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Polynuclear Architectures with Di- and Tricarbene Ligands

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Supporting Information

ABSTRACT: The 1,3,5-triimidazolium-substituted benzene cation in H₃-1(PF₆)₃ reacts with Hg(OAc)₂ to yield the cylinder-like trinuclear hexacarbene complex $[Hg_3(1)_2](PF_6)_6$. Reaction of imidazole with 1,4-dibromobenzene gives 1,4-bis(1-imidazo-lyl)benzene (2), which after dialkylation with ethyl bromide and salt metathesis yields the new diimidazolium salt H₂-3(PF₆)₂. Two equivalents of H₂-3(PF₆)₂ react with 2 equiv of Ag₂O to give the dinuclear Ag¹ tetracarbene complex $[Ag_2(3)_2](PF_6)_2$, which after transmetalation with $[AuCl(SMe_2)]$ yields the Au¹ tetracarbene complex $[Au_2(3)_2](PF_6)_2$. In contrast to the formation of the tetracarbene complexes of type $[M_2(3)_2]^{2+}$ (M = Ag^I, Au¹),



the diimidazolium salt H_2 -3(PF₆)₂ reacts with Hg(OAc)₂ to yield the dinuclear Hg^{II} dicarbene complex [Hg₂(OAc)₂(3)](PF₆)₂, where each mercury center is coordinated by one carbene carbon atom and one acetate oxygen atom. The crystal structure of [Hg₂(OAc)₂(3)](PF₆)₂ reveals that the complex forms a coordination polymer via intra- and intermolecular acetate bridges between Hg^{II} centers.

1. INTRODUCTION

N-heterocyclic carbenes have emerged as an important class of compounds over the last two decades, due to their utility as ligands in organometallic chemistry¹ and as nucleophiles and bases in organocatalysis.² NHC complexes have been used in different fields such as homogeneous catalysis³ and materials science⁴ and as biologically active compounds.⁵ Very recently, poly-NHC ligands have been employed as building blocks for the construction of three-dimensional metallosupramolecular structures of type [A]⁴⁺ (Figure 1) and related assemblies.⁶ Due to the high stability of selected M-C_{NHC} bonds compared to M-N/O bonds, it is conceivable that such three-dimensional organometallic frameworks (OMFs) featuring only M-C_{NHC} bonds could develop into superior types of host molecules for the encapsulation and catalytic transformation of selected substrates in comparison to related structures built from Werner-type metal complexes.

In addition to the structures of type $[A]^{4+}$, molecular rectangles of types $[B]^{4+}$ and $[C]^{4+}$ featuring a mixed donor set of rigid ditopic benzobis-NHC ligands and 4,4'-bipyridine or diphosphine ligands^{7a-c} and related structures have also been described.^{7d,e} Even macrocyclic ligands featuring NHC donor groups have been used for the construction of three-dimensional metallosupramolecular structures.⁸

Even though a mercury(II) complex was among the first complexes to be isolated bearing N-heterocyclic carbenes,⁹ mercury(II) NHC complexes belong to the less studied derivatives among the large variety of NHC metal complexes known today. Complexes of the type $[Hg^{II}(NHC)_2](CIO_4)_2$ were first prepared by the reaction of imidazolium perchlorates with $Hg(OAc)_2$.⁹ Almost



Figure 1. Selection of metallosupramolecular structures featuring $M{-}C_{\rm NHC}$ bonds.

all mercury(II) NHC complexes synthesized thereafter have been prepared from an azolium starting material and Hg(OAc)₂

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Figure 2. Examples of mononuclear $([D]^{2+})$ and dinuclear $([E]^{4+})$ Hg^{II} NHC complexes.



Figure 3. Di- and triimidazolium salts.

using a one-pot synthesis.^{10–14} Most of these mercury(II) NHC complexes are mononuclear with two NHC donors coordinated to a Hg center in a linear arrangement such as that found in $[\mathbf{D}]^{2+}$ (Figure 2),^{10–14} although some dinuclear Hg^{II} NHC complexes of type $[\mathbf{E}]^{4+}$ have been reported.¹²

Apart from complexes of type $[\mathbf{E}]^{4+}$, polynuclear mercury(II) NHC complexes are largely unknown. We became interested in the synthesis of such polynuclear Hg^{II} complexes from in situ generated poly-NHC ligands. Herein we report the synthesis and characterization of a trinuclear Hg^{II} complex from the tricarbene precursor H₃-1(PF₆)₃. In addition, we studied the coordination chemistry of the dicarbene ligand obtained from H₂-3(PF₆)₂ with Ag^I, Au^I, and Hg^{II} (Figure 3).

2. RESULTS AND DISCUSSION

2.1. Synthesis of Imidazolium Salts. We have previously described the preparation of the triimidazolium salt⁶ H_3 -1(PF₆)₃, which we intended to use for the preparation of trinuclear mercury(II) complexes. 1,4-Bis(1-imidazolyl)benzene (**2**) was obtained from the copper(I)-catalyzed reaction of imidazole with 1,4-dibromobenzene using the reported protocol.¹⁵ The diimidazolium salt H_2 -3(Br)₂ was synthesized by dialkylation of **2** with ethyl bromide and was obtained as a colorless solid in an excellent yield of 88% (Scheme 1). The compound H_2 -3(Br)₂ can be converted into H_2 -3(PF₆)₂ by reaction with NH₄PF₆. Methanol proved the ideal solvent for this metathesis reaction, since the starting materials H_2 -3(Br)₂ and NH₄PF₆ and the byproduct NH₄Br are soluble in MeOH, whereas the desired salt H_2 -3(PF₆)₂ is insoluble in MeOH and can thus be isolated by a simple filtration.

The ¹H NMR spectrum of H₂-3(Br)₂ in [D₆]DMSO shows the characteristic resonance for the imidazolium C2-H protons at δ 10.10 ppm. The corresponding signal was observed slightly upfield at δ 8.97 ppm for H₂-3(PF₆)₂ (in CD₃CN), which is





consistent with previous observations upon anion exchange.¹⁶ The imidazolium C4-H and C5-H protons were observed as pseudotriplets due to coupling of the C5-H/C4-H protons (${}^{3}J_{\rm H,H}$ = 1.9 Hz) and the C2-H proton (${}^{4}J_{\rm H,H}$ = 1.5 Hz). The imidazolium C2-H proton was also observed as a pseudotriplet (${}^{4}J_{\rm H,H}$ = 1.5 Hz), but this resonance is not well resolved due to the low ${}^{4}J_{\rm H,H}$ coupling constant. The ${}^{13}C\{{}^{1}H\}$ NMR spectrum of H₂-3(PF₆)₂ features the imidazolium C2 signal at δ 137.0 ppm, which is a typical value for this resonance. 1c,6a,6b The salt H₂-3(PF₆)₂ was also identified by ESI mass spectrometry (positive ions), showing peaks at m/z 413.1319 (calcd 413.1324) and 134.0870 (calcd 134.0844) for the molecular ions [H₂-3(PF₆)]⁺ and [H₂-3]²⁺, respectively.

