

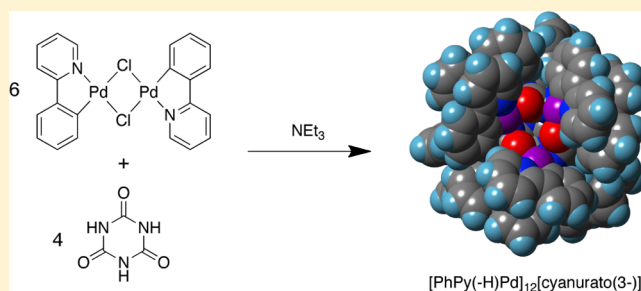
Pairwise Assembly of Organopalladium(II) Units with Cyanurato(3−) and Trithiocyanurato(3−) Ligands: Formation of Chiral Pd₁₂, Pd₁₀, and Pd₉ Cage-Molecules

Claire A. Murray, Christine J. Cardin, Barnaby W. Greenland, Andrew Swift, and Howard M. Colquhoun*

Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, United Kingdom

Supporting Information

ABSTRACT: The *o*-palladated, chloro-bridged dimers [Pd{2-phenylpyridine(-H)}-μ-Cl]₂ and [Pd{N,N-dimethylbenzylamine(-H)}-μ-Cl]₂ react with cyanuric acid in the presence of base to afford closed, chiral cage-molecules in which 12 organo-Pd(II) centers, located in pairs at the vertices of an octahedron, are linked by four tetrahedrally arranged cyanurato(3−) ligands. Incomplete (Pd₁₀) cages, having structures derived from the corresponding Pd₁₂ cages by replacing one pair of organopalladium centers with two protons, have also been isolated. Reaction of [Pd{2-phenylpyridine(-H)}-μ-Cl]₂ with trithiocyanuric acid gives an entirely different and more open type of cage-complex, trithiocyanurato(3−) ligands: cage-closure in this latter system



comprising only nine organopalladium centers and three appears to be inhibited by steric crowding of the thiocarbonyl groups.

INTRODUCTION

Recent decades have seen the emergence of a rapidly expanding area of coordination chemistry in which the electronic and geometric characteristics of ligands and metal centers are matched to afford large (sometimes very large) multinuclear complexes with well-defined polyhedral geometries.¹ The work of Fujita,² Stang,³ Raymond,⁴ Ward,⁵ and Schröder⁶ has been particularly notable in this regard. The assembly processes leading to polynuclear systems of this type are often reversible under the conditions of synthesis, so that reactions can be self-correcting and can lead to cage-structures representing true thermodynamic minima.¹

Here we describe a new class of highly symmetrical, yet chiral, cage-type complexes based on triply deprotonated cyanuric acid which can, in the present context, be regarded as a tribasic imide. Monobasic imides such as succinimide have long been known to react with *o*-metalated palladium(II) centers, in the presence of base, to give binuclear complexes via *N,O*-coordination of the imidato(1−) ligand.⁷ Extension of this type of chemistry to higher-nuclearity cage-complexes (Pd₆, Pd₈) also proved possible, with the di-imides parabanic acid and pyromellitimide, respectively.^{8,9} In such complexes, square-planar organopalladium(II) centers are linked in nonbonded pairs through a (deprotonated) imide-nitrogen atom and the oxygen of an adjacent carbonyl group.

The simplest possible *tribasic* imide is cyanuric acid (Scheme 1), and preliminary computational modeling studies suggested that the cyanurato(3−) ion could, by reaction with square-planar transition metal centers, give rise to large, three-dimensional cage structures. Ligands derived from cyanuric acid

have previously been explored to a surprisingly limited extent: for example, there appears to be no structurally characterized transition metal derivative of the triply deprotonated, cyanurato(3−) ligand.¹⁰ Even the cyanurato(2−) ligand is relatively rare in the literature, although it has been structurally characterized as a binucleating ligand in the copper(I) complex [Cu₂(C₃N₃O₃H)(H₂O)₂],¹¹ and as a tetranucleating ligand, linking pairs of molybdenum centers, in [Mo₄(*N,N'*-di-*p*-anisylformamidate)₆(C₃N₃O₃H)].¹² The cyanurato(1−) ligand has been identified crystallographically in a number of molecular complexes including [Cu(C₃N₃O₃H₂)₂(NH₃)₂],¹³ [Ni(C₃N₃O₃H₂)₂(NH₃)₄],¹⁴ and [Ag₄(C₃N₃O₃H₂)₄(4,4-bipyridyl)],¹⁵ and also in the network structure [Ag₂(C₃N₃O₃H₂)₂(4,4-bipyridyl)]_∞.¹⁶ Molecular cyanurato(1−) complexes have a tendency to form ribbon-like structures in the solid state, through hydrogen bonding between the residual pairs of cyanurate [NHCO] units.¹⁷

In the present work, molecular simulations suggested that 12 [organopalladium(II)]⁺ centers could, in principle, assemble with four cyanurato(3−) ligands to give a neutral, closed-cage complex. We now report the realization of two such dodecanuclear assemblies, together with crystallographic and spectroscopic evidence for stable intermediates (the homologous Pd₁₀ complexes), and the unexpected results of a parallel study using the trithiocyanurate(3−) ligand.

