\text{Ru}(\text{OAc})_2]$ (possibly as a CH_3CN adduct). The latter was not isolated but combined directly with 5-*tert*-butylisophthalic acid to give complex **9** in 71% yield (Scheme 1).

Scheme 1



Attempts to produce a solvent-free complex $[(\text{cymene})\text{Ru}(\mu\text{-}C_{12}H_{12}O_4)]_2$ were not successful. The addition of small amounts of water to the reaction mixture resulted in the formation of a defined species, which turned out to be the diaqua complex **9**. The high affinity for water is in line with what has been observed for the half-sandwich complex $[Cp^*Rh(OAc)_2]$, which rapidly forms the aqua adduct $[Cp^*Rh(OAc)_2(H_2O)]$.[24] The stability of the aqua complex is enhanced by two intramolecular hydrogen bonds between the aqua ligand and the carboxylate group, as evidenced by crystallographic analysis. The (cymene)ruthenium complex **9** likely benefits from similar interactions. Nevertheless, the aqua ligands can be easily replaced by other ligands. This was evidenced by the following observation: when complex **9** was dissolved in CD_3CN containing a small amount of D_2O, a single set of signals was observed by ^1H NMR spectroscopy. In pure CD_3CN, however, a mixture of complexes was detected by NMR. A likely explanation is that the aqua ligands can be replaced by acetonitrile ligands (Scheme 2).

Scheme 2



The facile formation of the CH_3CN adduct **10** was confirmed by X-ray analysis of crystals, which were obtained from an acetonitrile solution of complex **9**. A graphic representation of the molecular structure of complex **10** in the crystal is depicted in Figure 1. The dimeric complex shows

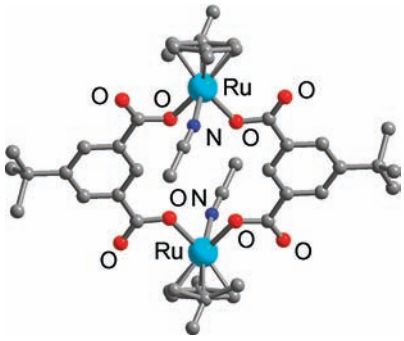


Figure 1. Molecular structure of complex **10** in the crystal. H atoms are not shown for clarity. The thermal ellipsoids are set at 50% probability.

a crystallographic inversion center. The two (cymene)-ruthenium fragments are connected by two bridging 3-*tert*-butylisophthalate ligands, forming a 16-membered macrocycle. All four carboxylate groups are bound in a η^1-type fashion with Ru–O distances of 2.096(3) and 2.110(3) Å. The coordination sphere of each metal center is completed with an acetonitrile ligand [Ru–N = 2.111(4) Å]. The two Ru centers are 8.101(2) Å apart from each other.

To test whether complex **9** is a suitable building block for more complex nanostructures, we first investigated a reaction with a "simple" ditopic N-donor ligand. Mixing a chloroform solution of complex **9** with 1,2-di-4-pyridylethylene (dpe) resulted in the formation of a new complex (**11**), which was isolated in 92% yield (Scheme 3). The NMR spectra of complex **11** showed a single set of signals for the 3-*tert*-butylisophthalate and dpe ligands, in accordance with a highly symmetrical structure. On the basis of the geometry that was

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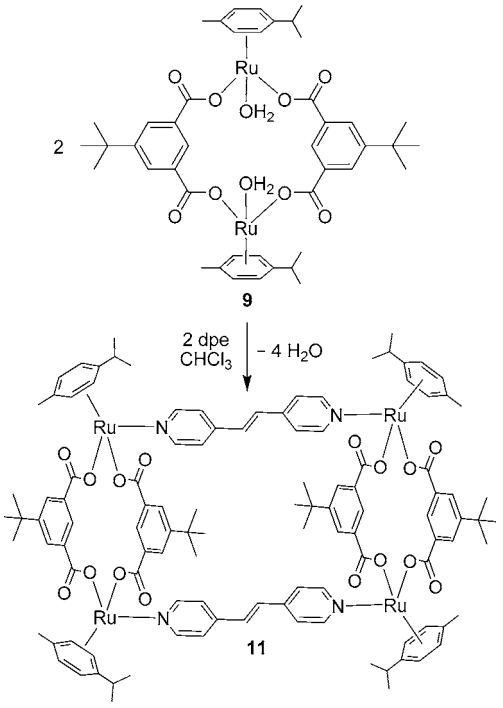
Scheme 3



determined for the acetonitrile adduct **10**, a tetranuclear structure was expected for complex **11**. This assumption was confirmed by single-crystal X-ray analysis of complex **11** (Figure 2). Two macrocyclic $\{(cymene)Ru(\mu\text{-}C_{12}H_{12}O_4)\}_2$ units are connected by two bridging dpe ligands. The latter are slightly bent. As a consequence, the distance between two opposite C atoms of the ethylene group is 9.4 Å, whereas the pyridyl N atoms are only 8.6 Å apart from each other. The distance between the two Ru atoms in the $\{(cymene)Ru(\mu\text{-}C_{12}H_{12}O_4)\}_2$ unit is only 8.1 Å and thus very similar to what was observed for the dimer **10**.

Next, we have investigated the reaction of complex **9** and the previously described complex $[\mathbf{8}(H_2O)(CH_3CN)]$ (the solvent-stabilized precursor of fragment **8**)[22] with the tritopic N-donor ligand 4-tpt. Simply mixing the dimers **8** and **9** with 4-tpt in $CDCl_3$ gave rise to new complexes (**12** and **13**) in high yield, as evidenced by in situ ^{1}H NMR spectroscopy measurements. The NMR data of the isolated complexes **12** (yield: 86%) and **13** (yield: 92%) were in line with the anticipated trigonal-prismatic cage structures: in both cases, the spectra showed signals for the (cymene)ruthenium fragments, for the dicarboxylate ligands, and for the N-donor ligands in a ratio 3:3:1.

The molecular structure of complex **12** in the crystal is depicted in Figure 3. The Ru atoms are positioned at the vertices of a nearly regular trigonal prism with edge lengths of 13.2 and 8.0 Å. The two coplanar 4-tpt ligands are orthogonal to the planes defined by the 3,4-dimethoxyfuran-2,5-dicarboxylate ligands. The ligands define a cavity that is accessible by portals near the edges of the trigonal prism. The average Ru–O (2.08 Å) and Ru–N bond lengths (2.11 Å) are similar to those found for the tetranuclear complex **11** ($Ru\text{–}O_{av}$ = 2.09 Å; $Ru\text{–}N_{av}$ = 2.13 Å).