Single crystals of H_2 -3(PF₆)₂ suitable for an X-ray structure determination have been grown by slow diffusion of diethyl ether into a saturated acetonitrile solution of the compound at ambient temperature. Figure 4 depicts the molecular structure of H_2 -3(PF₆)₂. The asymmetric unit contains a half of the formula unit of the compound related to the other half by a crystallographic inversion center. Important bond parameters in the diimidazolium cation fall in the range observed previously for imidazolium cations.^{1c,6b,16} In the solid-state structure of H_2 -3(PF₆)₂, the PF₆⁻ counterions are engaged in nonclassical hydrogen bonding¹⁶ interactions with the ring protons H7 and H3, with H7 · · · F2 and $H3 \cdots F3$ distances of 2.464 and 2.304 Å, respectively (Figure 4). The orientation of the imidazolium units with respect to the central phenyl ring appears to be influenced by these nonclassical hydrogen bonds, and the upfield shift of the imidazolium N-CH-N proton of H₂-3(PF₆)₂ compared to H₂-3(Br)₂ is most likely caused by the lack of hydrogen bonds involving the N-CH-N proton in H_2 -3(PF₆)₂.

2.2. Synthesis of a Trinuclear Mercury(II) Hexacarbene Complex. For the synthesis of a trinuclear mercury(II) hexacarbene complex, 2 equiv of the triimidazolium salt H_3 -1(PF₆)₃ was reacted with 3 equiv of Hg(OAc)₂ to give [Hg₃(1)₂](PF₆)₆ in 60% yield (Scheme 2). The reaction was carried out in refluxing



Figure 4. Molecular structure of H_2 -3(PF₆)₂ (ball and stick model) showing the nonclassical hydrogen bonding interaction of the PF₆⁻ counterions with protons H3 and H7 (H3···F3 = 2.304 Å and H7···F2 = 2.464 Å). Hydrogen atoms, except for those engaged in nonclassical hydrogen bonds and H1/H1*, have been omitted for clarity. Selected bond lengths (Å) and angles (deg): N1–C1 = 1.326(2), N2–C1 = 1.337(2); N1–C1–N2 = 108.68(15).

Scheme 2. Synthesis of the Trinuclear Hg^{II} Hexacarbene Complex $[Hg_3(1)_2](PF_6)_6$



CH₃CN and took 4 days for completion. The reaction time can be shortened by the addition of an external base such as NaOAc. The use of the hexafluorophosphate salt is beneficial here, as $[Hg_3(1)_2](PF_6)_6$ is insoluble in water and residual $Hg(OAc)_2$ can thus be removed by washing with water. Complex $[Hg_3(1)_2](PF_6)_6$ was isolated as an air-stable white solid which exhibits good solubility in organic solvents such as CH₃CN, acetone, and DMF, whereas it is less soluble in solvents such as MeOH, CH₂Cl₂, and Et₂O.

Formation of $[Hg_3(1)_2](PF_6)_6$ was indicated by the disappearance of the imidazolium C2 proton resonance in the ¹H NMR spectrum together with the appearance of a resonance at δ 174.3 ppm for the Hg^{II}-bound carbene carbon atom in the ¹³C{¹H} NMR spectrum.^{11,14} The remainder of the ¹H and ¹³C{¹H} resonances for the complex are in the range previously described for mercury(II) dicarbene complexes of the type $[Hg(NHC)_2]^{2+9,10}$

The molecular structure of the complex was established by an X-ray diffraction analysis. Crystals of $[Hg_3(1)_2](PF_6)_6 \cdot SCH_3CN$ were grown by slow diffusion of diethyl ether into a saturated acetonitrile solution of the compound at ambient temperature. The structure analysis confirmed the formation of a trinuclear complex where each mercury(II) ion is coordinated by two carbene carbon atoms from two different ligands (Figure 5). For both tricarbene ligands the planes of the NHC donors are rotated



Figure 5. Molecular structure of the hexacation $[Hg_3(1)_2]^{6+}$ (50% probability ellipsoids) in $[Hg_3(1)_2](PF_6)_6 \cdot 5CH_3CN$. Hydrogen atoms and solvent molecules have been omitted for clarity, and only the first atom of each of the *N*-ethyl substituents is depicted. Selected bond lengths (Å) and angles (deg): Hg-C_{NHC} = 2.050(10)-2.072(11); C_{NHC}-Hg-C_{NHC} = 173.6(4)-177.9(4), N-C_{NHC}-N = 104.7(9)-106.7(10).

out of the plane of the central phenyl ring. However, the NHC ring planes are not oriented perpendicularly with respect to the central phenyl ring; instead, all NHC donor planes are rotated in an anticlockwise direction from an imaginary perpendicular orientation with respect to the central phenyl. The resulting torsion angles between the NHC planes and the plane of the central phenyl ring range from $-51.322(15)^\circ$ to $-65.066(15)^\circ$. These torsion angles are large when compared to the equivalent angles observed for trinuclear complexes of the same tricarbene ligand with coinage metals (Ag^I, Cu^I, Au^I),⁶ resulting in an increased distance of 4.978 Å between the centroids of two phenyl rings.

The dihedral angles between two imidazolin-2-ylidene units coordinated to the same mercury(II) ion are 40.26, 42.44, and 44.35°. The coordination geometry around the mercury(II) centers is almost linear, with the $C_{\rm NHC}$ –Hg– $C_{\rm NHC}$ bond angles in the range 173.6(4)–177.9(4)°. These values, like the Hg– $C_{\rm NHC}$ bond distances (range 2.050(10)–2.072(11) Å), fall in the range previously reported for complexes of the type [Hg(NHC)₂]^{2+,10–14} The three mercury atoms form a distorted triangle with nonbonding Hg···Hg distances in the range 6.00–6.29 Å.

2.3. Synthesis of Dinuclear Ag¹ and Au¹ Tetracarbene Complexes. Basic Ag₂O was selected for the deprotonation of the imidazolium C2 carbon atoms in H₂-3(PF₆)₂. The Ag₂O method works for most imidazolium salts, giving the silver(I) NHC complexes in high yield.¹⁷ Reaction of equimolar amounts of H₂-3(PF₆)₂ and Ag₂O gave the disilver(I) tetracarbene complex [Ag₂(3)₂](PF₆)₂ (Scheme 3). The reaction was complete after 20 h at 55 °C in acetonitrile and gave [Ag₂(3)₂](PF₆)₂ as a slightly light sensitive white solid in 93% yield.

Formation of the carbene complex was detected by NMR spectroscopy. While the signal of the acidic imidazolium proton of H₂-3(PF₆)₂ (δ 8.97 ppm) was absent in the ¹H NMR spectrum, a new resonance at δ 180.6 ppm for the carbene carbon atom appeared in the ¹³C{¹H} NMR spectrum of [Ag₂(3)₂](PF₆)₂. No ¹³C-^{207/209}Ag coupling^{8a,18} was observed, which could be attributed to exchange processes which can take place in solutions of Ag¹–NHC complexes.¹⁹

In the ¹H NMR spectrum of $[Ag_2(3)_2](PF_6)_2$, the imidazole C4-H and C5-H proton signals were observed as doublets with a ³*J* coupling constant of 1.9 Hz, whereas these protons gave rise to pseudotriplets in the imidazolium salt H₂-3(PF₆)₂, due to coupling of these protons with the C2 imidazolium proton. This





observation can also be taken as an indication for the formation of a carbene complex. Additional NMR spectroscopic data for $[Ag_2(3)_2](PF_6)_2$ fall in the range of those in previous reports for $[Ag(NHC)_2]^+$ complexes.^{6,17} The HR-ESI mass spectrum (positive ions) of $[Ag_2(3)_2](PF_6)_2$ shows a signal at m/z374.0575 (calcd 374.0575) corresponding to the molecular fragment $[Ag_2(3)_2]^{2+}$ as the peak of highest intensity, which indicates the formation of a dinuclear tetracarbene complex.