Received: May 18, 2013

Published: September 5, 2013

Scheme 1. Formation of the Dodecapalladium and Decapalladium Cage-Complexes 1 and 2, Respectively, from Reaction of [Pd{2-phenylpyridine(-H)}- μ -Cl]₂ with Cyanuric Acid

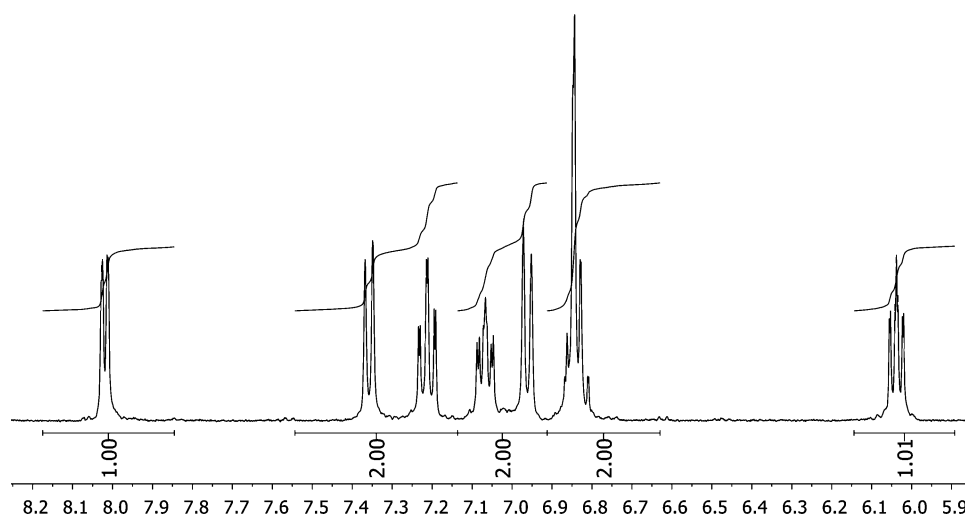
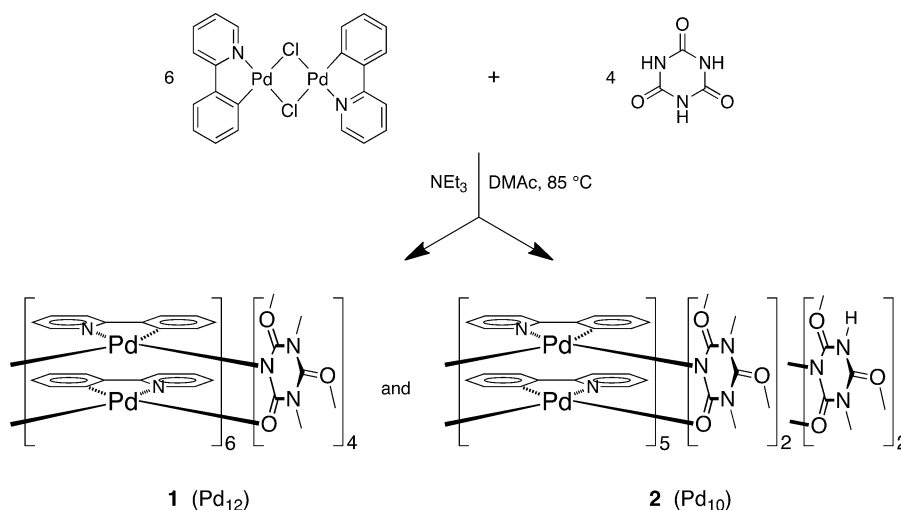


Figure 1. ¹H NMR spectrum of the dodecanuclear complex 1 (400 MHz, CD₂Cl₂). Resonances assignable to six of the eight protons associated with each [2-phenylpyridine(-H)] ligand are fully resolved, with the remaining two resonances overlapping between 6.8 and 6.9 ppm.

RESULTS AND DISCUSSION

Reaction of the *o*-palladated derivative of 2-phenylpyridine, [Pd{2-phenylpyridine(-H)}- μ -Cl]₂,¹⁸ (6 equiv) with cyanuric acid (4 equiv), in the presence of triethylamine as acid-acceptor (Scheme 1), afforded a deep orange crystalline complex (1). Mass spectroscopy of complex 1 confirmed that a dodecanuclear complex with 12 [2-phenylpyridine(-H)] ligands had been formed ([M + H]⁺: isotope distribution centered at *m/z* 3631). Analysis of 1 by ¹H NMR spectroscopy showed that the complex contains only eight different types of proton (Figure 1). These are assignable to just a single [2-phenylpyridine(-H)] ligand (see Supporting Information), indicating that all 12 such ligands in 1 must be present in geometrically equivalent environments.

Single crystal X-ray diffraction revealed a molecular structure (Figure 2a) in which the 12 organopalladium vertices are indeed geometrically equivalent, being located in nonbonded pairs about the vertices of an octahedron. The *o*-metalated phenylpyridine ligands are arranged in π -stacked antiparallel pairs, with the phenyl and pyridyl rings in near van der Waals contact (interatomic distances in the range 3.3–3.7 Å).

Molecule 1 has (noncrystallographic) point group symmetry *T*, and is therefore chiral. In this context, chirality may be defined by the rotational direction (clockwise or anticlockwise) of the angular C=O—Pd linkages about the center of the cyanurate(3-) ligand (Figure 3), viewed from outside the molecular cage.

In any one dodecamer (Figure 2a), the rotational direction is the same for all four such ligands,¹⁹ but the crystal, having the centrosymmetric space group *R* $\bar{3}$, contains equal numbers of “clockwise” and “anticlockwise” enantiomers and is therefore racemic. These enantiomers are stable in solution, as was demonstrated by use of the chiral NMR shift reagent (*S*)-(+)-trifluoro-1-(9-anthryl) ethanol.²⁰ The latter produced a well-defined splitting of the triplet ¹H resonance, originally at 6.04 ppm (Figure 1), to give two overlapping triplets of equal intensity (see Supporting Information). This effect is consistent with the shift reagent forming a hydrogen bond to the unused lone pair of a bridging (C=O—Pd) oxygen atom. The pairwise arrangement of 12 metal centers about the vertices of an octahedron has previously been identified in metal–metal bonded Mo(II) and Rh(II) complexes with the trianion of

