ORGANOMETALLICS

Synthesis of Nanometer-Sized Cylinder-Like Structures from a 1,3,5-Triphenylbenzene-Bridged Tris-NHC Ligand and Ag^I, Au^I, and Cu^I

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Supporting Information

ABSTRACT: The metal-controlled self-assembly of nanometer-sized trinuclear cylinder-like assemblies is described. The 1,3,5-triphenylbenzene-derived trisimidazolium salt [1](PF₆)₃ reacts with 1.5 equiv of Ag₂O to yield the trinuclear Ag^I hexacarbene complex [2](PF₆)₃, where three Ag^I ions are sandwiched in between two C_3 -symmetric tris-NHC ligands. Transmetalation of [2](PF₆)₃ with 3 equiv of [AuCl(SMe₂)] or CuI yields the trinuclear Au^I hexacarbene complex [3](PF₆)₃ or the trinuclear Cu^I hexacarbene complex [4](PF₆)₃, respectively, with retention of the metallosupramolecular structure. The 1,3,5-triphenylbenzene ligand in the gold complex adopts a nonplanar geometry to allow π interactions between the central phenyl rings.



INTRODUCTION

The metal-directed self-assembly of supramolecular architectures has become a field of intense research, starting with the early work by Lehn on the dinuclear helicate complex prepared from Cu^I and 2,2'-bipyridine.¹ Thereafter, the self-assembly of a large number of metallosupramolecular structures, with various shapes and sizes, has been independently reported by Fujita,² Raymond,³ Stang,⁴ Nitschke,⁵ and others.^{6,7} Selected metallosupramolecular structures can function as molecular hosts by encapsulating small guest molecules.^{3a,8} The stabilization of reactive intermediates and selected catalytic transformations have also been observed within the cavities of metallosupramolecular assemblies.^{9,10}

Most of the known metallosupramolecular hosts are built from Werner-type coordination compounds with metal centers coordinated by nitrogen and/or oxygen donor atoms of polydentate ligands. With the recent resurgence of interest in N-heterocyclic carbenes (NHCs)¹¹ discrete metallosupramolecular structures held together by M–C bonds between metal centers and poly-NHC ligands have recently emerged. Today, molecular squares and rectangles,¹² cylinders,¹³ and organometallic polymers¹⁴ built from polycarbene ligands are known.

The silver(I)-mediated self-assembly of supramolecular assemblies from poly-NHC ligands has developed into an emerging field of organometallic chemistry due to the facile synthesis of silver-NHC complexes via the Ag_2O method¹⁵ and the possibility to transmetalate the NHC ligands from silver to other transition metals.^{13e,f,15} This method was also used for the preparation of the cylinder-like assemblies **A** and **B** (Figure 1),^{13e,f} and even the analogous M₆ dodecacarbene

complexes have been described.¹⁶ Molecular assemblies derived from NHC-substituted phenylenes such as **A** and **B** feature a rather small cavity for the incorporation of molecular guests. We have therefore investigated tricarbene ligands having a larger π -conjugated backbone.

Werner-type tridentate ligands with such an enlarged backbone featuring a central triazine^{17a,b} or phenylene^{17c} linker have been described. Related tris-NHC ligands are rare although some C₃-symmetric ligands with different backbone groups been described.¹⁸ Here we describe the preparation of nanometer-sized cyclinder-like assemblies from the 1,3,5-triphenylbenzene-bridged trisimidazolium salt [1] (PF₆)₃ (Scheme 1)¹⁹ and Ag^I and the subsequent transmetalation of the tricarbene ligand to Au^I and Cu^I.

RESULTS AND DISCUSSION

The trisimidazolium carbene precursor $[1](PF_6)_3$ was synthesized by a three-step procedure starting from 1,3,5-tris(4-bromophenyl)benzene (Scheme 1). Treatment of 1,3,5-tris(4-bromophenyl)benzene with imidazole in the presence of CuSO₄·5H₂O and K₂CO₃ in the solid state at 160 °C for 24 h resulted in the formation of the known¹⁹ compound I in 68% yield as a colorless solid. The trisimidazolium salt $[1](Br)_3$ was obtained as an off-white solid in 66% yield upon heating of compound I with an excess of ethyl bromide at 100 °C for 48 h in DMF. Addition of NH₄PF₆ to a methanolic solution of $[1](Br)_3$ gave the trisimidazolium hexafluorophosphate salt $[1](PF_6)_3$ in an

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Figure 1. Cylinder-like assemblies from benzene-derived tris- or tetra-NHC ligands.