Attempts to characterize complex **13** crystallographically were initially not successful. Single crystals of complex **13** were obtained from $CHCl_3$, but the quality of the data was very low because of the presence of substantial amounts of disordered

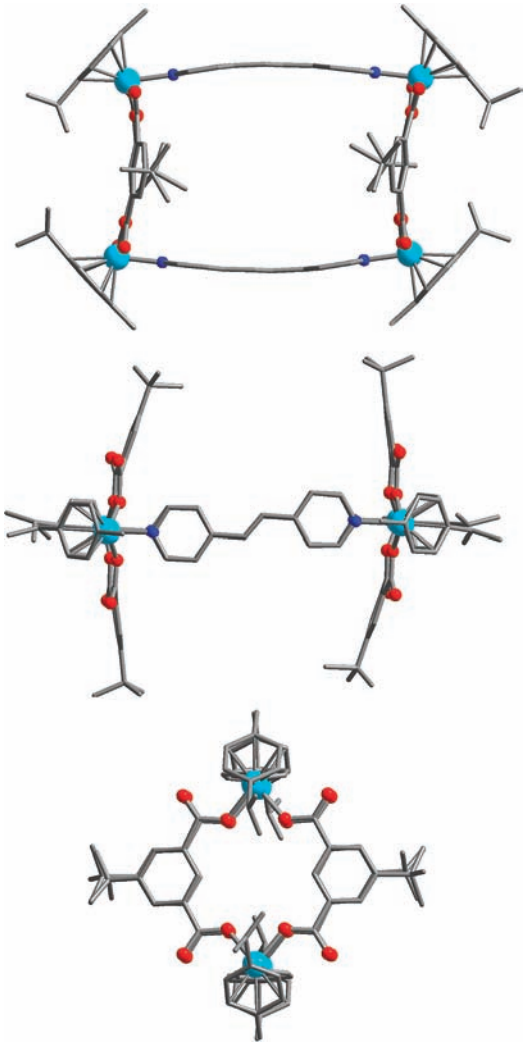


Figure 2. Molecular structure of complex **11** in the crystal with views along the three (pseudo)-C_2 axis. Color code: light blue, Ru; blue, N; red, O; gray, C. H atoms and solvent molecules (15.5 $CHCl_3$) are not shown for clarity.

solvent molecules (≥18 $CHCl_3$ per complex). Improved data were obtained for crystals grown from fluorobenzene. Again, a substantial amount of disordered solvent molecules was observed in the crystal (the electron density pointed to ~12 C_6H_5F per complex). However, utilization of the *SQUEEZE* algorithm[25] resulted in a reasonably precise structural determination of the nanometer-sized assembly. A graphic representation of the structure is shown in Figure 4.

The overall geometry (Ru···Ru distances: 13.3 and 8.1 Å) and the average Ru–O (2.09 Å) and Ru–N bond lengths (2.12 Å) are similar to those found for cage **12**.

Whereas 4-tpt is a frequently used N-donor ligand in supramolecular coordination chemistry,[1] the chemistry of the isomeric 2,4,6-tri-3-pyridyltriazine (3-tpt) ligand is less well explored.[26] A difficulty in using 3-tpt for metal-based self-assembly processes is the fact that 3-tpt can form conformational isomers with a different relative orientation of the N-donor groups. However, when 3-tpt was combined with either complex $[\mathbf{8}(H_2O)(CH_3CN)]$ or **9** in $CDCl_3$, a single new species was formed, as evidenced by in situ ^{1}H NMR spectroscopy. Isolation by precipitation provided complexes **14** and **15** in 75% and 89% yield, respectively.

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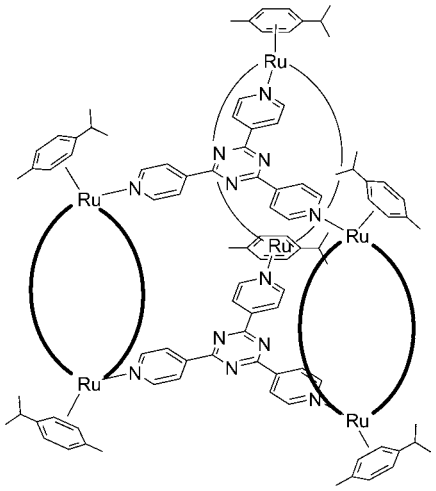


12 13

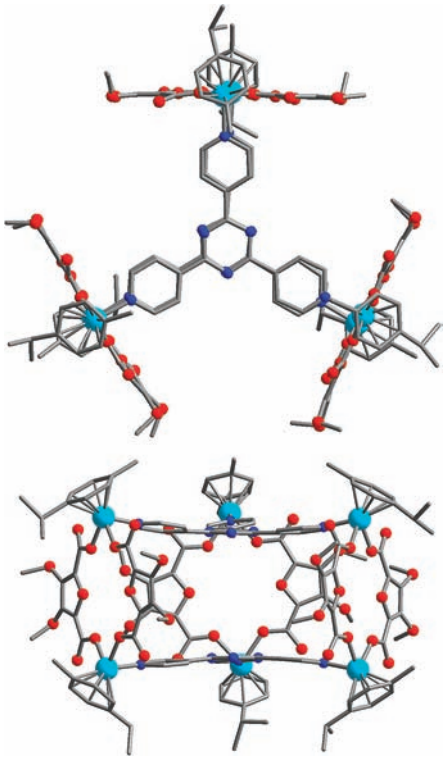


Figure 3. Molecular structure of complex **12** in the crystal. Top: view along the pseudo-C_3 axis. Bottom: view from the side. Color code: cyan, Ru; blue, N; red, O; gray, C. H atoms and solvent molecules are not shown for clarity.