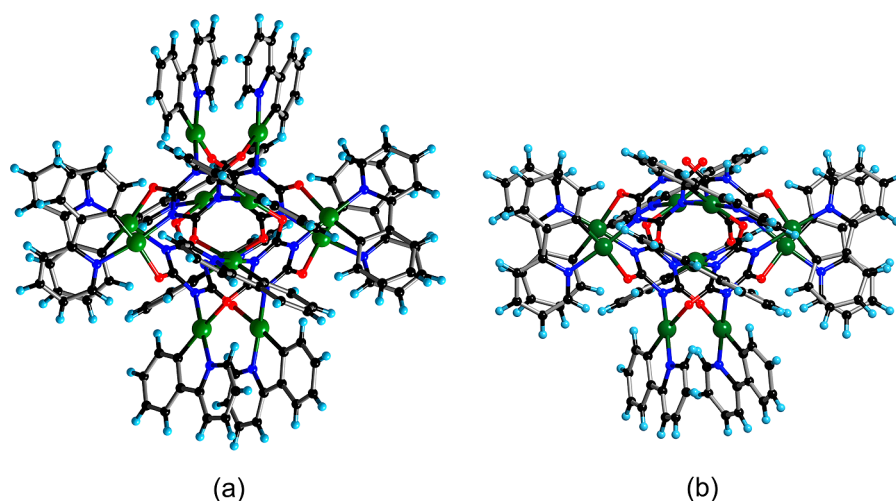


Figure 2. Single crystal X-ray structures of (a) the dodecanuclear complex **1** and (b) the decanuclear complex **2**. In **1**, the palladium atoms are grouped in six symmetrically equivalent pairs about the vertices of an octahedron, and are bridged by cyanurato(3⁻) ligands, [Pd–N–C=O–Pd], as shown in Scheme 1. Pairs of [2-phenylpyridine(-H)] ligands are stacked antiparallel to one another. Complex **2** contains ten palladium centers bridged by two cyanurato(3⁻) and two cyanurato(2⁻) ligands, leaving an open face with two “unused” [HN–C=O] residues.

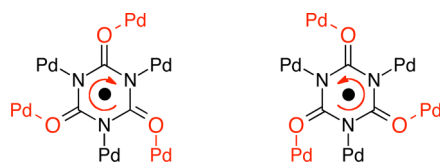


Figure 3. Helical chirality in complex **1**, showing “clockwise” and “anticlockwise” rotational enantiomers, viewed from outside the cage.

trimesic acid,²¹ and in a related metal–organic framework based on copper(II).²³ However, the symmetrical coordination mode of trimesate(3⁻) means that chirality analogous to that of **1** does not arise in such systems. Pairwise assemblies of 6 and 12 palladium(II) centers with polypyrazolate ligands have previously been reported to give [Pd₆]¹²⁺ and [Pd₁₂]¹²⁺ cages,^{23,24} though these are structurally unrelated to the present system.

Examination of a batch of complex **1** crystallized from dichloromethane/benzene revealed a small number of very thin, bright yellow crystals, distinctly different from those of the orange Pd₁₂ complex. Single crystal X-ray analysis using synchrotron radiation enabled this minor coproduct to be identified as the decapalladium complex **2** (Figure 2b). Its structure is derived from that of complex **1** by removing two organopalladium(II) centers and replacing them with two protons, leaving a polyhedron with a single open face, and there can be little doubt that **2** is the final precursor in the assembly of the closed-cage molecule **1**.

Complexes entirely analogous to **1** and **2** were isolated from the reaction of cyanuric acid with the dimeric complex [Pd{*N,N*-dimethylbenzylamine(-H)}-μ-Cl]₂.²⁵ The structure of the resulting dodecanuclear complex, **3**, was characterized both spectroscopically and crystallographically (see Supporting Information), and that of the decanuclear complex (**4**), by NMR and mass spectrometry. The *N*-methyl groups in **3** and **4** are very useful ¹H NMR probes, with the highly symmetrical Pd₁₂ complex **3** showing only two *N*-methyl singlet resonances. One type of methyl group (red in Figure 4) is strongly shielded by the aromatic ring current of its neighboring [*N,N*-dimethylbenzylamine(-H)] ligand, producing a marked upfield shift for the resonance arising from this group of protons. Both

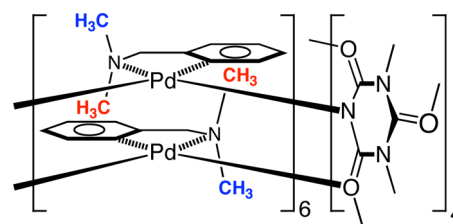


Figure 4. Complex **3**, showing the inequivalence of the two *N*-methyl groups on each [*N,N*-dimethylbenzylamine(-H)] ligand. This inequivalence arises from the “folded” geometry of the imide bridge,⁷ which brings one methyl group (red), but not the other (blue), into the ring-current shielding zone of the adjacent aromatic ligand.

3 and **4** show helical chirality, as described above for **1** and **2**, but addition of the same hydrogen-bonding chiral shift reagent to the racemic complex **3** had no effect whatever on its ¹H NMR spectrum. In keeping with this, a space-filling representation of the X-ray structure of **3** (Figure 5) shows the framework of the complex to be completely screened from possible hydrogen bonding interactions by the steric bulk of its 12 *ortho*-metalated *N,N*-dimethylbenzylamine ligands. The central cavity of the dodecapalladium cage is very small, but computational modeling indicates that it could readily accommodate an atom of helium, and that clathration of a neon atom should also be feasible. Synthetic approaches to noble-gas molecular clathrates of this type are currently under investigation.

Contrasting with the ¹H NMR spectrum of **3**, the homologous Pd₁₀ complex, **4**, shows 10 –CH₃ signals and 10 doublet –CH₂ resonances (two overlapping), arising from the five different environments of the *o*-palladated ligand (Figure 6 and Supporting Information). Moreover, the open face of complex **4**, with its two projecting carbonyl groups (cf., Figure 2b) offers clear possibilities for hydrogen bonding with (*S*)-(+)-trifluoro-1-(9-anthryl)ethanol. In practice, the latter reagent produced numerous splittings of the *N*-methyl and *N*-methylene resonances in the ¹H NMR spectrum of **4**, including an especially clear-cut splitting of two of the *N*-CH₂ resonances (Figure 6), confirming that the chirality of the open Pd₁₀ cage is fully retained in solution.