Scheme 1. Synthesis of the Ligand Precursor $[1](PF_6)_3$



excellent yield of 79% as a colorless solid. The formation of $[1](PF_6)_3$ was confirmed by NMR spectroscopy (¹H, ¹³C{¹H}, 2D NMR) and by high-resolution electrospray ionization (HR-ESI) mass spectrometry. The imidazolium C2–H resonance was observed as a singlet at δ 9.88 ppm, a value consistent with chemical shifts reported for related trisimidazolium hexafluorophosphate salts.^{13e,f} The ¹³C{¹H} NMR spectrum shows the resonance for the C2 carbon atom at δ 140.8 ppm.^{13e,f} The HR-ESI mass spectrum (positive ions) of $[1](PF_6)_3$ exhibits the most intense peak at m/z 197.1073 (calcd for $[1]^{3+} m/z$ 197.1079). The procedure described here for the synthesis of $[1](PF_6)_3$ differs slightly from that used for the synthesis of $[1](BF_4)_{3}$, which was described by some of us previously.¹⁹

The reaction of 2 equiv of salt $[1](PF_6)_3$ with 3 equiv of Ag_2O in acetonitrile under exclusion of light yielded the trinuclear Ag^I hexacarbene complex $[2](PF_6)_3$ in 77% yield as a colorless solid (Scheme 2; see also the Supporting Information). The formation

of complex $[2](PF_6)_3$ was confirmed by ¹H and ¹³C{¹H} NMR spectroscopy and by HR-ESI mass spectrometry. Upon formation of $[2](PF_6)_3$, the characteristic resonance for the C2–H proton of azolium salt $[1](PF_6)_3$ at δ 9.88 ppm (in DMSO- d_6) is no longer observed in the ¹H NMR spectrum. The ¹³C{¹H} spectrum shows the C_{NHC} resonance of $[2](PF_6)_3$ at δ 178.3 ppm (in DMSO- d_6), which is consistent with the values previously reported for Ag^I–NHC complexes.^{13e,f,h,16} The HR-ESI mass spectrum (positive ions) of $[2](PF_6)_3$ featured the most intense peak at m/z 500.4380 (calcd for $[2]^{3+} m/z$ 500.4390).

Since Ag^{I} -NHC complexes are good carbene transfer agents,¹⁵ we tried to substitute the Ag^{I} ions in $[2](PF_{6})_{3}$ for Au^{I} ions. Stirring of a mixture of $[2](PF_{6})_{3}$ and 3 equiv of $[AuCl(SMe_{2})]$ in acetonitrile for 16 h at ambient temperature led to the formation of the trinuclear gold(I) hexacarbene complex $[3](PF_{6})_{3}$ as an air- and moisture-stable white solid in Scheme 2. Synthesis of Complex $[2](PF_6)_3$ and Transmetalation of the Tris-NHC Ligand To Give $[3](PF_6)_3$ and $[4](PF_6)_3$



an excellent yield of 70%. The metallosupramolecular remained intact (Scheme 2).

The formation of complex $[3](PF_6)_3$ was confirmed by ¹H and ¹³C{¹H} NMR spectroscopy and by HR-ESI mass spectrometry. In the ¹³C{¹H} NMR spectrum, the resonance for the C_{NHC} carbon atoms was observed at δ 180.6 ppm (in DMSO- d_6), in the range observed for previously reported [Au¹(NHC)₂] complexes. ^{13e,f,h,16} The complete substitution of all three Ag^I ions by Au^I ions is also evident from the observation of only one C_{NHC} resonance in the ¹³C{¹H} spectrum. The HR-ESI mass spectrum (positive ions) confirmed the formation of [3](PF₆)₃ by exhibiting an intense peak at *m*/*z* 589.1665 (calcd for [3]³⁺ *m*/*z* 589.1666).

Single crystals of $[3](PF_6)_3 \cdot CH_3CN \cdot SEt_2O$ for an X-ray diffraction study were obtained by slow vapor diffusion of diethyl ether into a saturated acetonitrile solution of $[3](PF_6)_3$ at ambient temperature. The structure analysis revealed the expected molecular structure of the trinuclear gold(I) hexacarbene complex cation $[3]^{3+}$, which is shown in Figure 2.