Formation of monocarbene silver(I) complexes of the type $[Ag_2(L)_2(3)]$ was not observed during the synthesis of $[Ag_2(3)_2](PF_6)_2$, although dinuclear complexes of this type have been obtained in reactions of diimidazolium salts with Ag_2O .²⁰ A disilver(I) tetracarbene complex similar to $[Ag_2(3)_2](PF_6)_2$ has also been obtained via the Ag_2O method from a naphthalene bridged diimidazolium salt.²¹

Reaction of 1 equiv of $[Ag_2(3)_2](PF_6)_2$ with 2 equiv of [AuCl(SMe₂)] at ambient temperature gives an excellent yield of 89% of the transmetalation product $[Au_2(3)_2](PF_6)_2$ as a white powder (Scheme 3). Related transmetalation reactions of polynuclear polycarbene complexes with retention of the overall complex structure have been described.⁶ NMR spectroscopy did not unequivocally demonstrate the formation of the gold(I) carbene complex, as the ${}^{13}C{}^{1}H$ NMR spectrum showed the resonance for the carbon carbon atom only marginally shifted at δ 182.1 ppm compared to the equivalent resonance for $[Ag_2(3)_2](PF_6)_2$ (δ 180.6 ppm). The same is true for all additional NMR spectroscopic data, which are essentially identical for $[Au_2(3)_2](PF_6)_2$ and $[Ag_2(3)_2](PF_6)_2$. Formation of $[Au_2(3)_2](PF_6)_2$ was finally confirmed by ESI mass spectrometry, which showed peaks for the molecular fragments $[Au_2(3)_2(PF_6)]^+$ $(m/z \ 1071.2054)$ and $[Au_2(3)_2]^{2+}$ $(m/z \ 463.1189)$.



Figure 6. Molecular structure of the dication $[Au_2(3)_2]^{2+}$ (50% probability ellipsoids) in $[Au_2(3)_2](PF_6)_2$. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Au1-C1 = 2.034(8), Au1-C17 = 2.015(7), Au2-C10 = 2.026(8), Au2-C26 = 2.041(8); C1-Au1-C17 = 173.6(3), C10-Au2-C26 = 171.8(3), N1-C1-N2 = 105.7(7), N3-C10-N4 = 104.9(6), N5-C17-N6 = 104.1(6), N7-C26-N8 = 106.3(7).

Crystals of $[Au_2(3)_2](PF_6)_2$ were grown by slow diffusion of diethyl ether into a saturated solution of the complex in acetonitrile. The X-ray structure analysis (Figure 6) confirmed the conclusions drawn from the MS data. The Au–C_{NHC} bond lengths (2.015(7)-2.041(8) Å) fall in the typical range for $[Au(NHC)_2]^+$ complexes.^{6,18} The C_{NHC}–Au–C_{NHC} bond angles $(171.8(3) \text{ and } 173.6(3)^\circ)$ deviate only slightly from linearity. The dihedral angles between two imidazolin-2-ylidene donors coordinated to the same gold(I) ions measure 9.81 and 6.34°. Only few digold(I) tetracarbene complexes of the structural type found in $[Au_2(3)_2]^{2+}$ have been described. Among those are the dinuclear complexes with two naphthalene bridged di-NHC ligands²¹ and two 1,3-phenylene-bridged triazolin-5-ylidenes.²²

The two phenyl rings in $[Au_2(3)_2]^{2+}$ are not oriented in a coplanar fashion. They are rotated in opposite directions from an imaginary parallel orientation. This behavior brings one portion from each of the two phenyl rings (atoms C8 and C9 of the top phenyl ring and atoms C24 and C25 of the bottom phenyl ring; Figure 6) closer together (C8–C24 = 3.882 Å and C9–C25 = 3.853 Å), whereas the other parts (C5, C6 and C21, C22) of the two phenyl rings move apart from each other (C5-C21 = 7.254 Å)and C6-C22 = 7.285 Å). The complex cations $[Au_2(3)_2]^{2+}$ form an infinite layered structure via nonclassical hydrogen-bonding interactions between the hexafluorophosphate anions and the $[Au_2(3)_2]^{2+}$ cations and $\pi \cdots \pi$ interactions between phenyl rings from neighboring cations (Figure 7). In this layered structure, the two phenyl rings from two different $[Au_2(3)_2]^{24}$ cations are arranged in a coplanar fashion with an intermolecular transannular separation of 4.005 Å. In addition, one PF_6^- anion links four $[Au_2(3)_2]^{2+}$ cations via nonclassical hydrogen bonds.

2.4. Synthesis of a Dinuclear Mercury(II) Dicarbene Complex. Almost all mercury(II) NHC complexes described contain the Hg(NHC)₂ unit,¹¹⁻¹⁴ where each mercury center is coordinated by two NHC donors. We have now found that the deprotonation of the imidazolium groups in H₂-3(PF₆)₂ with Hg(OAc)₂ leads to the formation of a different type of mercury(II) NHC complex, [Hg₂(OAc)₂(3)](PF₆)₂, where each mercury atom is coordinated by one NHC and one acetate donor instead of two NHC donors (Scheme 4). The literature contains only one other example of this type of mercury coordination



Figure 7. Perspective view of the coordination polymer obtained from $[Au_2(3)_2]^{2+}$ and PF_6^- anions (ball and stick model). Hydrogen atoms, except for those involved in nonclassical hydrogen-bonding interactions, have been omitted for clarity.

Scheme 4. Synthesis of the Dinuclear Mercury(II) Complex [Hg₂(OAc)₂(3)](PF₆)₂



chemistry,^{12a} where the $[Hg^{II}(OAc)(NHC)]^+$ complex is an intermediate in the reaction leading to the $[Hg(NHC)_2]^{2+}$ complex. In the reaction of H_2 -3(PF₆)₂ with Hg(OAc)₂ [Hg₂(OAc)₂(3)](PF₆)₂ is the final reaction product and no dinuclear tetracarbene complex of type $[Hg_2(3)_2]^{4+}$ featuring Hg(NHC)₂ units has been observed.

The reaction of 1 equiv of H_2 -3(PF₆)₂ with 2.3 equiv of $Hg(OAc)_2$ in DMF (100 °C, 36 h) was found to be optimal for the preparation of $[Hg_2(OAc)_2(3)](PF_6)_2$. The reaction of H_2 -3(PF₆)₂ with less than 2 equiv of $Hg(OAc)_2$ always gave a mixture of products containing mainly $[Hg_2(OAc)_2(3)](PF_6)_2$ along with H_2 -3(PF₆)₂. The need to use more than 2 equiv of $Hg(OAc)_2$ indicates the high tendency of H_2 -3(PF₆)₂ to yield $[Hg_2(OAc)_2(3)](PF_6)_2$ rather than the tetracarbene complex $[Hg_2(3)_2](PF_6)_4$, which would only require the use of equimolar amounts of H_2 -3(PF₆)₂ and $Hg(OAc)_2$. $[Hg_2(OAc)_2(3)](PF_6)_2$ was isolated as a slightly hygroscopic white solid which is soluble in solvents such as acetonitrile, acetone, and DMF and almost insoluble in dichloromethane, THF, or MeOH.