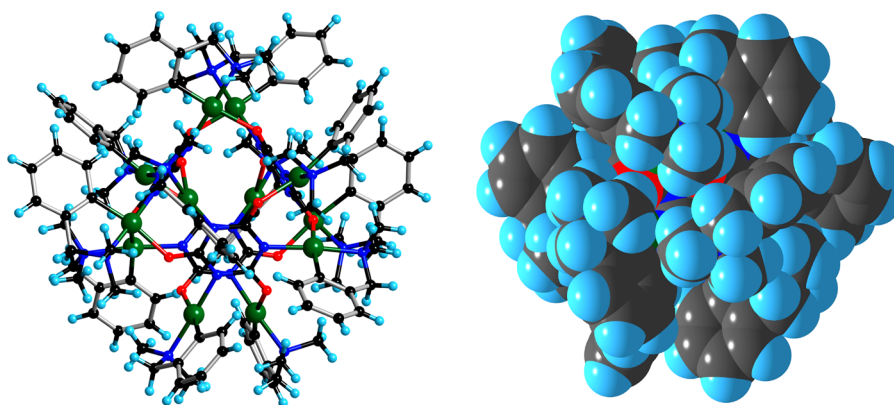


Figure 5. Ball-and-stick and space-filling representations of **3**, showing how the metal–ligand framework of this Pd₁₂ complex is screened from external interactions by the 12 peripheral [*N,N*-dimethylbenzylamine(-H)] ligands.

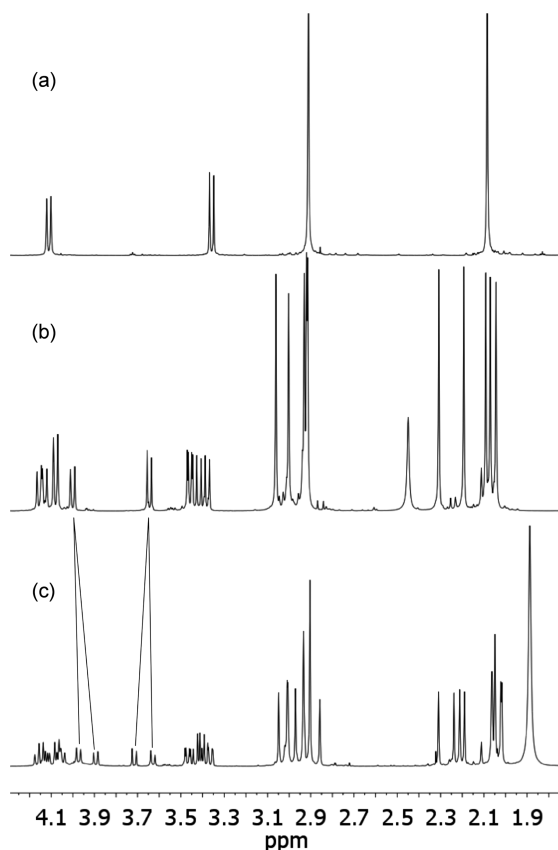


Figure 6. (a) 700 MHz ¹H NMR spectrum of the Pd₁₂ complex **3** (aliphatic region) in CD₂Cl₂. (b) Corresponding spectrum of the Pd₁₀ complex **4**. (c) Spectrum of **4** in the presence of the chiral shift reagent (*S*)-(+)-trifluoro-1-(9-anthryl)ethanol.

The limited yields of cage-molecules, and the presence of both “closed” (Pd₁₂) and “open” (Pd₁₀) cages in the final products, strongly suggest that the assembly processes involved do not reach true thermodynamic minima. Even though formation of a weak [C=O⋯Pd] coordinative bond will undoubtedly be reversible under very mild conditions, it seems unlikely that the same holds true for coordination of an anionic imido-nitrogen to palladium(II), with displacement of chloride. Consequently, achieving the (Pd₁₂) global energy minimum may not always be possible.

Replacement of cyanuric acid with its trithio-analogue in the reaction with [Pd{2-phenylpyridine(-H)}-μ-Cl]₂ was expected to give a closed Pd₁₂ cage entirely analogous to that seen in **1**. The single product isolated from this reaction did indeed contain organopalladium(II) centers and trithiocyanurato(3-) ligands in the same 3:1 molar ratio as found in **1** and **3**, but ¹H NMR, mass spectroscopy, and single crystal X-ray analysis showed that a completely different type of complex, now containing nine organo-palladium(II) centers (**5**), had been formed. The X-ray structure of **5** is shown in Figure 7, from

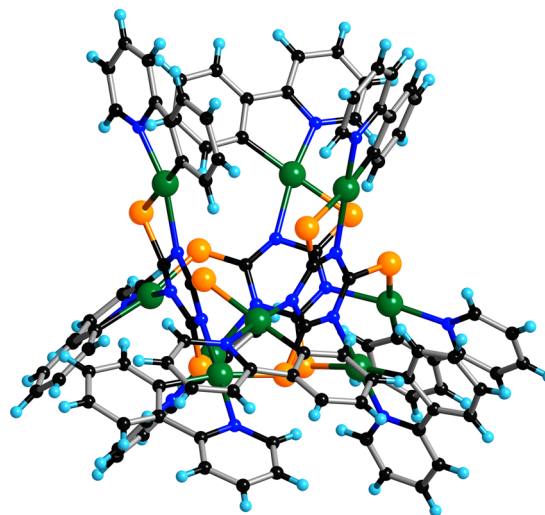


Figure 7. Single crystal X-ray structure of **5**. Six of the nine palladium atoms are grouped in pairs, with [Pd–N–C=S–Pd] bridges analogous to the [Pd–N–C=O–Pd] motif found in complex **1**. The three remaining metal centers, shown at the top of the structure, are each chelated by a single [N–C=S] group.

which it is evident that the three trithiocyanurato(3-) anions link three pairs of organopalladium centers, each ligand forming two [Pd–N–C=S–Pd] bridges. However, the coordination mode then changes so that the three remaining [N–C=S][–] groups (one on each trithiocyanurate ligand) act as chelating units, each for a single organopalladium center.²⁶