The metric parameters observed in the cation $[3]^{3+}$ (Au-C_{NHC}, 1.918(14)-2.096(14) Å; C_{NHC}-Au-C_{NHC}, 170.5(7)-178.6(5)°) fall in the ranges previously reported for dicarbene gold complexes.^{13e,f,h} The three gold atoms form a triangle featuring Au···Au separations of about 1.4 nm. The two central phenyl rings of the tris-NHC ligands are oriented in a nearly coplanar fashion featuring a centroid···centroid separation of about 3.644 Å. We take this short separation as an indication for the presence of $\pi \cdots \pi$ interactions between these rings. By assuming that cation [3]³⁺ possesses a pseudo-triangular-prismatic



Figure 2. Molecular structure (top view) of the trication $[3]^{3+}$ in $[3](PF_6)_3 \cdot CH_3CN \cdot SEt_2O$ (hydrogen atoms omitted for clarity, 50% probability ellipsoids). Selected bond distances (Å) and bond angles (deg): range Au-C_{NHC}, 1.918(14)–2.096(14); range C_{NHC}-Au-C_{NHC}, 170.5(7)–178.6(5); range N-C_{NHC}-N, 101.5(10)–105.1(12).

structure, we estimated the internal volume of the cavity to be 360 Å³, which is significantly larger than the internal volume estimated for the previously reported tri-Au^I structures (the internal volume of the cavity of the tri-Au complex with structure A is estimated as 72 Å³).

In addition, trinuclear cylinder-like assemblies related to $[3]^{3+}$ obtained from tris-NHC ligands but featuring only a phenylene linker (see A in Figure 1) exhibit a much larger separation of the midpoints of the central phenylene groups (M = Ag, 4.914 Å; M = Au, 4.762 Å; M = Cu, 4.239 Å) in comparison to that of $[3]^{3+}$ (3.644 Å).^{13e} To accommodate the $C_{\rm NHC}$ -Au- $C_{\rm NHC}$ bonds of about 4.0 Å, the carbene donors in $[3]^{3+}$ are pushed out of the plane of the central phenyl group toward the outside of the cylinder, giving the tricarbene a convex geometry (Figure 3).



Figure 3. Schematic representation of the molecular structure (side view) of the cation $[3]^{3+}$ showing the $\pi \cdots \pi$ interactions between two central phenyl rings and the nonplanar geometry of the tricarbene ligands.

This convex distortion is only possible with the 1,3,5triphenylbenzene backbone. In addition, the NHC donors are not oriented perpendicular to the aromatic backbone, also contributing to the short separation of the central phenylene rings.

Transmetalation of the trisilver complex $[2](PF_6)_3$ with 3 equiv of CuI in acetonitrile at ambient temperature yielded the trinuclear copper(I) hexacarbene complex $[4](PF_6)_3$ as a white solid in 63% yield with retention of the metallosupramolecular structure (Scheme 2). The formation of complex $[4](PF_6)_3$ was also confirmed by ¹H and ¹³C{¹H} NMR spectroscopy and HR-ESI mass spectrometry. In the ¹³C{¹H} NMR spectrum, the resonance for the C_{NHC} atoms was observed at δ 174.3 ppm (in DMSO- d_6), in agreement with previously reported chemical shifts for C_{NHC} atoms in moieties of the type {Cu(NHC)₂}.^{13e,20} The magnetic equivalence of the resonance for the C_{NHC} atoms is consistent with the 3-fold symmetry of the complex cation (for a full set of NMR spectra see the Supporting Information).

CONCLUSIONS

In summary, we prepared a nanometer-sized cylinder-like trinuclear AgI hexacarbene complex via metal-controlled selfassembly. The trinuclear silver complex undergoes transmetalation with [AuCl(SMe2)] or CuI to form the homotrinuclear hexacarbene complexes $[3](PF_6)_3$ and $[4](PF_6)_3$ with retention of the cylinder-like architecture. Use of the 1,3,5triphenylbenzene backbone leads to large (1.4 nm) M…M separations in the trinuclear complexes. In addition, the aromatic backbone is flexible enough to adopt a nonplanar geometry in the metal complexes to allow for $\pi \cdots \pi$ interactions between the central phenylene rings. The new structures may be related to previously reported, cylinder-like hexa-NHC structures developed by us, but here we developed a suitable method for increasing the M…M separation. Potentially, this could lead to an increased internal volume of the cavity while maintaining the inherent reactivity properties of the molecule. Such an increase was, however, not observed for the gold complex $[3](PF_6)_3$ due to the $\pi \cdots \pi$ interactions of the central phenyl rings. It remains to

be seen if addition of suitable aromatic guest molecules leads to encapsulation and a breakup of the observed $\pi \cdots \pi$ interactions.