[Hg₂(OAc)₂(3)](PF₆)₂ was characterized by NMR spectroscopy, mass spectrometry, elemental analysis, and single-crystal X-ray crystallography. The ¹H NMR spectrum, as expected, shows no resonances for the C2-H imidazolium protons of H₂-3(PF₆)₂, and the ¹³C{¹H} NMR spectrum exhibits a new signal at δ 163.9 ppm for the carbene carbon atom. The resonance at δ 177.2 ppm, which falls in the range reported for the mercury(II)bound carbene carbon atoms, ^{11,13,14} was assigned to the acetate (C(O)O) carbon atom on the basis of 2D correlation spectra. In the ¹H NMR spectrum the signals for the protons bound to the



Figure 8. Molecular structure of the dication $[Hg_2(OAC)_2(3)]^{2+}$ (50% probability ellipsoids) in $[Hg_2(OAC)_2(3)](PF_6)_2 \cdot 1.5CH_3OH$. Hydrogen atoms and noncoordinated solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Hg1-C1 = 2.052(7), Hg1-O22 = 2.069(5), Hg1-O21 = 2.589(7), Hg1 \cdot \cdot \cdot O25 = 2.715(5), N1-C1 = 1.343(9), N2-C1 = 1.337(9), O22-C22 = 1.304(10), O23-C22 = 1.233(10), Hg2-C9 = 2.017(8), Hg2-O24 = 2.031(5), N3-C9 = 1.335(10), N4-C9 = 1.363(9), O24-C24 = 1.315(9), O25-C24 = 1.217(9); C1-Hg1-O22 = 171.5(2), N1-C1-N2 = 106.8(6), C9-Hg2-O24 = 174.5(3), N3-C9-N4 = 105.5(7).

imidazole C4 and C5 atoms appear as doublets with a ${}^{3}J$ coupling constant of 1.9 Hz at δ 8.06 and 8.14 ppm, respectively. The remaining 1 H and 13 C{ 1 H} NMR spectroscopic data for [Hg₂(OAc)₂(3)](PF₆)₂ fall in the range previously reported for similar compounds. ${}^{10-14}$ The MALDI mass spectrum of [Hg₂(OAc)₂(3)](PF₆)₂ exhibits peaks at m/z = 1076, 930, and 785 for the molecular fragments [Hg₂(OAc)₂(3)(PF₆)₂]⁺, [Hg₂(OAc)₂(3)(PF₆)]⁺, and [Hg₂(OAc)₂(3) – H]⁺, respectively.

The connectivity in complex $[Hg_2(OAc)_2(3)](PF_6)_2$ was unambiguously established by an X-ray diffraction analysis of single crystals grown by slow diffusion of diethyl ether into a acetonitrile/methanol solution of the complex at room temperature. The X-ray diffraction analysis of $[Hg_2(OAc)_2(3)]$ - $(PF_6)_2 \cdot 1.5CH_3OH$ (Figure 8) shows that each mercury(II) ion is coordinated by an acetate oxygen atom and a carbene carbon atom in an almost linear fashion (angles $C_{\rm NHC}$ –Hg– $O_{\rm acetate} =$ 171.5(2) and 174.5(3)°). The Hg– $C_{\rm NHC}$ (range 2.017(8) and 2.052(7) Å)^{11,12} and Hg– $O_{\rm acetate}$ (2.069(5)–2.031(5) Å)^{12a} bond lengths fall in the ranges previously reported for such bonds. In addition, Hg1 is coordinated by a methanol molecule (Hg1–O21 = 2.589(7) Å) and the second oxygen atom of the



Figure 9. Perspective drawing (ball and stick model) of the 1D coordination polymer formed by the dication $[Hg_2(OAc)_2(3)]^{2+}$. Hydrogen atoms and solvent molecules have been omitted for clarity.



Figure 10. View of the supramolecular 1D helical chain of $[Hg_2(OAc)_2-(3)]^{2+}$ cations.

acetate anion coordinating to Hg2 (Hg1 \cdots O25 = 2.715(5) Å). The two imidazolin-2-ylidene rings are not coplanar with the phenyl ring. They are rotated out of the phenyl ring plane by about 80°.

The $[Hg_2(OAc)_2(3)]^{2+}$ dications form indefinite helical chains in the solid state by an intermolecular interaction of oxygen atom O23 with atom Hg2 of a neighboring dinuclear dication (Hg2···O23* = 2.581(6) Å). The resulting helical polymer is depicted in Figure 9. This interaction leads to Hg^{II} ions with differing coordination numbers (CN = 4 for Hg1, CN = 3 for Hg2).

The acetate anions act as intramolecular (O24-C24-O25)and intermolecular (O22-C22-O23) bridges. The resulting intramolecular and intermolecular Hg····Hg distances were found to be 5.387 and 5.094 Å, respectively. An interesting feature is the helical arrangement of the dications in the solid state (Figure 10). The hexafluorophosphate counterions maintain nonclassical hydrogen-bonding interactions with cations from neighboring helical chains with the H···F distances ranging from 2.30 to 2.50 Å thereby holding two adjacent helical chains together. The reasons for the stability of a complex featuring $[Hg(OAc)-(NHC)]^+$ coordination are not completely clear at this time. We assume that a combination of steric and electronic parameters leads to the observed stability. Electronically, the presence of the acetate anion leads to a complex with a reduced 1+ charge in comparison to the classical $[Hg(NHC)_2]^{2+}$ complexes. In addition, the formation of a polymer made up from $[Hg_2(OAC)_2(3)]^{2+}$ building blocks does contribute to the stability of the complex.

3. CONCLUSIONS

We have shown that di- and tricarbene ligands in the presence of linearly coordinated metal ions (Ag^I, Au^I, and Hg^{II}) can be utilized as building blocks for the generation of metallosupramolecular architectures. Such structures, exclusively held together by $M-C_{NHC}$ bonds, could serve as a new type of molecular host for the encapsulation of selected substrates or anions. The trinuclear hexacarbene complex $[Hg_3(1)_2](PF_6)_6$ was obtained from the salt H_3 -1(PF₆)₃ and mercury(II) acetate. The cylinderlike complex cation $[Hg_3(1)_2]^{6+}$, however, does not possess a cavity large enough for the encapsulation of multiatom substrates. Anion encapsulation was also not detected, which most likely is caused by the use of the large PF_6^- anions. The dicarbene ligand 3 obtained from the diimidazolium salt H_2 -3(PF₆)₂ reacts with Ag¹ ions to give the dinuclear tetracarbene complex $[Ag_2(3)_2](PF_6)_2$, which undergoes transmetalation with [AuCl(SMe₂)] to yield the Au¹ tetracarbene complex $[Au_2(3)_2](PF_6)_2$. In contrast to this, the diimidazolium salt H_2 -3(PF₆)₂ reacts with Hg(OAc)₂ under formation of complex $[Hg_2(OAc)_2(3)](PF_6)_2$, featuring the rare Hg(OAc)(NHC) coordination. The dinuclear complex $[Hg_2(OAc)_2(3)](PF_6)_2$ forms a helical coordination polymer in the solid state via intra- and intermolecular acetate bridges between the mercury atoms.

4. EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under an argon atmosphere using standard Schlenk techniques or in a glovebox. Glassware was oven-dried at 130 °C. Solvents were freshly distilled by standard procedures prior to use. ¹H and ¹³C{¹H} NMR spectra were recorded on Bruker AC 200, Bruker AVANCE I 400, and Bruker AVANCE III 400 spectrometers. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent as an internal standard. All coupling constants are expressed in hertz and are only given for ¹H–¹H couplings unless mentioned otherwise. Mass spectra were obtained with MicroTof (Bruker Daltonics, Bremen), Quattro LCZ (Waters-Micromass, Manchester, U.K.), Bruker Reflex IV, and Varian MAT 212 spectrometers. The compounds H₃-1(PF₆)₃,⁶⁶ 1,4-bis(1-imidazolyl)benzene,¹⁵ and [AuCl(SMe₂)]²³



Figure 11. Assignment of NMR resonances.

were prepared as described. Imidazole, 1,4-dibromobenzene, *N*,*N*-dimethylglycine hydrochloride, ethyl bromide, NH₄PF₆, Ag₂O, and Hg(OAc)₂ were purchased from commercial sources and were used as received without further purification. For assignment of the NMR resonances, see Figure 11. In accord with previous observations, consistent micronalytical data could not be obtained for most of the complexes containing PF₆⁻ anions, due to the large amount of fluorine present. The purity of these compounds was established by a full NMR spectroscopic (¹H, ¹³C) and HRMS characterization.

Synthesis of 1,4-Bis(1-imidazolyl)benzene (2).¹⁵. A mixture composed of CuI (0.78 g, 4.1 mmol), N,N-dimethylglycine hydrochloride (1.12 g, 8.02 mmol), K2CO3 (11.1 g, 80.3 mmol), 1,4-dibromobenzene (4.72 g, 20.0 mmol), and imidazole (3.4 g, 49.9 mmol) in 50 mL of DMSO was heated to 110 °C for 48 h. The reaction mixture was then partitioned between water and ethyl acetate. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic phases were washed with brine and dried over MgSO₄, and all solvents were removed in vacuo. The residue was loaded on a silica gel column and eluted with CH₂Cl₂/CH₃OH (10/1) to give compound **2** as a white solid. Yield: 2.14 g (10.2 mmol, 51%). ¹H NMR (400 MHz, CDCl₃): δ 7.87 (s, 2H, NCHN), 7.51 (s, 4H, Ar CH), 7.29 (s, 2H, imidazole H4/H5), 7.22 ppm (s, 2H, imidazole H4/H5). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 136.4 (Ar CN), 135.5 (NCN), 130.9 (imidazole C4/C5), 123.8 (imidazole C4/C5), 118.1 (Ar CH) ppm. MS (EI, 20 eV): m/z (%) 210 (100) [2]⁺. Anal. Calcd for 2: C, 68.55; H, 4.80; N, 26.66. Found: C, 68.45; H, 4.85; N, 26.61. The spectroscopic data match those reported in ref 15.

Synthesis of 1,4-Bis(3-ethyl-1-imidazolium)benzene Dibromide (H₂-3(Br)₂). A Schlenk flask was charged with 1,4-bis-(1-imidazolyl)benzene (2; 1.13 g, 5.4 mmol) and an excess of ethyl bromide (3.53 g, 32.0 mmol). To this mixture was added DMF (10 mL), and the reaction mixture was heated to 95 °C for 3 h. During this time a white compound precipitated, which was filtered off, washed with diethyl ether (2 × 10 mL), and dried in vacuo to give H₂-3(Br)₂ as a white solid. Yield: 2.035 g (4.75 mmol, 88%). ¹H NMR (200 MHz, [D₆]DMSO): δ 10.10 (pseudo-t, 2H, NCHN), 8.47 (pseudo-t, 2H, imidazole H4/HS), 8.17 (s, 4H, Ar H), 8.14 (pseudo-t, 2H, imidazole H4/HS), 4.32 (q, ³J = 7.27 Hz, 4H, NCH₂), 1.54 ppm (t, ³J = 7.27 Hz, 6H, CH₃). H₂-3(Br)₂ was not further characterized but was immediately used for the synthesis of H₂-3(PF₆)₂.

Synthesis of 1,4-Bis(3-ethyl-1-imidazolium)benzene Bis-(hexafluorophosphate) (H₂-3(PF₆)₂). The bromide salt was converted to H₂-3(PF₆)₂ by adding a solution of NH₄PF₆ (1.78 g, 10.9 mmol) in methanol (8 mL) to a methanolic solution of H₂-3(Br)₂ (2.035 g, 4.75 mmol in 20 mL of methanol). The white hexafluorophosphate salt H₂-3(PF₆)₂ precipitated immediately. The precipitated solid was collected by filtration, washed with small portions of cold methanol and diethyl ether, and dried in vacuo. Yield: 1.94 g (3.47 mmol, 73%). ¹H NMR (400 MHz, CD₃CN): δ 8.97 (pseudo-t, 2H, N–CH-N), 7.88 (s, 4H, Ar H), 7.84 (pseudo-t, 2H, imidazole H4/H5), 7.65 (pseudo-t, 2H, imidazole H4/H5), 4.32 (q, ³J = 7.34 Hz, 4H, NCH₂), 1.57 ppm (t, ³J = 7.34 Hz, 6H, CH₃). ¹³C{¹H} NMR (100 MHz, CD₃CN): δ 137.0 (NCN), 135.8 (Ar CN), 125.5 (Ar CH), 124.3 (imidazole C4/C5), 122.9 (imidazole C4/C5), 46.7 (NCH₂), 15.3 ppm (CH₃). HRMS (ESI, positive ions): *m/z* 413.1319 (calcd for [H₂-3(PF₆)]⁺ 413.1324), 239.1284 (calcd for $[\rm H_2\mathchar`-Et]^+$ 239.1297), 134.0870 (calcd for $[\rm H_2\mathchar`-3]^{2+}$ 134.0844).