Formation of the expected thiocyanurate-Pd₁₂ cage appears to be inhibited by the substantially greater van der Waals radius of sulfur (1.80 Å) relative to oxygen (1.52 Å). In the structure of complex **5**, the “bridging” coordination mode of the trithiocyanurate ligand brings three sulfur atoms into van der

Waals contact ($S\cdots S = 3.57, 3.53, \text{ and } 3.52 \text{ \AA}$), while in complex **1** the corresponding ($O\cdots O$) distances are in a similar range but for much smaller atoms. Computational modeling (*Cerius2* Universal Force Field) and energy-minimization of the hypothetical Pd_{12} -trithiocyanurate complex shows that cage-closure would force the sulfur atoms well into sub-van-der-Waals contact. The energy of the hypothetical Pd_{12} (trithiocyanurate)₄ complex is in fact calculated to be some $380 \text{ kcal mol}^{-1}$ higher than that of the Pd_{12} (cyanurate)₄ complex, **1**. While energies based on molecular mechanics calculations cannot be quantitative for such complex molecules, this result is certainly consistent with the severe steric crowding of sulfur atoms ($S\cdots S < 3.30 \text{ \AA}$) seen in the modeled Pd_{12} -trithiocyanurate complex.

Intriguingly, the electrospray mass spectra of the Pd_{10} cage-molecules **2** and **4** both show subsidiary series of ions with half-integral mass numbers, corresponding to doubly charged dimers in the form of disodium adducts (see Supporting Information). This ability of metal ions to link pairs of Pd_{10} (but not Pd_{12}) cages highlights the fact that the relationship between a closed Pd_{12} and an open Pd_{10} cage is somewhat analogous to that between a *closo*- and a *nido*-carbaborane.²⁷ It is thus possible that the decanuclear complexes **2** and **4** could be doubly deprotonated to give reactive “*nido*-like” dianions, with the ability to act as ligands for bonded metal centers such as $[\text{Rh}-\text{Rh}]^{4+}$ or $[\text{Mo}\equiv\text{Mo}]^{4+}$ (or indeed for nonbonded pairs such as $[\text{Pd}^{2+}]_2$ or $[\text{Pt}^{2+}]_2$) that are already known to form stable binuclear complexes with imidato-type ligands).^{7–9,12,28} The *commo*-type systems that are predicted to be formed in such reactions (see Supporting Information) would seem to have no precedent in transition metal coordination chemistry, and are currently being sought in our laboratory.

EXPERIMENTAL SECTION

Instrumentation and Analysis. Single crystal X-ray data for **1** and **3** were collected using an Agilent Technologies Gemini Ultra-S CCD instrument with Cu $K\alpha$ radiation for **1** and Mo $K\alpha$ radiation for **3**. Data for **2** were obtained on beamline 11.3.1 of the Advanced Light Source, Berkeley, CA, and data for **5** on beamline I19 of the Diamond Light Source, Harwell, U.K. Full details of data collection, structure solution and refinement for **1**, **2**, **3**, and **5** are given as Supporting Information and in the deposited .cif files CCDC 929579, 929577, 929578, and 929576, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at: www.ccdc.cam.ac.uk/data_request/cif. Proton and carbon NMR spectra were acquired on a Bruker Nanobay 400 operating at 400 and 100 MHz for ^1H and ^{13}C nuclei, respectively, or on a Bruker Avance III 700 operating at 700 and 175 MHz for ^1H and ^{13}C nuclei, respectively. Chemical shifts are reported relative to the residual protic solvent signal in the specified deuterated solvent. The numbers of protons in each environment are reported as relative values. High resolution mass spectra (electrospray ionization, ESI) were acquired on a Bruker micrOTOF-Q instrument, working in positive ion mode.

Starting Materials and Intermediates. Palladium(II) chloride (anhydrous), 2-phenylpyridine, *N,N*-dimethylbenzylamine, cyanuric acid, and trithiocyanuric acid were obtained from Aldrich and used as received. The *ortho*-palladated dimers $[\text{Pd}\{2\text{-phenylpyridine}(\text{-H})\}\text{-}\mu\text{-Cl}]_2$ and $[\text{Pd}\{N,N\text{-dimethylbenzylamine}(\text{-H})\}\text{-}\mu\text{-Cl}]_2$ were synthesized as described in the literature.^{29,30}

$[\text{Pd}\{2\text{-phenylpyridine}(\text{-H})\}]_{12}[\text{C}_3\text{N}_3\text{O}_3]_4$ (1**).** $[\text{Pd}\{2\text{-phenylpyridine}(\text{-H})\}\text{-}\mu\text{-Cl}]_2$ (0.21 g, 0.36 mmol) and cyanuric acid (0.032 g, 0.25 mmol) were dissolved in *N,N*-dimethylacetamide (10 mL), triethylamine (0.2 mL) was added, and the mixture was stirred under N_2 at $85 \text{ }^\circ\text{C}$ for seven hours. The cloudy solution was filtered through Celite and washed through with dichloromethane, and the combined filtrate and washings were then concentrated to *ca.* 3 mL

under reduced pressure. Methanol (20 mL) was added, and the solution was held at $4 \text{ }^\circ\text{C}$ overnight. The resulting orange precipitate was collected by filtration, washed with methanol (20 mL), and dried under vacuum. The product, **1**, was isolated by column chromatography on silica ($\text{CH}_2\text{Cl}_2/\text{MeOH } 100:5 \text{ v/v}$) as a bright orange, crystalline solid (0.067 g, 29%) ($R_f = 0.3$). $^1\text{H NMR}$ (CD_2Cl_2 400 MHz): $\delta = 8.02$ (dd, 1H, 5.6 and 1.0 Hz), 7.35 (d, 1H, 7.6 Hz), 7.21 (dt, 1H, 7.6 and 1.4 Hz), 7.09–7.04 (m, 1H), 6.96 (d, 1H, 7.6 Hz), 6.87–6.82 (m, 2H), 6.06–6.02 (m, 1H). $^{13}\text{C NMR}$ (CD_2Cl_2 175 MHz): $\delta = 169.6, 163.7, 154.7, 150.3, 145.4, 136.5, 134.8, 128.0, 122.7, 122.5, 120.3, 116.6$. MS (ESI, positive ion mode) Calcd for $\text{C}_{145}\text{H}_{96}\text{N}_{24}\text{O}_{12}\text{Pd}_{12}$ ($[\text{M} + \text{H}]^+$) = 3623.6058. Found = 3623.5902. Anal. Calcd for $\text{C}_{144}\text{H}_{96}\text{N}_{24}\text{O}_{12}\text{Pd}_{12}\cdot 2\text{CH}_2\text{Cl}_2$: C 46.13, H 2.65, N 8.84. Found: C 45.87, H 2.70, N 9.10%.