The development of methods for efficient control of the shape and volume of cavities is of crucial interest for the design of metalosupramolecular structures that can function as molecular hosts for molecular recognition and selective catalysis. Further studies will be directed toward the utilization of the flexibility observed in $[3]^{3+}$ for the encapsulation of aromatic guests inside the cavity of these synthetic organometallic receptors.

EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Glassware was oven-dried at 130 °C. Solvents were distilled by standard procedures prior to use. ¹H and ¹³C{¹H} NMR spectra were recorded at 298 K on Bruker AVANCE I 400, Bruker AVANCE III 400, and Bruker AVANCE II 200 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 an Orbitrap LTQ XL (Thermo Scientific) spectrometer. 1,3,5-Tris(4-bromophenyl)benzene, [AuCl(SMe₂)], and Ag₂O were used as received from commercial sources. Satisfactory microanalytical data for [1](PF₆)₃ and the metal complexes could not be obtained, due to the large fluorine content in the hexafluorophosphate counterions. A complete set of NMR spectra is provided in the Supporting Information.

Synthesis of Compound I.



Samples of 1,3,5-tris(4-bromophenyl)benzene (0.272 g, 0.5 mmol), imidazole (0.204 g, 3.0 mmol), K₂CO₃ (0.346 g, 2.5 mmol), and CuSO₄· $5H_2O$ (0.025 g, 0.1 mmol) were mixed in a 50 mL Schlenk flask, and the solid mixture was heated to 160 °C for 24 h under an argon atmosphere. The reaction mixture was then cooled to ambient temperature and was washed three times with water (10 mL each). The remaining solid residue was extracted with methanol (150 mL). The solvent was removed to give compound I as a colorless solid. Yield: 0.171 g (0.339 mmol, 68%). ¹H NMR (400 MHz, DMSO- d_6): δ 8.36 (s, 3H, H1), 8.06 $(d, {}^{3}J = 8.5 Hz, 6H, H6), 8.01 (s, 3H, H9), 7.84 (s, 3H, H3), 7.80 (d, {}^{3}J =$ 8.5 Hz, 6H, H5), 7.15 ppm (s, 3H, H2). ¹³C{¹H} NMR (100 MHz, DMSO-d₆): 140.6 (C8), 138.3 (C7), 136.4 (C4), 135.5 (C1), 129.9 (C2), 128.6 (C6), 124.4 (C9), 120.6 (C5), 117.9 ppm (C3). HRMS (ESI, positive ions): m/z 505.2132 (calcd for $[I + H]^{+}$ 505.2141). Anal. Calcd for M·H₂O (C₃₃H₂₄N₆·H₂O): C, 75.84; H, 5.01; N, 16.09. Found: C, 75.86; H, 5.03; N, 15.99.

Synthesis of [1](Br)₃.



A sample of compound I (0.316 g, 0.626 mmol) and ethyl bromide (0.409 g, 3.756 mmol) were dissolved in DMF (10 mL), and the solution was heated to 100 °C for 48 h. A white solid precipitated over this period. After the reaction mixture was cooled to ambient temperature, the white precipitate was filtered off, washed with diethyl ether, and dried in vacuo to give the salt [1](Br)₃. Yield: 0.344 g (0.414 mmol, 66%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 10.05 (s, 3H, H1), 8.46 (s, 3H, H3), 8.29 (d, ³*J* = 8.7 Hz, 6H, H6), 8.17 (s, 3H, H9), 8.14 (s, 3H, H2), 8.00 (d, ³*J* = 8.7 Hz, 6H, H5), 4.35 (q, ³*J* = 7.3 Hz, 6H, H10), 1.56 ppm (t, ³*J* = 7.3 Hz, 9H, H11). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 140.7 (C7), 140.1 (C8), 135.1 (C1), 134.3 (C4), 128.9 (C6), 125.3 (C9), 123.0 (C2), 122.1 (C5), 121.0 (C3), 44.8 (C10), 14.8 ppm (C11). HRMS (ESI, positive ions): *m*/*z* 197.1073 (calcd for [1]³⁺ 197.1079). Anal. Calcd for [1]Br₃·H₂O (C₃₉H₃₉N₆Br₃·H₂O): C, 55.14; H, 4.87; N, 9.90. Found: C, 55.11; H, 5.25; N, 9.94.