Synthesis of $[Hg_3(1)_2](PF_6)_6$. Samples of H_3 -1(PF₆)₃ (0.120 g, 0.15 mmol) and Hg(OAc)₂ (0.96 g, 0.30 mmol) were suspended in CH₃CN (10 mL). The reaction mixture was heated under reflux for 4 days. Subsequently, the mixture was cooled to ambient temperature and the solvent was removed in vacuo. The solid residue was washed with water $(3 \times 5 \text{ mL})$ and dried in vacuo. Analytically pure $[Hg_3(1)_2](PF_6)_6$ was obtained after repeated recrystallization from acetonitrile/diethyl ether. Yield: 0.099 g (0.045 mmol, 60%). ¹H NMR (400 MHz, CD₃CN): δ 7.93 (s, 3H, Ar H), 7.79 (d, ³*J* = 1.97 Hz, 3H, imidazole H4/H5), 7.66 (d, ${}^{3}J$ = 1.97 Hz, 3H, imidazole H4/H5), 4.53 (q, ${}^{3}J$ = 7.25 Hz, 6H, NCH₂), 1.65 ppm (t, ${}^{3}J$ = 7.25 Hz, 9H, CH₃). ${}^{13}C{}^{1}H$ NMR (100 MHz, CD₃CN): δ 174.3 (NCN), 140.6 (Ar CN), 126.7 (imidazole C4/C5), 125.9 (imidazole C4/C5), 125.3 (Ar CH), 48.7 (NCH₂), 16.1 ppm (CH₃). HRMS (ESI, positive ions): *m*/*z* 951.0903 (calcd for $[Hg_3(1)_2(PF_6)_4]^{2+}$ 951.0886), 585.7382 (calcd for $[Hg_3(1)_2 (PF_6)_3]^{3+}$ 585.7375), 403.0623 (calcd for $[Hg_3(1)_2(PF_6)_2]^{4+}$ 403.0625).

Synthesis of [Ag₂(3)₂](PF₆)₂. A sample of H₂-3(PF₆)₂ (0.112 g, 0.2 mmol) was dissolved in 10 mL of CH₃CN, and to this solution was added Ag₂O (0.051 g, 0.22 mmol). The resulting suspension was heated to 55 °C for 20 h with the exclusion of light. After cooling, the suspension obtained was filtered slowly through Celite to obtain a clear solution. The filtrate was concentrated to 3 mL, and diethyl ether (20 mL) was added. This led to the precipitation of a white solid. The solid was collected by filtration, washed with diethyl ether, and dried in vacuo. Yield: 0.097 g (0.093 mmol, 93%). ¹H NMR (200 MHz, CD₃CN): δ 7.66 (s, 4H, Ar H), 7.53 (d, ²J = 1.89 Hz, 2H, imidazole H4/H5), 7.45 (d, ${}^{2}J$ = 1.89 Hz, 2H, imidazole H4/H5), 4.30 (q, ${}^{3}J$ = 7.35 Hz, 4H, NCH₂), 1.54 ppm (t, ${}^{3}J$ = 7.35 Hz, 6H, CH₃). ${}^{13}C{}^{1}H$ NMR (50 MHz, CD₃CN): δ 180.6 (NCN), 141.1 (Ar CN), 126.1 (Ar CH), 123.4 (imidazole C4/C5), 123.0 (imidazole C4/C5), 48.4 (NCH2), 17.4 ppm (CH₃). HRMS (ESI, positive ions): *m*/*z* 374.0575 (calcd for $[\mathrm{Ag}_2(\mathbf{3})_2]^{2+} 374.0575).$

Synthesis of $[Au_2(3)_2](PF_6)_2$. A solution of $[Ag_2(3)_2](PF_6)_2$ (0.052 g, 0.05 mmol) in acetonitrile (10 mL) was treated with solid [AuCl(SMe₂)] (0.030 g, 0.1 mmol). During the addition a white solid precipitated from the reaction mixture. The reaction mixture was stirred at ambient temperature for 12 h and then slowly filtered to obtain a clear filtrate. The filtrate was added slowly to diethyl ether (20 mL). Upon this addition a white solid precipitated, which was collected by filtration, washed with diethyl ether, and dried in vacuo without heating to give $[Au_2(3)_2](PF_6)_3$ as a colorless solid. Yield: 0.054 g (0.045 mmol, 90%). ¹H NMR (400 MHz, CD₃CN): δ 7.80 (s, 4H, Ar H), 7.55 (d, ²J = 1.99 Hz, 2H, imidazole H4/H5), 7.49 (d, ^{2}J = 1.99 Hz, 2H, imidazole H4/H5), 4.41 (q, ${}^{3}J$ = 7.36 Hz, 4H, NCH₂), 1.61 ppm (t, ${}^{3}J$ = 7.36 Hz, 6H, CH₃). ¹³C{¹H} NMR (100 MHz, CD₃CN): δ 182.1 (NCN), 139.2 (Ar CN), 125.5 (Ar CH), 122.4 (imidazole C4/C5), 122.2 (imidazole C4/C5), 47.0 (NCH₂), 16.1 ppm (CH₃). HRMS (ESI, positive ions): m/z 1071.2054 (calcd for $[Au_2(3)_2(PF_6)]^+$ 1071.2030), 463.1189 (calcd for $[Au_2(3)_2]^{2+}$ 463.1192).

Synthesis of $[Hg_2(OAc)_2(3)](PF_6)_2$. To a mixture of H_2 -3(PF₆)₂ (0.112 g, 0.2 mmol) and Hg(OAc)₂ (0.147 g, 0.46 mmol) was added DMF (4 mL), and the mixture was heated to 100 °C for 36 h. After the mixture was cooled to ambient temperature, the solvent was stripped in vacuo and the remaining residue was washed with a small amount of H_2O . The solid residue was eaxtracted with acetone (5 mL), and the liquid phase was filtered slowly through a short pad of Celite. The filtrate was collected, and removal of the solvent gave $[Hg_2(OAc)_2(3)](PF_6)_2$ as a white powder. Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a solution of $[Hg_2(OAc)_2(3)](PF_6)_2$ in acetonitrile/methanol. Yield: 0.172 g (0.16 mmol, 80%). ¹H NMR (400 MHz, $[D_6]_a$ cetone): δ 8.14 (d, ³J = 1.9 Hz, 2H, imidazole H5), 8.09 (s, 4H, Ar H), 8.06 (d, ³J =

1.9 Hz, 2H, imidazole H4), 4.64 (q, ${}^{3}J$ = 7.3 Hz, 4H, NCH₂), 1.91 (s, 6H, acetate CH₃), 1.63 ppm (t, ${}^{3}J$ = 7.3 Hz, 6H, CH₃). ${}^{13}C{}^{1}H$ } NMR (100 MHz, [D₆]acetone): δ 177.2 (C=O), 163.9 (NCN), 140.0 (Ar CN), 128.5 (Ar CH), 125.9 (imidazole C5), 125.4 (imidazole C4), 47.8 (NCH₂), 21.9 (acetate CH₃), 16.5 ppm (CH₃). MS-MALDI (DCTB, positive ions): m/z 1076 [Hg₂(OAc)₂(3)(PF₆)₂]⁺, 930 [Hg₂(OAc)₂(3) - H⁺]⁺, 527 [Hg₂(OAc)₂(3) - Hg(OAc)]⁺. Anal. Calcd for [Hg₂(OAc)₂(3)](PF₆)₂: C, 22.32; H, 2.25; N, 5.21. Found: C, 21.49; H, 2.24; N, 5.25.

X-ray Crystal Structure Determinations. X-ray diffraction data were collected at T = 153(2) K with a Bruker AXS APEX CCD diffractometer equipped with a rotating anode using monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Diffraction data were collected over the full sphere and were corrected for absorption. Structure solutions were found with the SHELXS-97²⁴ package using direct methods and were refined with SHELXL-97²⁴ against $|F^2|$ using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms (for exceptions, see the descriptions of the individual molecular structures). Hydrogen atoms were added to the structure models on calculated positions.