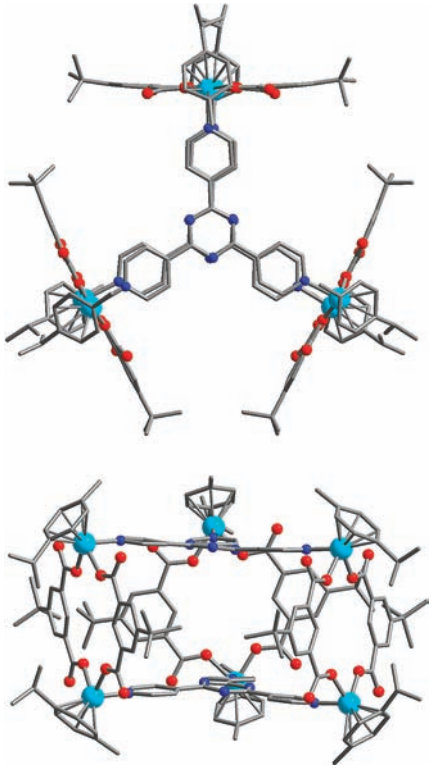
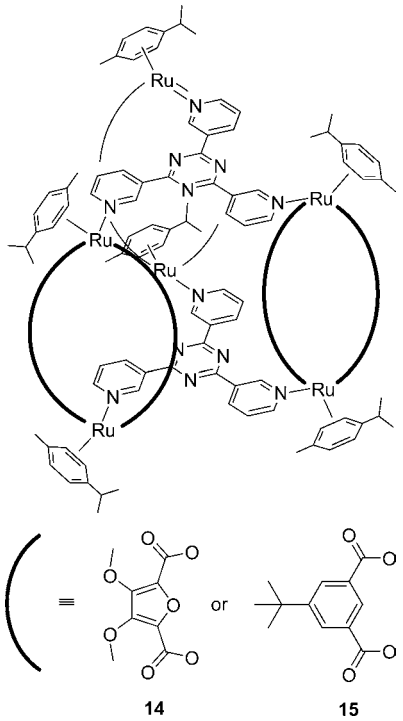


Figure 4. Molecular structure of complex **13** in the crystal. Top: view along the pseudo-C_3 axis. Bottom: view from the side. Color code: cyan, Ru; blue, N; red, O; gray, C. H atoms are not shown for clarity.



14 15

The apparent symmetry of **14** and **15**, as deduced by NMR spectroscopy, was lower than that of **12** and **13**. Two sets of signals were observed for the bridging carboxylate ligands of **14** and **15**, whereas only one set of signals was observed for **12** and **13**. These data are in line with geometry A but not with geometry B (the latter complexes would display even lower symmetry).

The formation of assemblies of type A was confirmed by single-crystal X-ray analyses of **14** and **15** (Figure 5). As in the case of **12** and **13**, the six metal centers in **14** and **15** form a trigonal prism. Dicarboxylate ligands that bridge the same two metal centers are again nearly coplanar, and the average Ru−N and Ru−O bond distances are within the expected range. However, the dimensions of the prisms are smaller (8.0 × 11.3 Å^2

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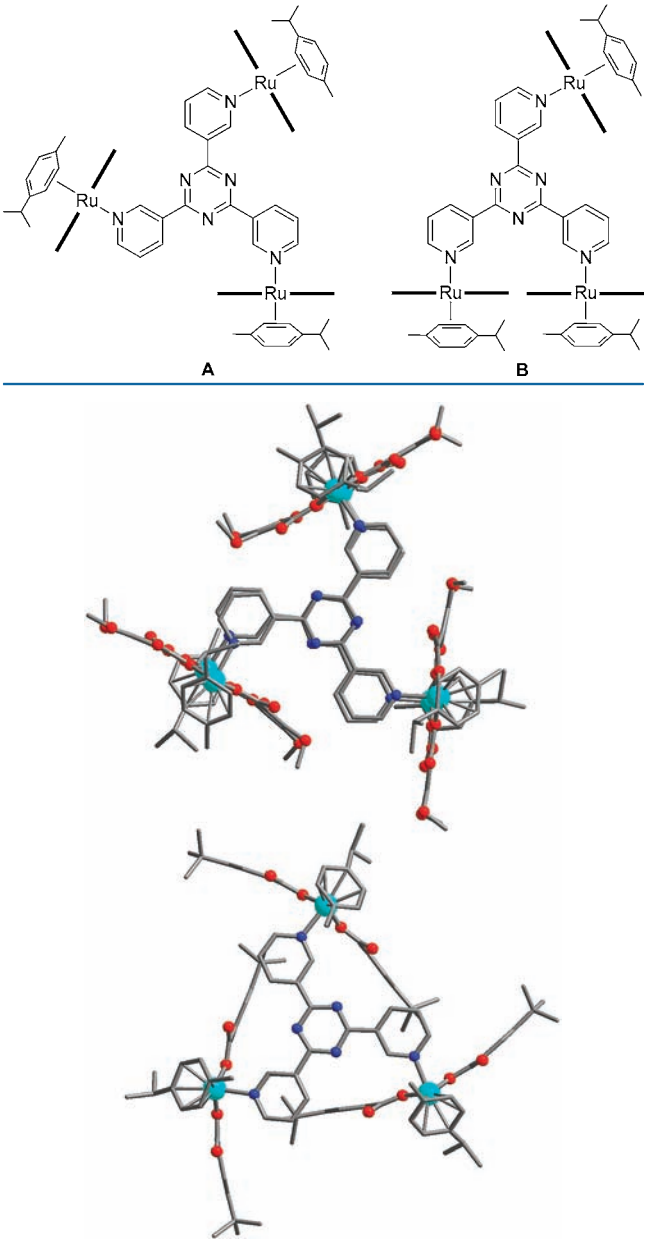

Figure 5. Molecular structures of complexes **14** (top) and **15** (bottom) in the crystal. Color code: cyan, Ru; blue, N; red, O; gray, C. H atoms and solvent molecules are not shown for clarity.

for **14** and 8.1 × 11.2 Å^2 for **15**) than those obtained with the 4-tpt ligand. Because of the relative orientation of the dicarboxylate ligands, the cage interior is well shielded from the outside. Complex **15**, in particular, has only very small portals because of the size and orientation of the *tert*-butyl groups, whose protons make a number of close contacts (H···centroid ≤3 Å) with the aromatic π systems on adjacent 3-tpt and 5-*tert*-butylisophthalate ligands. The complexes thus adopt an overall more compact structure, the interior cavity and portal dimensions of which suggesting that they are much less amenable to accommodating guest species than their 4-tpt analogues. In the case of **15**, this is reflected by the fact that the crystal is marginally solvated, with only several disordered chloroform molecules filling interstitial positions outside the cage. Crystals of **14** do, however, contain a large number of dichloromethane solvates (≥7), one of which occupies a well-defined position inside the cage interior.