$[\text{Pd}\{N,N\text{-dimethylbenzylamine}(\text{-H})\}]_{12}[\text{C}_3\text{N}_3\text{O}_3]_4$ (3**) and $[\text{Pd}\{N,N\text{-dimethylbenzylamine}(\text{-H})\}]_{10}[\text{C}_3\text{N}_3\text{O}_3]_2$ $[\text{C}_3\text{N}_3\text{O}_3\text{H}]_2$ (**4**).** Cyanuric acid (0.032 g, 0.25 mmol) was dissolved with stirring in a mixture of dichloromethane (15 mL) and methanol (15 mL) at $35 \text{ }^\circ\text{C}$, and then triethylamine (0.2 mL) and $[\text{Pd}\{N,N\text{-dimethylbenzylamine}(\text{-H})\}\text{-}\mu\text{-Cl}]_2$ (0.200 g, 0.36 mmol) were added. After stirring for 72 h at $35 \text{ }^\circ\text{C}$, the yellow solution was cooled and concentrated to *ca.* 10 mL at which point a fine yellow precipitate began to form. The resulting suspension was held at $4 \text{ }^\circ\text{C}$ overnight and the solid (A) collected by filtration. The filtrate was retained and further concentrated to give a further quantity of yellow solid (B). Column chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH } 100:2.5 \text{ v/v}$) of fraction A resulted in isolation of the Pd_{12} complex **3** (0.105 g, 52%, $R_f = 0.9$), whereas column chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH } 100:2.5 \text{ v/v}$) of fraction B gave only the Pd_{10} species, **4**, which was finally recrystallized from *N,N*-dimethylacetamide and methanol (0.018 g, 8%, $R_f = 0.3$). Complex **3** (Pd_{12}) data follow. $^1\text{H NMR}$ (CD_2Cl_2 700 MHz): $\delta = 6.92$ – 6.89 (m, 1H), 6.79– 6.76 (m, 3H), 4.11 (d, 1H, 14 Hz), 3.36 (d, 1H, 14 Hz), 2.91 (s, 3H), 2.08 (s, 3H). ^{13}C (CD_2Cl_2 175 MHz): $\delta = 168.6, 147.0, 146.9, 135.3, 124.1, 121.9, 120.0, 72.8, 51.7, 51.0$. MS (ESI, positive ion mode) Calcd for $\text{C}_{120}\text{H}_{145}\text{N}_{24}\text{O}_{12}\text{Pd}_{12}$ ($[\text{M} + \text{H}]^+$) = 3384.0010. Found = 3383.9961. Anal. Calcd for $\text{C}_{120}\text{H}_{144}\text{N}_{24}\text{O}_{12}\text{Pd}_{12}$: C 42.50, H 4.28, N 9.91. Found: C 42.25, H 4.21, N 9.91%. Data for complex **4** (Pd_{10}) follow. $^1\text{H NMR}$ (CD_2Cl_2 700 MHz): $\delta = 8.91$ (s, 1H), 6.94– 6.64 (m, 20 H), 4.15 (d, 1H, 14 Hz), 4.13 (d, 1H, 14 Hz), 4.04 (d, 1H, 14 Hz), 4.03 (d, 1H, 14 Hz), 3.95 (d, 1H, 14 Hz), 3.73 (d, 1H, 14 Hz), 3.51 (d, 1H, 14 Hz), 3.47 (d, 1H, 14 Hz), 3.44 (d, 1H, 14 Hz), 3.40 (d, 1H, 14 Hz), 3.03 (s, 3H), 3.02 (s, 3H), 2.94 (s, 3H), 2.91 (s, 3H), 2.90 (s, 3H), 2.30 (s, 3H), 2.21 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (CDCl_3 175 MHz): $\delta = 168.94, 168.92, 168.90, 168.1, 161.7, 157.9, 147.9, 147.38, 147.35, 147.2, 147.1, 146.2, 145.3, 145.11, 145.07, 144.4, 135.1, 134.94, 134.89, 134.1, 124.67, 124.62, 124.41, 124.27, 124.14, 123.18, 123.04, 123.03, 122.79, 122.49, 121.07, 120.99, 120.83, 120.60, 72.98, 72.85, 72.83, 72.63, 51.85, 51.71, 51.69, 51.47, 51.44, 51.38$. MS (ESI positive ion mode) Calcd for $\text{C}_{102}\text{H}_{123}\text{N}_{22}\text{O}_{12}\text{Pd}_{10}$ = 2913.0035. Found = 2913.0037. Anal. Calcd for $\text{C}_{102}\text{H}_{122}\text{N}_{22}\text{O}_{12}\text{Pd}_{10}\cdot\text{MeCONMe}_2$: C 39.83, H 4.13, N 10.08. Found: C 40.10, H 3.92, N 9.94%.