 H_2 -**3**($PF_6)_2$. Crystals suitable for an X-ray diffraction study were obtained by diffusion of diethyl ether into a saturated solution of H₂-3(PF_6)₂ in acetonitrile: C₁₆H₂₀N₄F₁₂P₂, *M* = 558.30, colorless crystal, 0.22 \times 0.07 \times 0.05 mm³, monoclinic, space group $P2_1/n$, *Z* = 2, a = 8.5008(4) Å, b = 12.3583(6) Å, c = 10.4088(5) Å, β = 98.2340(10)°, V = 1082.23(9) Å³, $\rho_{\rm calcd}$ = 1.713 g cm⁻³, Mo K α radiation (λ = 0.71073 Å), μ = 0.317 mm⁻¹, ω and φ scans, 12.311 measured intensities (5.1° \leq 2 θ \leq 60.0°), semiempirical absorption correction (0.934 \leq *T* \leq 0.984), 3148 independent ($R_{\rm int}$ = 0.0158) and 2788 observed intensities ($I \geq 2\sigma(I)$), refinement of 155 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions, R = 0.0524, $R_{\rm w}$ = 0.1468, $R_{\rm all}$ = 0.0572, $R_{\rm w,all}$ = 0.1521. The asymmetric unit contains a half formula unit of H₂-3(PF_6)₂ related to the other half by a crystallographic inversion center.

 $[Hq_3(1)_2](PF_6)_6 \cdot 5CH_3CN$. Crystals suitable for an X-ray diffraction study were obtained by diffusion of diethyl ether into a saturated solution of $[Hg_3(1)_2](PF_6)_6$ in acetonitrile: $C_{52}H_{63}N_{17}Hg_3F_{36}P_6$, M =2397.74, colorless crystal, 0.12 \times 0.10 \times 0.05 mm³, orthorhombic, space group *Iba*2, *Z* = 8, *a* = 30.443(2) Å, *b* = 18.8901(15) Å, *c* = 29.089(2) Å, V = 16729(2) Å³, $\rho_{calcd} = 1.902$ g·cm⁻³, Mo K α radiation ($\lambda = 0.71073$ Å), $\mu = 5.733$ mm⁻¹, ω and φ scans, 83789 measured intensities (2.5° \leq 2 θ \leq 55.8°), semiempirical absorption correction $(0.546 \le T \le 0.762)$, 19954 independent ($R_{int} = 0.0536$) and 16357 observed intensities $(I \ge 2\sigma(I))$, refinement of 991 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions, R = 0.0533, $R_w = 0.1429$, $R_{all} = 0.0697$, $R_{w,all} = 0.1551$. The asymmetric unit contains one molecule of $[Hg_3(1)_2](PF_6)_6$. Five of the six PF₆⁻ anions reside on general positions, and two additional PF₆⁻ anions reside on special positions (2-fold rotation axis, SOF = 0.5). One of the acetonitrile molecules is disordered over two positions. No hydrogen positions were calculated for the disordered acetonitrile molecule. The structure was refined as a twin containing 80% and 20% of the two possible helical complex cations.

 $\begin{bmatrix} Au_2(\mathbf{3})_2 | (PF_6)_2. \text{ Crystals suitable for an X-ray diffraction study were obtained by diffusion of diethyl ether into a saturated acetonitrile solution of <math display="block"> \begin{bmatrix} Au_2(3)_2 \end{bmatrix} (PF_6)_2: \mathbb{C}_{32}H_{36}N_8Au_2F_{12}P_2, M = 1216.56, \text{ colorless crystal}, 0.06 \times 0.05 \times 0.02 \text{ mm}^3, \text{ triclinic, space group } P\overline{1}, Z = 2, a = 11.4827(10) \text{ Å}, b = 11.7727(10) \text{ Å}, c = 15.0753(13) \text{ Å}, a = 80.1770(10)^\circ, \beta = 72.3180(10)^\circ, \gamma = 84.0760(10)^\circ, V = 1910.3(3) \text{ Å}^3, \rho_{\text{calcd}} = 2.115 \text{ g cm}^{-3}, \text{ Mo } K\alpha \text{ radiation } (\lambda = 0.71073 \text{ Å}), \mu = 7.851 \text{ mm}^{-1}, \omega \text{ and } \varphi \text{ scans}, 20111 \text{ measured intensities } (2.9^\circ \leq 2\theta \leq 57.0^\circ), \text{ semiempirical absorption correction } (0.650 \leq T \leq 0.859), 9656 \text{ independent } (R_{\text{int}} = 0.0351) \text{ and } 6620 \text{ observed intensities } (I \geq 2\sigma(I)), \text{ refinement of 509 parameters against } |F^2| \text{ of all measured intensities}$

with hydrogen atoms on calculated positions, R = 0.0425, $R_w = 0.0972$, $R_{\rm all} = 0.0755$, $R_{\rm w,all} = 0.1112$. The asymmetric unit contains one molecule of $[Au_2(3)_2](PF_6)_2$.

 $[Hg_2(OAc)_2(\mathbf{3})](PF_6)_2 \cdot 1.5CH_3OH$. Crystals suitable for an X-ray diffraction study were obtained by diffusion of diethyl ether into a acetonitrile/ methanol solution of the complex [Hg₂(OAc)₂(3)](PF₆)₂: C_{21.5}H_{27.5}N₄- $Hg_2F_{12}O_{5.5}P_2$, M = 1121.09, colorless crystal, 0.15 × 0.10 × 0.07 mm³, monoclinic, space group P2₁/c, Z = 4, a = 17.5961(8) Å, b = 13.4202(6) Å, c = 14.5061(7) Å, $\beta = 104.9020(10)^{\circ}$, V = 3310.3(3) Å³, $\rho_{calcd} =$ 2.249 g cm⁻³, Mo K α radiation ($\lambda = 0.71073$ Å), $\mu = 9.469$ mm⁻¹, ω and φ scans, 33 877 measured intensities (2.4° $\leq 2\theta \leq 60.0^{\circ}$), semiempirical absorption correction (0.331 $\leq T \leq$ 0.557), 9634 independent ($R_{int} =$ 0.0305) and 6714 observed intensities $(I \ge 2\sigma(I))$, refinement of 438 parameters against $|\vec{F}|$ of all measured intensities with hydrogen atoms on calculated positions, R = 0.0499, $R_w = 0.1336$, $R_{all} = 0.0776$, $R_{w,all} =$ 0.1518. The asymmetric unit contains one dication $[Hg_2(OAc)_2(3)]^{2+}$, two PF_6^{-} ions, and 1.5 molecules of methanol, one of which is coordinated to Hg1 while the methanol half-molecule in the asymmetric unit is disordered. In addition, one of the methyl groups of one ethyl substituent of the dicarbene ligand is disordered. No hydrogen atoms were added to the structure model for the disordered molecules or groups.

ASSOCIATED CONTENT

Supporting Information. CIF files giving X-ray crystallographic data for H_2 -3(PF₆)₂ [Hg₃(1)₂](PF₆)₆·5CH₃CN, [Au₂(3)₂](PF₆)₂, and [Hg₂(OAc)₂(3)](PF₆)₂·1.5CH₃OH. This material is available free of charge via the Internet at http://pubs. acs.org.