The host properties of complexes **12**–**15** were explored using the polycyclic compounds pyrene, triphenylene, and coronene as potential guests. These flat, aromatic compounds were chosen because they might slip in between the coplanar tpt ligands. One should note that π stacks of this kind have frequently been observed for prismatic cages based on tpt ligands.[1,12,27] When a solution of complex **13** (1.6 mM) and 1.25 equiv of pyrene, triphenylene, or coronene in $CDCl_3$ was investigated by ^{1}H NMR spectroscopy, formation of a 1:1 adduct between the polycyclic aromatic compound and complex **13** was observed. The host–guest complex gave rise to a new set of signals, indicating that guest exchange is slow on the NMR time scale (see Figure 6 for an example). Integration of the signals of the free cage and of the host–guest complex allowed the binding constants to be calculated. The value for pyrene in $CDCl_3$ was $K_a = (1.3 \pm 0.5) \times 10^3$ M^{-1} and the association constant for triphenylene $K_a = (4.2 \pm 0.5) \times 10^3$ M^{-1}. The interaction between coronene and complex **13** was stronger. Even low amounts of coronene resulted in the quantitative formation of the host–guest complex ($K_a > 10^4$ M^{-1}). The binding of pyrene and triphenylene to complex **13** is affected by the solvent: when the more polar solvent mixture $CD_3OD/CDCl_3$ (1:1) was used instead of pure $CDCl_3$, the binding constants increased to K_a(pyrene) = $(4.5 \pm 0.5) \times 10^3$ M^{-1} and K_a(triphenylene) = $(1.5 \pm 0.5) \times 10^4$ M^{-1}.

NMR experiments with cage **12** revealed that it is a better host than complex **13**. The addition of 1.25 equiv of pyrene or triphenylene to a solution of complex **12** (Figure 7) in $CDCl_3$ (1.6 mM) lead to quantitative formation of the host–guest complex ($K_a > 10^4$ M^{-1}).

As anticipated from their structures (vide supra), the smaller and less accessible cages **14** and **15** were found to be poor hosts for aromatic guests. Attempts to encapsulate pyrene, triphenylene, or coronene were unsuccessful. Even smaller aromatic compounds such as naphthalene, 2,7-dimethoxynaphthalene, anthracene, caffeine, 1,3,5-tribromobenzene, and phenanthrene were not encapsulated by **14** and **15**.

The host–guest complex coronene⊂**12** was also characterized by single-crystal X-ray diffraction analysis. Crystals of coronene⊂**12** scattered weakly because of large amounts of disordered solvent in the lattice. An estimated 34 chloroform moieties (per asymmetric unit) were identified in the electron density map, many of which were removed using the *SQUEEZE* function because of unstable refinement.[25] The diffuse solvent clearly impacts the two complex molecules occupying the asymmetric unit, both of which likewise display significant librational disorder. The data were, nonetheless, sufficient to confidently resolve their overall molecular structures and reveal the coronene guests, which reside in their central cavities, sandwiched between the 4-tpt ligands. The guests are not centrally located with respect to the 4-tpt ligands; instead, they are displaced toward one of the three sides of the pyramidal structure. Relative orientations between the host and guest do not vary largely between the two crystallographically unique complexes, and it is likely because of the large amounts of randomly distributed chlorinated solvent that the crystal does not feature higher symmetry. However, the overall cage structures do not differ significantly from their unoccupied guest-free analogues, implying that accommodation of the planar guest does not impose significant conformational strain on the complex.

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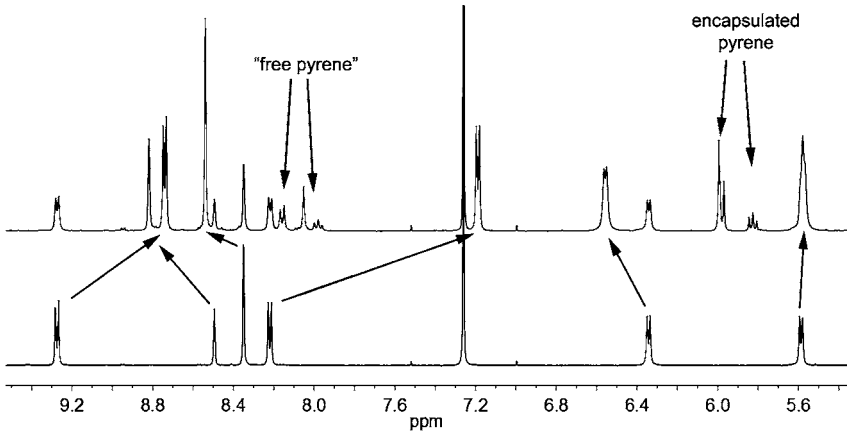

Figure 6. Part of the ^{1}H NMR spectrum ($CDCl_3$) of complex **13** (bottom) and of a mixture of complex **13** (1.6 mM) and pyrene (2.0 mM) (top).

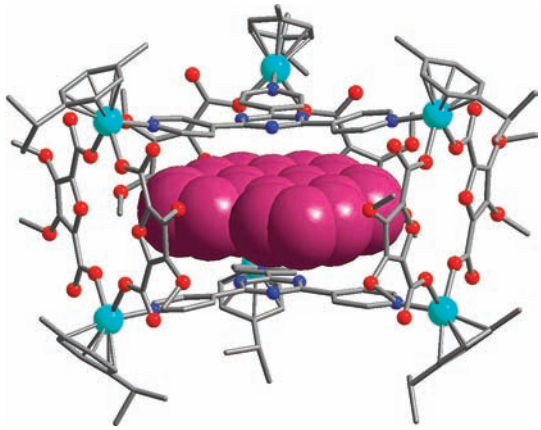

Figure 7. Molecular structure of complex **12** with encapsulated coronene. Color code: cyan, Ru; blue, N; red, O; gray, C; coronene, purple. H atoms and solvent molecules are not shown for clarity.

CONCLUSION AND OUTLOOK

We have shown that the dimeric (cymene)ruthenium complexes [**8**(H_2O)(CH_3CN)] and **9** can be used as versatile building blocks for the construction of supramolecular assemblies. A molecular rectangle was obtained with the ditopic ligand dpe, whereas trigonal-prismatic cages were formed with the tritopic ligands 4-tpt and 3-tpt. Compared to other prismatic structures based on (arene)ruthenium complexes, our assemblies have two distinct features. First of all, they are not charged, whereas previously reported cages are mostly polycationic. Consequently, our complexes have a completely different solubility profile (soluble in organic solvents), and counteranions do not interfere with guest binding. Second, our dimeric building blocks are themselves macrocyclic complexes, and the assemblies have thus a more complex topology. It is conceivable that the (cymene) ruthenium complex can be replaced by other (arene)ruthenium or (cyclopentadienyl)M (M = Rh, Ir) complexes, which would allow one to modulate the solubility and the redox properties of the assemblies. The size of the structures could be altered by using different bridging dicarboxylate ligands. It remains to be seen whether interesting applications will emerge. The straightforward synthesis of the assemblies **11**−**15** is in any case further evidence for the vast potential of organometallic half-sandwich complexes in supramolecular coordination chemistry.