Synthesis of $[1](PF_6)_3$.



A methanolic solution of NH₄PF₆ (0.270 g, 1.656 mmol in 5 mL of MeOH) was added to a methanolic solution of $[1](Br)_3$ (0.344 g, 0.414 mmol in 10 mL of MeOH). The hexafluorophosphate salt $[1](PF_6)_3$ precipitated as a white solid. The solid was collected by filtration, washed with cold methanol and diethyl ether, and dried in vacuo. Yield: 0.334 g (0.325 mmol, 79%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.88 (s, 3H, H1), 8.42 (s, 3H, H3), 8.29 (d, ³*J* = 8.6 Hz, 6H, H6), 8.18 (s, 3H, H9), 8.10 (s, 3H, H2), 7.96 (d, ³*J* = 8.6 Hz, 6H, H5), 4.33 (q, ³*J* = 7.3 Hz, 6H, H10), 1.56 ppm (t, ³*J* = 7.3 Hz, 9H, H11). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 140.8 (C7), 140.1 (C8), 135.1 (C1), 134.4 (C4), 128.9 (C6), 125.3 (C9), 123.0 (C2), 122.1 (C5), 121.1 (C3), 44.8 (C10), 14.7 ppm (C11). HRMS (ESI, positive ions): *m*/*z* 197.1073 (calcd for $[1]^{3+}$ 197.1079).

Synthesis of $[2](PF_6)_3$.



To a mixture of $[1](PF_6)_3$ (0.080 g, 0.078 mmol) and Ag₂O (0.027 g, 0.117 mmol) was added acetonitrile (10 mL). The resulting suspension was heated to 60 °C for 48 h under exclusion of light. After the reaction mixture was cooled to ambient temperature, the obtained suspension was filtered through a pad of Celite to give a clear solution. The filtrate was concentrated to 3 mL, and addition of 15 mL of diethyl ether resulted in the precipitation of a white solid. The precipitate was filtered off, washed with diethyl ether, and dried in vacuo. Yield: 0.058 g (0.030 mmol, 77%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.97 (s, 6H, H3), 7.87 (s, 6H, H2), 7.79 (s br, 24H, H5, H6), 7.66 (s, 6H, H9), 4.43 (q, ³J = 7.3 Hz, 12H, H10), 1.60 ppm (t, ³J = 7.3 Hz, 18H, H11). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 178.3 (C1), 138.8 (C7), 138.6

(C4), 138.5 (C8), 127.2 (C6), 123.5 (C5), 122.8 (C9), 122.7 (C2), 122.0 (C3), 46.8 (C10), 16.9 ppm (C11). HRMS (ESI, positive ions): m/z 500.4380 (calcd for [2]³⁺ 500.4390); m/z 823.1402 (calcd for [2]PF₆]²⁺ 823.1406).

Synthesis of [3](PF₆)₃.



To a solution of $[2](PF_6)_3$ (0.058 g, 0.030 mmol) in acetonitrile (5 mL) was added solid $[AuCl(SMe_2)]$ (0.027 g, 0.092 mmol). Immediately after the addition a white solid started to precipitate. The reaction mixture was stirred at ambient temperature for 16 h and was then slowly filtered through a pad of Celite until a clear filtrate was obtained. The filtrate was added slowly to diethyl ether (20 mL) to give a white solid, which was collected by filtration, washed with diethyl ether, and dried in vacuo. Yield: 0.046 g (0.021 mmol, 70%). ¹H NMR (400 MHz, DMSO- d_6): δ 7.96 (s, 6H, H3), 7.90 (s, 6H, H2), 7.84 (d, ³J = 8.3 Hz, 12H, H6), 7.77 (d, ³J = 8.3 Hz, 12H, H5), 7.71 (s, 6H, H9), 4.49 (q, ³J = 7.3 Hz, 12H, H10), 1.63 ppm (t, ³J = 7.3 Hz, 18H, H11). ¹³C{¹H} NMR (100 MHz, DMSO- d_6): δ 180.6 (C1), 138.7 (C7), 138.4 (C8), 137.9 (C4), 126.9 (C6), 124.4 (C5), 122.8 (C2), 122.7 (br, C3, C9), 46.4 (C10), 16.7 ppm (C11). HRMS (ESI, positive ions): m/z 589.1665 (calcd for $[3]^{3+}$ 589.1666); m/z 956.2329 (calcd for $[[3]PF_6]^{2+}$ 956.2320).