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REFERENCES

 (a) Melaimi, M.; Soleilhavoup, M.; Bertrand, G. Angew. Chem., Int. Ed. 2010, 49, 8810–8849.
 (b) de Frémont, P.; Marion, N.; Nolan, S. P. Coord. Chem. Rev. 2009, 253, 862–892.
 (c) Hahn, F. E.; Jahnke, M. C. Angew. Chem., Int. Ed. 2008, 47, 3122–3172.

(2) (a) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* 2007, 107, 5606–5655. (b) Marion, N.; Díez-González, S.; Nolan, S. P. *Angew. Chem., Int. Ed.* 2007, 46, 2988–3000.

(3) (a) Herrmann, W. A. Angew. Chem., Int. Ed. 2002, 41, 1290–1309. (b) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. Angew. Chem., Int. Ed. 2007, 46, 2768–2813. (c) Díez-González, S.; Marion, N.; Nolan, S. P. Chem. Rev. 2009, 109, 3612–3576. (d) Poyatos, M.; Mata, J. A.; Peris, E. Chem. Rev. 2009, 109, 3677–3707.

(4) (a) Boydston, A. J.; Williams, K. A.; Bielawski, C. W. *J. Am. Chem. Soc.* **2005**, *127*, 12496–12497. (b) Boydston, A. J.; Bielawski, C. W. *Dalton Trans.* **2006**, 4073–4077. (c) Tennyson, A. G.; Kamplain, J. W.; Bielawski, C. W. *Chem. Commun.* **2009**, 2124–2126. (d) Mercs, L.; Neels, A.; Stoeckli-Evans, H.; Albrecht, M. *Dalton Trans.* **2009**, 7168–7178.

(5) (a) Hindi, K. M.; Panzner, M. J.; Tessier, C. A.; Cannon, C. L.; Youngs, W. J. Chem. Rev. 2009, 109, 3859–3884. (b) Ray, S.; Mohan, R.; Singh, J. K.; Samantary, M. K.; Shaikh, M. M.; Panda, D.; Ghosh, P. J. Am. Chem. Soc. 2007, 129, 15042–15053. (c) Hickey, J. L.; Ruhayel, R. A.; Barnard, P. J.; Baker, M. V.; Berners-Price, S. J.; Filipovska, A. J. Am. Chem. Soc. 2008, 130, 12570–12571. (d) Deng, L.; Holm, R. H. J. Am. Chem. Soc. 2008, 130, 9878–9886.

(6) (a) Rit, A.; Pape, T.; Hahn, F. E. J. Am. Chem. Soc. 2010, 132, 4572–4573. (b) Rit, A.; Pape, T.; Hepp, A.; Hahn, F. E. Organometallics 2011, 30, 334–347.

(7) (a) Hahn, F. E.; Radloff, C.; Pape, T.; Hepp, A. Organometallics 2008, 27, 6408–6410. (b) Radloff, C.; Hahn, F. E.; Pape, T.; Fröhlich, R. Dalton Trans. 2009, 7215–7222. (c) Radloff, C.; Weigand, J. J.; Hahn, F. E. Dalton Trans. 2009, 9392–9394. (d) Han, Y.; Lee, L. J.; Huynh, H. V. Organometallics 2010, 29, 6020–6027. (e) Dan, Y.; Huynh, H. V. Chem. Eur. J. 2010, 16, 771–773.

(8) (a) Hahn, F. E.; Radloff, C.; Pape, T.; Hepp, A. *Chem. Eur. J.* 2008, *14*, 10900–10904. (b) Wang, D.; Zhang, B.; He, C.; Wu, P.; Duan, C. *Chem. Commun.* 2010, *46*, 4728–4730. (c) Radloff, C.; Gong, H.-Y.; Schulte to Brinke, C.; Pape, T.; Lynch, V. M.; Sessler, J. L.; Hahn, F. E. *Chem. Eur. J.* 2010, *16*, 13077–13081.

(9) Wanzlick, H.-W.; Schönherr, H.-J. Angew. Chem., Int. Ed. Engl. 1968, 7, 141–142.

(10) Arduengo, A. J., III; Harlow, R. L.; Marshall, W. J.; Prakasha, T. K. *Heteroat. Chem.* **1996**, *7*, 421–426.

(11) Wan, X.-J.; Xu, F.-B.; Li, Q.-S.; Song, H.-B.; Zhang, Z.-Z. Organometallics 2005, 24, 6066–6068.

(12) (a) Chen, J. C. C.; Lin, I. J. B. Dalton Trans. 2000, 839–840. (b) Lee, K.-M.; Chen, J. C. C.; Lin, I. J. B. J. Organomet. Chem. 2001, 617–618, 364–375.

(13) Catalano, V. J.; Malwitz, M. A.; Etogo, A. O. Inorg. Chem. 2004, 43, 5714–5724.

(14) Baker, M. V.; Brown, D. H.; Haque, R. A.; Simpson, P. V.; Skelton, B. W.; White, A. H.; Williams, C. C. *Organometallics* **2009**, *28*, 3793–3803.

(15) Zhang, S.; Yang, S.; Lan, J.; Yang, S.; You, J. Chem. Commun. 2008, 6170–6172.

(16) (a) Fliedel, C.; Braunstein, P. Organometallics 2010,

29, 5614-5626. (b) Baker, M. V.; Brown, D. H.; Haque, R. A.; Skelton,

B. W.; White, A. H. J. Incl. Phenom. Macrocycl. Chem. 2009, 65, 97–109.
(c) Scheele, U. J.; Dechert, S.; Meyer, F. Inorg. Chim. Acta 2006, 359, 4891–4900.

(17) (a) Wang, H. M. J.; Lin, I. J. B. Organometallics 1998, 17, 972–975.
(b) Lin, I. J. B.; Vasam, C. S. Coord. Chem. Rev. 2007, 251, 642–670.

(c) Garrison, J. C.; Youngs, W. J. Chem. Rev. **2005**, 105, 3978–4008.

(18) Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.;

Hwang, W. S.; Lin, I. J. B. *Chem. Rev.* **2009**, *109*, 3561–3598.

(19) Warsink, S.; Chang, I.-H.; Weigand, J. J.; Hauwert, P.; Chen, J.-T.; Elsevier, C. J. Organometallics **2010**, *29*, 4555–4561.

(20) Deißler, C.; Rominger, F.; Kunz, D. Dalton Trans. 2009, 7152–7167.
(21) Saito, S.; Saika, M.; Yamasaki, R.; Azumaya, I.; Masu, H.

Organometallics 2011, 30, 1366–1373.
(22) Kilpin, K. J.; Paul, U. S. D.; Lee, A.-L.; Crowley, J. D. Chem.
Commun. 2010, 47, 328–330. Subsequent studies by the same authors indicated that this complex is actually a trinuclear species built from

three dicarbene ligands and three silver(I) cations: Crowley, J. D. Personal communication.

(23) Nishina, N.; Yamamoto, Y. Synlett 2007, 11, 1767–1770.

(24) SHELXS-97, SHELXL-97: Sheldrick, G. M. Acta Crystallogr., Sect. A 2008, 64, 112–122.