EXPERIMENTAL SECTION

General Procedures. Commercial reagents were purchased from Aldrich, Fluka, or TCI and were used as received. The complexes [(cymene)RuCl(μ-Cl)]$_2$[28] and [**8**(H_2O)(CH_3CN)],[21] as well as the ligands 2,4,6-tri-4-pyridyltriazine (4-tpt)[29] and 2,4,6-tri-3-pyridyltriazine (3-tpt),[29] were prepared according to literature procedures. All solvents were dried using a solvent purification system from Innovative Technologies, Inc. The syntheses of the complexes were carried out under an atmosphere of dry dinitrogen using standard Schlenk techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) and are calibrated relative to solvent residual peaks. Combustion analyses were performed with a Thermo Scientific Flash 2000 organic elemental analyzer.

[(Cymene)Ru(μ-$C_{12}H_{12}O_4$)(H_2O)]$_2$ (9). Silver acetate (300 mg, 1.80 mmol) was added to a solution of complex [(cymene)RuCl(μ-Cl)]$_2$ (245 mg, 0.40 mmol) in acetonitrile (50 mL). The mixture was stirred for 1 h at room temperature under protection from light. AgCl was removed by filtration via Celite. Solid 5-*tert*-butylisophthalic acid (178 mg, 0.80 mmol) was added to the filtrate, and the mixture was stirred for 2 h at 50 °C. The volume was reduced to 15 mL, and water (0.5 mL) was added. The mixture was stirred for 1 h at 40 °C. The orange product precipitated upon the addition of diethyl ether (40 mL) and was collected by filtration, washed with diethyl ether, and dried under vacuum (134 mg, 71%). ^{1}H NMR (400 MHz, CD_3CN/D_2O, 100:2): δ 8.38 (s, 2H, CH, isophthalate), 8.15 (s, 4H, CH, isophthalate), 6.01 (d, J = 6.0 Hz, 4H, CH, cymene), 5.79 (d, J = 6.0 Hz, 4H, CH, cymene), 2.80 (sept, J = 6.8 Hz, 2H, C*H*(CH_3)$_2$, cymene), 2.26 (s, 6H, CH_3, cymene), 1.40 (s, 18H, C(CH_3)$_3$, isophthalate), 1.28 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$, cymene). ^{13}C NMR (50 MHz, CD_3CN/D_2O, 100:2): δ 173.3, 150.1, 135.2, 129.1, 128.0, 100.5, 96.8, 82.9, 80.1, 34.4, 31.1, 30.7, 21.5, 18.1. Anal. Calcd for $C_{44}H_{56}O_{10}Ru_2$: C, 55.80; H, 5.96. Found: C, 55.88l, H, 5.80. Single crystals of complex [(cymene)Ru(μ-$C_{12}H_{12}O_4$)(CH_3CN)]$_2$ (**10**) were obtained by the slow vapor diffusion of diethyl ether into a saturated solution of complex **9** in acetonitrile.

[{(Cymene)Ru(μ-$C_{12}H_{12}O_4$)}$_2$(μ-dpe)]$_2$ (11). A solution of complex **9** (28 mg, 30 μmol) and dpe (5.5 mg, 30 μmol) in chloroform (5 mL) was stirred for 2 h at 40 °C. The yellow product precipitated upon the addition of diethyl ether (15 mL) and was collected by filtration, washed with diethyl ether, and dried under vacuum (32 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96 (d, J = 7.0 Hz, 8H, NCH, dpe), 8.54 (s, 4H, CH, isophthalate), 8.29 (s, 8H, CH, isophthalate), 7.09 (d, J = 7.0 Hz, 8H, CH, dpe), 7.00 (s, 4H, C_2H_2, dpe), 6.32 (d, J = 6.0 Hz, 8H, CH, cymene), 5.55 (d, J = 6.0 Hz, 8H, CH, cymene), 2.60 (sept, J = 7.0 Hz, 4H, C*H*(CH_3)$_2$, cymene), 1.67 (s, 12H, CH_3, cymene), 1.43 (s, 36 H, C(CH_3)$_3$, isophthalate), 1.20 (d, J = 7.0 Hz, 24H, CH(C*H*$_3$)$_2$, cymene). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.7, 154.4, 149.3, 143.7, 134.7, 130.3, 129.4, 128.9, 97.7, 97.3, 89.1 (br), 34.8, 31.5, 31.3, 22.7, 18.2. Anal. Calcd for $C_{112}H_{124}N_4O_{16}Ru_4$·$CHCl_3$: C,

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58.86; H, 5.46; N, 2.43. Found: C, 58.97; H, 5.67; N, 2.59. Single crystals were obtained by the slow vapor diffusion of diethyl ether into a solution of complex **11** in chloroform.

[{(Cymene)Ru(μ-$C_8H_6O_7$)}$_6$(μ-4-tpt)$_2$] (12). A solution of complex **8** (40 mg, 42 μmol) and 4-tpt (8.7 mg, 28 μmol) in CH_2Cl_2 (24 mL) was stirred for 2 h at 41 °C. Subsequently, the solvent was reduced to 10 mL under reduced pressure. Complex **12** precipitated in the form of a dark-orange powder upon the addition of diethyl ether (30 mL) and pentane (20 mL). The precipitate was isolated, washed with diethyl ether (20 mL) and pentane (20 mL), and dried under vacuum (43 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.21 (d, J = 6.8 Hz, 12H, NCH), 8.21 (d, J = 6.8 Hz, 12H, CH), 6.30 (d, J = 6.0 Hz, 12H, CH, cymene), 5.74 (d, J = 6.0 Hz, 12H, CH, cymene), 4.11 (s, 36H, CH_3, furan), 2.68 (sept, J = 6.8 Hz, 6H, CH(CH_3)$_2$, cymene), 1.75 (s, 18H, CH_3, cymene), 1.21 (d, J = 6.8 Hz, 36H, CH(CH_3)$_2$, cymene). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 166.2, 155.5, 143.9, 142.4, 134.2, 123.2, 100.1, 96.4, 86.1, 78.3, 61.3, 31.1, 22.6, 18.1. Anal. Calcd for $C_{144}H_{144}N_{12}O_{42}Ru_6{\cdot}3CH_2Cl_2$: C, 49.37; H, 4.23; N, 4.70. Found: C, 48.96; H, 3.93; N, 4.84. Single crystals were obtained by the slow vapor diffusion of pentane into a solution of complex **12** in chloroform.