Synthesis of [4](PF₆)₃.



A sample of $[2](PF_6)_3$ (0.058 g, 0.030 mmol) was dissolved in 10 mL of acetonitrile, and to this solution was added solid CuI (0.018 g, 0.095 mmol). The reaction mixture was stirred for 16 h at ambient temperature. The resulting suspension was slowly filtered through a pad of Celite to give a clear solution. The filtrate was concentrated to 2 mL, and addition of 10 mL of diethyl ether resulted in the precipitation of a white solid. The white solid was filtered off, washed with diethyl ether, and dried in vacuo. Yield: 0.034 g (0.019 mmol, 63%). ¹H NMR (200 MHz, DMSO- d_6): δ 7.98 (s, 6H, H3), 7.83 (s, 6H, H2), 7.78 (s, br, 24H, H5, H6), 7.64 (s, 6H, H9), 4.45 (q, 3J = 7.2 Hz, 12H, H10), 1.61 ppm (t, 3J = 7.2 Hz, 18 H, H11). ¹³C{¹H} NMR (50 MHz, DMSO- d_6): δ 174.3 (C1), 137.9 (C7), 137.3 (br, C4, C8), 126.1 (C6), 122.3 (C5), 121.9 (C9), 121.5 (C2), 120.6 (C3), 45.9 (C10), 16.4 ppm (C11). HRMS (ESI, positive ions): m/z 455.7953 (calcd for [4]³⁺ 455.7964).

X-ray Crystallography. Single crystals of $[3](PF_6)_3 \cdot CH_3CN \cdot SEt_2O$ for an X-ray diffraction study have been obtained by slow vapor diffusion of diethyl ether into a saturated acetonitrile solution of $[3](PF_6)_3$ at ambient temperature. X-ray diffraction data were collected at T = 153(2) K with a Bruker APEX-II CCD diffractometer equipped with a rotation anode using graphite-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-97 package²¹ using direct methods and were refined with SHELXL-97²¹ against $|F^2|$ values of all data using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions.

Crystal data and structure refinement details for compound $[\mathbf{3}](\mathbf{PF}_6)_3 \cdot \mathbf{CH}_3 \mathbf{CN} \cdot 5\mathbf{Et}_2 \mathbf{O}: C_{100} \mathbf{H}_{125} \mathbf{N}_{13} \mathbf{Au}_3 \mathbf{F}_{18} \mathbf{O}_5 \mathbf{P}_3, M_r = 2614.94, \text{ color$ less crystal, $0.23 \times 0.07 \times 0.03 \text{ mm}^3$, monoclinic, space group $P2_1/n$, Z = 4, a = 20.4029(11) Å, b = 13.2486(8) Å, c = 33.885(2) Å, $\beta = 93.936(3)^\circ$, V = 9137.8(9) Å³, $\rho_{calcd} = 1.901$ g cm⁻³, $\mu = 4.960$ mm⁻¹ ω and φ scans, 131138 measured intensities $(2.3^{\circ} \le 2\theta \le 62.1^{\circ})$, 28577 independent intensities ($R_{int} = 0.0841$), and 17844 observed intensities $(I \ge 2\sigma(I))$, refinement of 996 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0585, $R_{\rm w} = 0.1473$, $R_{\rm all} = 0.1105$, and $R_{\rm wall} = 0.1632$. The asymmetric unit contains one formula unit of compound $[3](PF_6)_{3}$, one molecule of acetonitrile, and five molecules of diethyl ether. Three of the six N-ethyl substituents, two imidazolin-2-ylidene rings, and two hexafluorophosphate anions are disordered. The positional parameters of disordered atoms were refined with isotropic displacement parameters, and no hydrogen positions were calculated for disordered carbon atoms. The electron density of five diethyl ether molecules was removed from the least-squares calculations by means of the SQUEEZE function of the PLATON program.

ASSOCIATED CONTENT

Supporting Information

Figures giving NMR spectra of all new compounds and a CIF file containing the X-ray crystallographic data for $[3](PF_6)_3$ · CH₃CN·SEt₂O.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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REFERENCES

(1) Lehn, J.-M.; Rigault, A.; Siegel, J.; Harrowfield, J.; Chevrier, B.; Moras, D. Proc. Natl. Acad. Sci. U.S.A. **198**7, 84, 2565–2569.