$[\text{Pd}\{2\text{-phenylpyridine}(\text{-H})\}]_9[\text{C}_3\text{N}_3\text{S}_3]_3$ (5**).** $[\text{Pd}\{2\text{-phenylpyridine}(\text{-H})\}\text{-}\mu\text{-Cl}]_2$ (0.118 g, 0.200 mmol) was dissolved in dichloromethane (6 mL) to give a bright yellow solution. Trithiocyanuric acid (0.024 g, 0.134 mmol) was added and washed in with dichloromethane (9 mL). Triethylamine (1.5 mL) was added to give a dark orange-brown solution which was stirred for 6 days. The resulting suspension was filtered and the filtrate then concentrated to small volume on a rotary evaporator and refrigerated for 48 h. The solid was filtered off, washed with methanol, and dried under vacuum for 3 h to give the product, **5**, as a dark red powder. Yield = 0.0639 g, 67%). An analytical sample was obtained by low-temperature recrystallization from dichloromethane. $^1\text{H NMR}$ (CD_2Cl_2 700 MHz): $\delta = 10.37$ (d, 1H), 7.94 (d, 1H), 7.93 (d, 1H), 7.68 (t, 1H), 7.45 (t, 1H), 7.40 (t, 1H), 7.38 (t, 1H), 7.26 (m, 3H), 7.15 (d, 1H), 7.14 (d, 1H), 7.10 (m, 2H), 6.97 (m, 2H), 6.89 (m, 3H), 6.72 (t, 1H), 6.67 (t, 1H), 6.57 (t, 1H), 6.31 (t, 1H), 6.14 (t, 1H). ^{13}C NMR (CD_2Cl_2 700 MHz): $\delta = 117.9, 118.9, 119.2, 121.6, 122.0, 122.9, 123.1, 123.3, 123.4, 124.1, 128.4, 128.5, 128.7, 135.1, 135.8, 136.5,$

137.8, 138.0, 138.4, 146.8, 147.4, 154.2. MS (ESI positive ion mode) Calcd for $C_{108}H_{73}N_{18}S_9Pd_9 = 2962.5064$. Found = 2962.5060.

Crystal Data: Crystal data for **1** follow. $C_{144}H_{96}N_{24}O_{12}Pd_{12} \cdot 3(CH_2Cl_2)$, $M_r = 3886.10$, trigonal, $R\bar{3}$, $a = 18.1579(4)$ Å, $c = 76.3832(17)$ Å, $V = 21\,810.1(8)$ Å³, $T = 150(2)$ K, $Z = 6$, $D_c = 1.775$ g cm⁻³, $\mu(Cu\ K\alpha) = 13.230$ mm⁻¹, $F(000) = 11\,412$, independent measured reflections 7782, $R_1 = 0.0406$, $wR_2 = 0.0749$ for 6315 independent observed reflections ($R_{int} = 0.062$) [$2\theta \leq 62.820^\circ$, $I > 2\sigma(I)$]. CCDC 929579. Crystal data for **2** follow. $C_{122}H_{82}N_{22}O_{12}Pd_{10} \cdot 5(C_6H_6)$, $M_r = 3502.70$, monoclinic, $C2/c$, $a = 26.620(6)$ Å, $b = 37.337(9)$ Å, $c = 16.594(4)$ Å, $\beta = 113.678(3)^\circ$, $V = 15\,105(6)$ Å³, $T = 100(2)$ K, $Z = 4$, $D_c = 1.540$ g cm⁻³, $\mu(\text{synchrotron}) = 1.225$ mm⁻¹, $F(000) = 6936$, independent measured reflections 14 313, $R_1 = 0.0643$, $wR_2 = 0.1318$ for 6315 independent observed reflections ($R_{int} = 0.060$) [$2\theta \leq 28.196^\circ$, $I > 2\sigma(I)$]. CCDC 929577. Crystal data for **3** follow. $2(C_{120}H_{144}N_{24}O_{12}Pd_{12}) \cdot CHCl_3$, $M_r = 6902.61$, cubic, $P\bar{a}3$, $a = 29.4972(2)$ Å, $V = 25\,665.0(3)$ Å³, $T = 150(2)$ K, $Z = 4$, $D_c = 1.786$ g cm⁻³, $\mu(Mo\ K\alpha) = 1.735$ mm⁻¹, $F(000) = 13\,672$, independent measured reflections 14 765, $R_1 = 0.0842$, $wR_2 = 0.2017$ for 11 138 independent observed reflections ($R_{int} = 0.106$) [$2\theta \leq 30.114^\circ$, $I > 2\sigma(I)$]. CCDC 929578. Crystal data for **5** follow. $C_{108}H_{72}N_{18}Pd_9S_9$, $M_r = 2868.08$, monoclinic, $P2_1/c$, $a = 23.4882(9)$ Å, $b = 16.5223(8)$ Å, $c = 31.0850(12)$ Å, $\beta = 101.680(3)^\circ$, $V = 11\,813.7(9)$ Å³, $T = 100(2)$ K, $Z = 4$, $D_c = 1.612$ g cm⁻³, $\mu(\text{synchrotron}) = 1.546$ mm⁻¹, $F(000) = 5616$, independent measured reflections 57 495, $R_1 = 0.1117$, $wR_2 = 0.1314$ for 18 978 independent observed reflections ($R_{int} = 0.134$) [$2\theta \leq 28^\circ$, $I > 2\sigma(I)$]. CCDC 929576.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional spectroscopic data, computational studies, and crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

■ Corresponding Author

*E-mail: h.m.colquhoun@rdg.ac.uk.

■ Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

■ Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Diamond Light Source Ltd., EPSRC, and the University of Reading (studentship to C.A.M.), and by the Royal Society (travel grant to C.J.C.). At the University of Reading, we thank Dr. John Mckendrick and Mr. Trevor Gibson (mass spectrometry), and Mr. Peter Heath (NMR spectroscopy). We thank Dr. Dave Allan and Diamond Light Source for access to beamline I19 (MT7786-1), and Dr. Simon Teat and the Advanced Light Source for access to beamline 11.3.1. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract DE-AC02-05CH11231.

■ REFERENCES

- (1) (a) Stang, P. J. *J. Am. Chem. Soc.* **2012**, *134*, 11829–11830. (b) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, *111*, 6810–6918.
- (2) (a) Murase, T.; Nishijima, Y.; Fujita, M. *J. Am. Chem. Soc.* **2012**, *134*, 162–164. (b) Fujita, D.; Takahashi, A.; Sato, S.; Fujita, M. *J. Am. Chem. Soc.* **2011**, *133*, 13317–13319. (c) Suzuki, K.; Takao, K.; Sato,

S.; Fujita, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 4858–4861. (d) Suzuki, K.; Sato, S.; Fujita, M. *Nat. Chem.* **2010**, *2*, 25–29. (e) Suzuki, K.; Takao, K.; Sato, S.; Fujita, M. *J. Am. Chem. Soc.* **2010**, *132*, 2544–2545.