Coronene⊂12. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (d, J = 6.4 Hz, 12H, NCH, 4-tpt), 7.32 (s, 12H, CH, coronene), 6.66 (d, J = 6.4 Hz, 12H, CH, 4-tpt), 6.44 (br s, 12H, CH, cymene), 5.74 (br s, 12H, CH, cymene), 4.44 (s, 36H, CH_3, furan), 2.69 (br s, 6H, CH(CH_3)$_2$, cymene), 1.83 (br s, 18H, CH_3, cymene), 1.20 (d, J = 6.0 Hz, 36H, CH(CH_3)$_2$, cymene). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 165.7, 153.7, 144.5, 140.3, 134.4, 127.5, 125.8, 121.3, 120.3, 100.9 (br), 96.0 (br), 85.0 (br), 78.0 (br), 61.8, 31.0, 22.8, 17.7. Anal. Calcd for $C_{168}H_{156}N_{12}O_{42}Ru_6{\cdot}3CHCl_3$: C, 51.61; H, 4.03; N, 4.22. Found: C, 51.57; H, 4.25; N, 4.49. Single crystals were obtained by the slow vapor diffusion of pentane into a solution of coronene⊂**12** in chloroform.

[{(Cymene)Ru(μ-$C_{12}H_{12}O_4$)}$_6$(μ-4-tpt)$_2$] (13). A solution of complex **9** (28 mg, 30 μmol) and 4-tpt (6.2 mg, 20 μmol) in dichloromethane (15 mL) was stirred for 2 h at 40 °C. The red product precipitated upon the addition of hexane (15 mL) and was collected by filtration, washed with diethyl ether, and dried under vacuum (33 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.27 (d, J = 6.8 Hz, 12H, NCH, 4-tpt), 8.50 (s, 6H, CH, isophthalate), 8.35 (s, 12H, CH, isophthalate), 8.22 (d, J = 6.8 Hz, 12H, CH, 4-tpt), 6.34 (d, J = 5.6 Hz, 12H, CH, cymene), 5.58 (d, J = 5.6 Hz, 12H, CH, cymene), 2.56 (sept, J = 6.8 Hz, 6 H, CH(CH_3)$_2$, cymene), 1.63 (s, 18H, CCH_3, cymene), 1.49 (s, 54 H, C(CH_3)$_3$, isophthalate), 1.16 (d, J = 6.8 Hz, 36 H, CH(CH_3)$_2$, cymene). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.6, 169.8, 155.6, 149.0, 142.3, 134.4, 129.6, 129.1, 123.2, 97.7, 97.2, 89.7 (br), 34.8, 31.8, 31.3, 22.7, 18.1. Anal. Calcd for $C_{168}H_{180}N_{12}O_{42}Ru_6{\cdot}3CH_2Cl_2$: C, 56.85; H, 5.19; N, 4.65. Found: C, 57.01; H, 5.49; N, 4.89. Single crystals were obtained by the slow vapor diffusion of pentane into a solution of complex **13** in fluorobenzene.

Pyrene⊂13. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (s, 6H, CH, isophthalate), 8.75 (d, J = 6.0 Hz, 12H, NCH, 4-tpt), 8.55 (s, 12H, CH, isophthalate), 7.19 (d, J = 6.0 Hz, 12H, CH, 4-tpt), 6.56 (d, J = 5.0 Hz, 12H, CH, cymene), 6.00 (s, 4H, pyrene), 5.98 (d, J = 8.0 Hz, 4H, pyrene), 5.84 (t, J = 8.0 Hz, 4H, pyrene), 5.58 (d, J = 5.0 Hz, 12H, CH, cymene), 2.65 (sept, J = 7.0 Hz, 6H, CH(CH_3)$_2$, cymene), 1.63 (s, 54H, C(CH_3)$_3$, isophthalate), 1.38 (s, 18H, CH_3, cymene), 1.23 (d, J = 7.0 Hz, 36 H, CH(CH_3)$_2$, cymene).

Triphenylene⊂13. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (d, J = 7.0 Hz, 12H, NCH, tpt), 8.77 (s, 6H, CH, isophthalate), 8.52 (s, 12H, CH, isophthalate), 7.36 (d, J = 7.0 Hz, 12H, CH, 4-tpt), 6.58−6.53 (m, 18H, CH, cymene, triphenylene), 5.78 (dd, J = 6.0 and 3.0 Hz, 6H, triphenylene), 5.58 (d, J = 5.0 Hz, 12H, CH, cymene), 2.64 (sept, J = 6.0 Hz, 6 H, CH(CH_3)$_2$, cymene), 1.60 (s, 54H, C(CH_3)$_3$, isophthalate), 1.50 (s, 18H, CH_3, cymene), 1.21 (d, J = 6.0 Hz, 36 H, CH(CH_3)$_2$, cymene).

Coronene⊂13. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (s, 6H, CH, isophthalate), 8.65 (s, 12H, CH, isophthalate), 8.62 (d, J = 6.0 Hz, 12H, NCH, 4-tpt), 6.95 (s, 12H, coronene), 6.60 (d, J = 5.0 Hz, 12H, CH, cymene), 6.56 (d, J = 6.0 Hz, 12H, CH, 4-tpt), 5.54 (d, J = 5.0 Hz, 12H, CH, cymene), 2.67 (sept, J = 6.0 Hz, 6H, CH(CH_3)$_2$, cymene), 1.72 (s, 54H, C(CH_3)$_3$, isophthalate), 1.55 (s, 18H, CH_3, cymene), 1.24 (d, J = 6.0 Hz, 36H, CH(CH_3)$_2$, cymene).