(2) (a) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. Acc. Chem. Res.
2005, 38, 371–380. (b) Fujita, M. Chem. Soc. Rev. 1998, 27, 417–425.
(3) (a) Pluth, M. D.; Raymond, K. N. Chem. Soc. Rev. 2007, 36, 161–

171. (b) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* 1999, 32, 975–982.
(4) (a) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* 2011,

(4) (a) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. Chem. Rev. 2011, 111, 6810–6918. (b) Leininger, S.; Olenyuk, B.; Stang, P. J. Chem. Rev. 2000, 100, 853–908.

(5) (a) Smulders, M. M. J.; Riddell, I. A.; Browne, C.; Nitschke, J. R. *Chem. Soc. Rev.* **2013**, *42*, 1728–1754. (b) Nitschke, J. R. *Acc. Chem. Res.* **2007**, *40*, 103–112.

(6) De, S.; Mahata, K.; Schmittel, M. Chem. Soc. Rev. 2010, 39, 1555–1575.

(7) Ward, M. D. Chem. Commun. 2009, 4487-4499.

(8) (a) Birkmann, B.; Fröhlich, R.; Hahn, F. E. *Chem.*—*Eur. J.* **2009**, *15*, 9325–9329. (b) Han, Y.-F.; Jia, W.-G.; Lin, Y.-J.; Jin, G.-X. *Angew. Chem., Int. Ed.* **2009**, *48*, 6234–6238. (c) Leeland, J. W.; White, F. J.; Love, J. B. *J. Am. Chem. Soc.* **2011**, *133*, 7320–7323. (d) Mal, P.; Breiner, B.; Rissanen, K.; Nitschke, J. R. *Science* **2009**, *324*, 1697–1699.

(9) (a) Pluth, M. D.; Bergman, R. G.; Raymond, K. N. Science 2007, 316, 85–88. (b) Yoshizawa, M.; Tamura, M.; Fujita, M. Science 2006, 312, 251–254.

(10) Yoshizawa, M.; Klosterman, J. K.; Fujita, M. Angew. Chem., Int. Ed. 2009, 48, 3418–3438.

(11) (a) Jahnke, M. C.; Hahn, F. E. *Top. Organomet. Chem.* **2010**, *30*, 95–129. (b) Melaimi, M.; Soleilhavoup, M.; Bertrand, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 8810–8849. (c) Mercs, L.; Albrecht, M. *Chem. Soc. Rev.* **2010**, *39*, 1903–1912. (d) Poyatos, M.; Mata, J. A.; Peris, E. *Chem. Rev.* **2009**, *109*, 3677–3707. (e) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122–3172.

(12) (a) Han, Y.-F.; Jin, G.-X.; Hahn, F. E. J. Am. Chem. Soc. 2013, 135, 9263-9266. (b) Schmidtendorf, M.; Pape, T.; Hahn, F. E. Dalton Trans. 2013, 42, 16128-16141. (c) Schmidtendorf, M.; Pape, T.; Hahn, F. E. Angew. Chem., Int. Ed. 2012, 51, 2195-2198. (d) Gierz, V.; Maichle-Mössmer, C.; Kunz, D. Organometallics 2012, 31, 739-747. (e) Cure, J.; Poteau, R.; Gerber, I. C.; Gornitzka, H.; Hemmert, C. Organometallics 2012, 31, 619-626. (f) Conrady, F. M.; Fröhlich, R.; Schulte to Brinke, C.; Pape, T.; Hahn, F. E. J. Am. Chem. Soc. 2011, 133, 11496-11499. (g) Rit, A.; Pape, T.; Hahn, F. E. Organometallics 2011, 30, 6393-6401. (h) Liu, Q.-X.; Yao, Z.-Q.; Zhao, X.-J.; Chen, A.-H.; Yang, X.-Q.; Liu, S.-W.; Wang, X.-G. Organometallics 2011, 30, 3732-3739. (i) Saito, S.; Saika, M.; Yamasaki, R.; Azumaya, I.; Masu, H. Organometallics 2011, 30, 1366-1373. (j) Radloff, C.; Weigand, J. J.; Hahn, F. E. Dalton Trans. 2009, 9392-9394. (k) Radloff, C.; Hahn, F. E.; Pape, T.; Fröhlich, R. Dalton Trans. 2009, 7215-7222. (1) Hahn, F. E.; Radloff, C.; Pape, T.; Hepp, A. Organometallics 2008, 27, 6408-6410.