(3) (a) Zheng, Y.-R.; Zhao, Z.; Wang, M.; Ghosh, K.; Pollock, J. B.; Cook, T. R.; Stang, P. J. *J. Am. Chem. Soc.* **2010**, *132*, 16873–16882. (b) Northrop, B. H.; Zheng, Y. R.; Chi, K. W.; Stang, P. J. *Acc. Chem. Res.* **2009**, *42*, 1554–1563. Siedel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972–983.

(4) (a) Wang, Z. J.; Brown, C. J.; Bergman, R. G.; Raymond, K. N.; Toste, F. D. *J. Am. Chem. Soc.* **2011**, *133*, 7358–7360. (b) Hastings, C. J.; Pluth, M. D.; Bergman, R. G.; Raymond, K. N. *J. Am. Chem. Soc.* **2010**, *132*, 6938–6940.

(5) (a) Stephenson, A.; Argent, S. P.; Riis-Johannessen, T.; Tidmarsh, I. S.; Ward, M. D. *J. Am. Chem. Soc.* **2011**, *133*, 858–870. (b) Stephenson, A.; Ward, M. D. *Dalton. Trans.* **2011**, *40*, 7824–7826. (c) Stephenson, A.; Ward, M. D. *Dalton. Trans.* **2011**, *40*, 10360–10369.

(6) Argent, S. P.; Greenaway, A.; Gimenez-Lopez, M. C.; Lewis, W.; Nowell, H.; Khlobystov, A. N.; Blake, A. J.; Champness, N. R.; Schröder, M. *J. Am. Chem. Soc.* **2012**, *134*, 55–58.

(7) Adams, H.; Bailey, N. A.; Briggs, T. N.; McCleverty, J. A.; Colquhoun, H. M. *J. Chem. Soc., Dalton Trans.* **1986**, 813–819.

(8) Colquhoun, H. M.; Powell, C. T.; Zhu, Z.; Cardin, C. J.; Gan, Y.; Tootell, P.; Tsang, J. S. W.; Boag, N. M. *Eur. J. Inorg. Chem.* **2009**, 999–1002.

(9) Colquhoun, H. M.; Fairman, R. A.; Tootell, P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1999**, 2651–2652.

(10) Cyanurato(3-) complexes of antimony(V) and zinc(II) have, however, been characterized by X-ray crystallography. See: (a) Müller, U. Z. *Anorg. Allgem. Chem.* **1976**, *422*, 141–148. (b) Aoki, S.; Shiro, M.; Koike, T.; Kimura, E. *J. Am. Chem. Soc.* **2000**, *122*, 576–584, respectively.

(11) Yang, E.; Zhuang, R. Q.; Chen, Y. E. *Acta Crystallogr.* **2006**, *E62*, m2901–m2903.

(12) Cotton, F. A.; Donahue, J. P.; Murillo, C. A.; Pérez, L. M.; Yu, R. *J. Am. Chem. Soc.* **2003**, *125*, 8900–8910.

(13) Slade, P. G.; Raupach, M.; Radoslovich, E. W. *Acta Crystallogr.* **1973**, *B29*, 279–286.

(14) Falvello, L. R.; Hitchman, M. A.; Palacio, F.; Pascual, I.; Schultz, A. J.; Stratemeier, H.; Tomás, M.; Urriolabeitia, E. P.; Young, D. M. *J. Am. Chem. Soc.* **1999**, *121*, 2808–2819.

(15) Zhang, J.; Shen, Y. C.; Qin, Y. Y.; Liab, Z. J.; Yao, Y. G. *CrystEngComm* **2007**, *9*, 636–639.

(16) Sivashankar, K. *Proc.—Indian Acad. Sci., Chem. Sci.* **2000**, *112* (147), 151.

(17) Falvello, L. R.; Pascual, I.; Tomás, M.; Urriolabeitia, E. P. *J. Am. Chem. Soc.* **1997**, *119*, 11894–11902.

(18) Kasahara, A. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1272.

(19) The concept of facial chirality in polynuclear complexes has been investigated recently by Stang and also by Raymond. See: (a) Caskey, D. C.; Yamamoto, T.; Addicott, C.; Shoemaker, R. K.; Vacek, J.; Hawkrige, A. M.; Muddiman, D. C.; Kottas, G. S.; Michl, J.; Stang, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 7620–7628. (b) Davis, A. V.; Fiedler, D.; Ziegler, M.; Terpin, A.; Raymond, K. N. *J. Am. Chem. Soc.* **2007**, *129*, 15354–15363.

(20) Pirkle, W. H.; Sikkenga, D. L.; Pavlin, M. S. *J. Org. Chem.* **1977**, *42*, 384–387.

(21) Cotton, F. A.; Lin, C.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 6413–6417.

(22) Chui, S. S. Y.; Lo, S. M. F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148–1150.

(23) Bar, A. K.; Chakrabarty, R.; Mukherjee, P. S. *Inorg. Chem.* **2009**, *48*, 10880–10882.

(24) Yu, S.-Y.; Jiao, Q.; Li, S.-H.; Huang, H.-P.; Li, Y.-Z.; Pan, Y.-J.; Sei, Y.; Yamaguchi, K. *Org. Lett.* **2007**, *9*, 1379–1382.

(25) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909–913.

- (26) Chelating trithiocyanurato ligands are relatively well-known. See, for example: Trivedi, M.; Pandey, D. S.; Zou, R. Q.; Xu, Q. *Inorg. Chem. Commun.* **2008**, *11*, 526–530 and references therein.
- (27) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1–66.
- (28) Dohta, Y.; Kodaka, M.; Okada, T.; Okamoto, K.; Okuno, H. *Inorg. Chim. Acta* **1996**, *252*, 5–7.
- (29) Kasahara, A. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1272.
- (30) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909–913.