[{(Cymene)Ru(μ-$C_8H_6O_7$)}$_6$(μ-3-tpt)$_2$] (14). A solution of complex **8** (40 mg, 42 μmol) and 3-tpt (8.7 mg, 28 μmol) in CH_2Cl_2 (20 mL) was stirred for 2 h at 41 °C. Subsequently, the solvent was reduced to 5 mL under reduced pressure. Complex **14** precipitated in the form of a yellow powder upon the addition of diethyl ether (10 mL) and pentane (20 mL). The precipitate was isolated, washed with diethyl ether (30 mL) and pentane (30 mL), and dried under vacuum (36 mg, 75%). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 9.89 (br s, 6H, NCH, 3-tpt), 9.06 (br d, J = 8.0 Hz, 6H, NCH, 3-tpt), 8.76 (d, J = 4.8 Hz, 6H, NCH, 3-tpt), 7.63 (dd, J = 8.0 and 5.6 Hz, 6H, CH, 3-tpt), 6.43 (br s, 6H, CH, cymene), 6.35 (br s, 6H, CH, cymene), 5.90 (br s, 6H, CH, cymene), 5.75 (br s, 6H, CH, cymene), 4.15 (s, 18H, CH_3, furan), 3.99 (s, 18H, CH_3, furan), 2.73 (br, 6H, CH(CH_3)$_2$, cymene), 1.74 (br s, 18H, CH_3, cymene), 1.25 (d, J = 6.8 Hz, 18H, CH(CH_3)$_2$, cymene), 1.21 (d, J = 6.8 Hz, 18H, CH(CH_3)$_2$, cymene). ^{13}C NMR (100 MHz, CD_2Cl_2, 298 K): δ 168.8, 165.9, 165.5, 156.4, 154.3, 143.9, 143.8, 139.2, 133.7, 133.4, 132.8, 126.7, 100.1 (br), 96.25 (br), 84.2 (br), 78.1 (br), 61.5, 61.3, 30.6, 22.5, 22.4, 17.9. Anal. Calcd for $C_{144}H_{144}N_{12}O_{42}Ru_6{\cdot}CH_2Cl_2{\cdot}H_2O$: C, 50.86; H, 4.36; N, 4.91. Found: C, 50.99; H, 4.84; N, 4.55. Single crystals were obtained by the slow vapor diffusion of pentane into a solution of complex **14** in dichloromethane/acetonitrile (1:1).

[{(Cymene)Ru(μ-$C_{12}H_{12}O_4$)}$_6$(μ-3-tpt)$_2$] (15). A solution of complex **9** (28 mg, 30 μmol) and 3-tpt (6.2 mg, 20 μmol) in CH_2Cl_2 (15 mL) was stirred for 2 h at 41 °C. Subsequently, the solvent was reduced to 5 mL under reduced pressure. Complex **15** precipitated in the form of a yellow powder upon the addition of diethyl ether (15 mL) and pentane (20 mL). The precipitate was isolated, washed with diethyl ether (30 mL) and pentane (30 mL), and dried under vacuum (30 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 10.32 (d, J = 1.6 Hz, 6H, NCH, 3-tpt), 9.54 (br d, J = 8.0 Hz, 6H, NCH, 3-tpt), 9.49 (d, J = 5.2 Hz, 6H, NCH, 3-tpt), 8.65 (br s, 3H, CH, isophthalate), 8.32 (d, J = 1.6 Hz, 6H, CH, isophthalate), 8.24 (br s, 3H, CH, isophthalate), 7.82 (dd, J = 8.0 and 5.6 Hz, 6H, CH, 3-tpt), 7.16 (d, J = 1.6 Hz, 6H, CH, cymene), 6.39 (d, J = 5.6 Hz, 6H, CH, cymene), 6.35 (d, J = 5.6 Hz, 6H, CH, cymene), 5.73 (d, J = 5.6 Hz, 6H, CH, cymene), 5.66 (d, J = 5.6 Hz, 6H, CH, cymene), 2.66 (sept, J = 6.8 Hz, 6H, CH(CH_3)$_2$, cymene), 1.75 (s, 18H, CH_3, cymene), 1.43 (s, 27H, C(CH_3)$_3$, isophthalate, 1.25 (m, 36H, CH(CH_3)$_2$, cymene), −0.67 (s, 27H, C(CH_3)$_3$, isophthalate). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 175.0, 174.6, 169.1 (2C), 158.0, 155.2, 149.8, 138.2, 135.6, 134.6, 132.1, 129.7, 128.34, 128.29, 127.9, 125.9, 98.0 (br), 96.5 (br), 87.1 (br), 34.8, 32.8, 31.5, 31.2, 28.7, 22.8, 18.3. Anal. Calcd for $C_{168}H_{180}N_{12}O_{24}Ru_6{\cdot}H_2O$: C, 59.77; H, 5.43; N, 4.98. Found: C, 59.44; H, 5.91; N, 4.83. Single crystals were obtained by the slow vapor diffusion of pentane into a solution of complex **15** in dichloromethane/1,2,4-trichlorobenzene (1:2).

Crystallographic Investigations. The relevant details of the crystals, data collection, and structure refinement can be found in Tables 1−3. Data collections for all compounds have been measured at low temperature using Mo Kα radiation. The equipment used were an Oxford Diffraction Sapphire/KM4 CCD (complexes **11**, **12**, and coronene⊂**12**) and a Bruker APEX II CCD (complexes **10** and **13**−**15**), both having κ geometry goniometers. Semiempirical[30] absorption correction was applied to all data sets. Structure solutions, refinements, and geometrical calculations have been carried out by *SHELXTL*.[31] All structures were refined using full-matrix least squares on F^2 with all non-H atoms anisotropically defined. The H atoms were placed in calculated positions using the "riding model" with U_{iso} = aU_{eq} (where a is 1.5 for −CH_3 and −OH moieties and 1.2 for others). The structures were all treated by the *SQUEEZE* algorithm[25] in order to remove the scattering contributions from very disordered solvent molecules (CH_3CN for **10**, $CHCl_3$ for **11**, **12**, **14**, **15**, and coronene⊂**12**, and C_6H_5F for **13**). In certain cases, disorder problems concerning *tert*-butyl and isopropyl moieties have been treated by resolving the group into two components and/or applying an extensive regime of

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Table 1. Crystallographic Data for Complexes 10−12