(13) (a) Schulte to Brinke, C.; Pape, T.; Hahn, F. E. Dalton Trans. 2013, 42, 7330–7337. (b) Maity, R.; Rit, A.; Schulte to Brinke, C.; Daniliuc, C. G.; Hahn, F. E. Chem. Commun. 2013, 49, 1011–1013. (c) Ahamed, B. N.; Dutta, R.; Ghosh, P. Inorg. Chem. 2013, 52, 4269– 4276. (d) Wei, S.; Li, X.; Yang, Z.; Lan, J.; Gao, G.; Xue, Y.; You, J. Chem. Sci. 2012, 3, 359–363. (e) Rit, A.; Pape, T.; Hepp, A.; Hahn, F. E. Organometallics 2011, 30, 334–347. (f) Rit, A.; Pape, T.; Hahn, F. E. J. Am. Chem. Soc. 2010, 132, 4572–4573. (g) 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. (h) Hahn, F. E.; Radloff, C.; Pape, T.; Hepp, A. Chem.—Eur. J. 2008, 14, 10900–10904.

(14) (a) Gonell, S.; Poyatos, M.; Peris, E. Chem.—Eur. J. 2014, 20, 5746–5751. (b) Zhang, C.; Wang, J.-J.; Liu, Y.; Ma, H.; Yang, X.-L.; Xu, H.-B. Chem.—Eur. J. 2013, 19, 5004–5008. (c) Karimi, B.; Akhavan, P. F. Chem. Commun. 2011, 47, 7686–7688. (d) Choi, J.; Yang, H. Y.; Kim, H. J.; Son, S. U. Angew. Chem., Int. Ed. 2010, 49, 7718–7722. (e) Mercs, L.; Neels, A.; Stoeckli-Evans, H.; Albrecht, M. Dalton Trans. 2009, 7168–7178. (f) Williams, K. A.; Boydston, A. J.; Bielawski, C. W. Chem. Soc. Rev. 2007, 36, 729–744. (g) Boydston, A. J.; Bielawski, C. W. Dalton Trans. 2006, 4073–4077. (h) Boydston, A. J.; Williams, K. A.; Bielawski, C. W. J. Am. Chem. Soc. 2005, 127, 12496–12497. (i) Guerret, O.; Solé, S.; Gornitzka, H.; Teichert, M.; Trinquier, G.; Bertrand, G. J. Am. Chem. Soc. 1997, 119, 6668–6669.

(15) (a) 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. (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.

(16) Segarra, C.; Guisado-Barrios, G.; Hahn, F. E.; Peris, E. Organometallics 2014, 33, 5077-5080.

(17) (a) Fujita, M.; Oguro, D.; Miyazawa, M.; Oka, H.; Yamaguchi, K.; Ogura, K. *Nature* **1995**, 378, 469–471. (b) Yoshizawa, M.; Tamura, M.; Fujita, M. *J. Am. Chem. Soc.* **2004**, *126*, 6846–6847. (c) Kumazawa, K.; Yamanoi, Y.; Yoshizawa, M.; Kusukawa, T.; Fujita, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 5936–5940.

(18) (a) Wang, Y.-T.; Chang, M.-T.; Lee, G.-H.; Peng, S.-M.; Chiu, C.-W. Chem. Commun. 2013, 49, 7258–7260. (b) Gonell, S.; Alabau, R. G.; Poyatos, M.; Peris, E. Chem. Commun. 2013, 49, 7126–7128. (c) Gonell, S.; Poyatos, M.; Peris, E. Angew. Chem., Int. Ed. 2013, 52, 7009–7013. (d) Segarra, C.; Linke, J.; Mas-Marza, E.; Kuck, D.; Peris, E. Chem. Commun. 2013, 49, 10572–10574. (e) Williams, K. A.; Bielawski, C. W. Chem. Commun. 2010, 46, 5166–5168.

Organometallics

(19) (a) Mejuto, C.; Guisado-Barrios, G.; Peris, E. Organometallics
2014, 33, 3205–3211.
(20) Hu, X.; Castro-Rodriguez, I.; Olsen, K.; Meyer, K. Organometallics

(20) Hu, X., Casto-Rounguez, I., Olsen, R., Meyer, R. Organometantes
2004, 23, 755–764.
(21) SHELXS-97, SHELXL-97: Sheldrick, G. M. Acta Crystallogr., Sect. A 2008, 64, 112–122.