	10	**11**·15.5$CHCl_3$	**12**·8$CHCl_3$
empirical formula	$C_{48}H_{58}N_2O_8Ru_2$	$C_{127.5}H_{139.5}Cl_{46.5}N_4O_{16}Ru_4$	$C_{152}H_{152}Cl_{24}N_{12}O_{42}Ru_6$
mol wt/g mol^{-1}	993.10	4036.64	4276.09
cryst size/mm^3	0.38 × 0.22 × 0.13	0.20 × 0.15 × 0.10	0.41 × 0.18 × 0.15
cryst syst	monoclinic	orthorhombic	triclinic
space group	*I*2/*a*	*Pbca*	$P\bar{1}$
a/Å	12.089(2)	24.8929(10)	15.589(3)
b/Å	28.812(6)	27.2133(8)	17.849(4)
c/Å	14.424(4)	28.4169(12)	41.003(8)
α/deg	90	90	88.71(3)
β/deg	97.526(19)	90	89.42(3)
γ/deg	90	90	88.87(3)
volume/$Å^3$	4980.9(19)	19250.1(13)	11403(4)
Z	4	4	2(1)
density/g cm^{-3}	1.324	1.393	1.246
temperature/K	100(2)	140(2)	140(2)
abs coeff/mm^{-1}	0.656	1.002	0.729
Θ range/deg	3.40−27.54	2.49−26.37	2.25−23.53
index ranges	−15 → 15, 0 → 37, 0 → 18	0 → 31, 0 → 33, 0 → 35	−16 → 17, −20 → 20, −45 → 45
reflns collected	5722	19627	53282
abs corrn	semiempirical	semiempirical	none
max and min transmn	1.0000 and 0.6837	1.0000 and 0.90237	
data/restraints/param	5722/73/309	19627/120/924	31040/3167/1832
GOF on F^2	1.104	0.802	1.073
final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0588, w*R*2 = 0.1185	*R*1 = 0.0877, w*R*2 = 0.2097	*R*1 = 0.1186, w*R*2 = 0.2097
R indices (all data)	*R*1 = 0.0778, w*R*2 = 0.1257	*R*1 = 0.2194, w*R*2 = 0.2447	*R*1 = 0.1588, w*R*2 = 0.3437
largest diff peak and hole/e $Å^{-3}$	1.573 and −1.308	1.562 and −0.762	1.460 and −0.802

Table 2. Crystallographic Data for Complexes 13−15

	13	**14**·5CH_2Cl_2·2$CHCl_3$·2MeCN	**15**·$CHCl_3$
empirical formula	$C_{168}H_{180}N_{12}O_{24}Ru_6$	$C_{157}H_{162}Cl_{16}N_{14}O_{42}Ru_6$	$C_{169}H_{181}Cl_3N_{12}O_{24}Ru_6$
mol wt/g mol^{-1}	3357.66	4066.61	3477.03
cryst size/mm^3	0.51 × 0.41 × 0.37	0.42 × 0.35 × 0.34	0.35 × 0.33 × 0.32
cryst syst	orthorhombic	triclinic	trigonal
space group	$P2_12_12$	$P\bar{1}$	*P*31*c*
a/Å	26.992(8)	19.045(3)	21.122(2)
b/Å	21.207(5)	19.277(3)	21.122(2)
c/Å	22.203(6)	29.182(5)	24.400(6)
α/deg	90	72.488(12)	90
β/deg	90	80.260(14)	90
γ/deg	90	60.829(10)	120
volume/$Å^3$	12709(6)	8918(3)	9427(3)
Z	2	2(1)	2(1/3)
density/g cm^{-3}	0.877	1.514	1.225
temperature/K	100(2)	100(2)	100(2)
abs coeff/mm^{-1}	0.392	0.812	0.572
Θ range/deg	3.36−24.00	3.10−22.00	3.06−27.50
index ranges	−30 → 30, 0 → 24, 0 → 25	−20 → 20, −20 → 20, −30 → 30	−27 → 27, −27 → 27, −31 → 31
reflns collected	19407	75630	157317
abs corrn	semiempirical	semiempirical	semiempirical
max and min transmn	0.865 and 0.610	0.744 and 0.638	0.745 and 0.680
data/restraints/param	19407/90/957	20743/2084/2089	14424/181/704
GOF on F^2	1.074	1.053	1.026
final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0678, w*R*2 = 0.1765	*R*1 = 0.0833, w*R*2 = 0.1845	*R*1 = 0.0497, w*R*2 = 0.1199
R indices (all data)	*R*1 = 0.0977, w*R*2 = 0.1975	*R*1 = 0.1313, w*R*2 = 0.2088	*R*1 = 0.0646, w*R*2 = 0.1291
largest diff peak and hole/e $Å^{-3}$	1.338 and −0.735	1.471 and −1.196	0.611 and −1.057

restraints. Concerning the latter, typically 1,2 and 1,3 distances were restrained (DFIX and/or SAME) to appropriate target values obtained from an analogous fragment in the CSD, while atoms making up cyclic aromatic groups were restrained to be coplanar (FLAT). Where data were of sufficient quality to refine anisotropic displacement parameters, displacement parameter restraints (SIMU and ISOR) were liberally applied to all light atoms. For coronene⊂**12**, only the Ru and Cl atoms were refined with anisotropic displacement parameters. For

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Table 3. Crystallographic Data for Coronene⊂12

	coronene⊂12
empirical formula	$C_{168}H_{156}N_{12}O_{42}Ru_6 \cdot 13CHCl_3$
mol wt/g mol^{-1}	5173.25
cryst size/mm^3	0.42 × 0.35 × 0.32
cryst syst	monoclinic
space group	$P2_1/c$
a/Å	31.172(6)
b/Å	41.914(8)
c/Å	35.082(7)
α/deg	90
β/deg	90.59(3)
γ/deg	90
volume/Å^3	45834(16)
Z	8
density/g cm^{-3}	1.499
temperature/K	140(2)
abs coeff/mm^{-1}	0.909
Θ range/deg	2.09 to 23.93
index ranges	−34 → 34, −47 → 47, −39 → 39
reflns collected	66671
abs corrn	semiempirical
max and min transmn	0.865 and 0.610
data/restraints/param	66671/4354/2294
GOF on F^2	0.934
final R indices [$I > 2\sigma(I)$]	$R1$ = 0.1156, $wR2$ = 0.3010
R indices (all data)	$R1$ = 0.2154, $wR2$ = 0.3544
largest diff peak and hole/e Å^{-3}	1.460 and −0.802

complexes **11** and coronene⊂**12**, a large amount of solvent was located and fully treated, although some restraints (SIMU and DFIX cards) were used in order to control the geometry and anisotropy.

■ ASSOCIATED CONTENT

Supporting Information

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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Notes

The authors declare no competing financial interest.

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