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Construction of Hetero-Four-Layered Tripalladium(II) Cyclophanes by Transannular π···π Interactions

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Abstract: *A synthetic strategy for the generation of new molecular species utilizing a provision of nature is presented. Nano-dimensional* $(23(2)\times 21(1)\times 16(1)\ \text{Å}^3)$ *hetero-four-layered trimetallacyclophanes were constructed by proof-of-concept experiments that utilize a suitable combination of π···π interactions between the central aromatic rings, tailor-made short/long spacer tridentate donors, and the combined helicity. The behavior of the unprecedented four-layered metallacyclophane system offers a landmark in the development of new molecular systems.*

The burgeoning need of an efficient synthetic strategy for construction of unprecedented novel molecular architectures has stimulated many chemists over the course of more than half a century.[1] A comprehensive understanding of the formation process and driving forces behind such molecular assemblies can enable advantageous alteration of their functional properties. For example, cyclophanes are intriguing molecular systems that, via transannular π···π interactions, donor–acceptor, electron-transfer processes, through-space effects, and molecular strain, provide a basis for the relationships between physicochemical phenomena and detailed molecular structures.[2] A novel method for the creation of innovatory cyclophane molecules by a specific driving force has been developed, for both extension of concept and the following task-specific applications: molecular recognition and encapsulation, molecular reaction flasks, catalysts and magnetic materials, photoreactions, stereo-selective synthesis, DNA detection, and molecular electronics.[3] In particular, a major advantage of metallacyclophanes over the organic cyclophanes is a facile modularity that fine-tunes dimensions, topology, and binding selectivity.[1d,4] The coordination-driven self-assembly of palladium(II) ions with tridentate nitrogen-donor ligands, for instance, is a successful strategy for the construction of highly symmetrical metallacages with well-defined shapes and cavity sizes; this strategy also has given rise to simple two-layered palladium(II) cyclophanes.[1e,5] Even though the final products of the self-assembly reactions have been dependent on the nature of tridentate ligands, guest molecules, mole ratio, solvent, and temperature,[6] the systematic π···π interaction effects on construction of Pd^{II}-pyridyl multi-layered cyclic systems remains unexplored. Such multi-layered π···π interactions may a clue to the elucidation of electron transfer phenomena, including photo- and electro-luminescence. In this context, to establish an unprecedented hetero-multi-layered metallacyclophane system, we designed and constructed hetero-four-layered tripalladium(II) cyclophane molecules by the combined concept of π···π interactions and tailor-made C_3-symmetric tridentate donors as short/long spacers. Herein we report proof-of-concept experiments on the strategic construction of M_3L_4 hetero-four-layered tripalladium(II) cyclophanes using a direct, stepwise, or substitution reactions. Significantly, this synthetic strategy represents an effective method for construction of desirable hetero-multi-layered metallacyclophanes.

Self-assembly of square planar palladium(II) ions with inner-short/outer-long C_3-symmetric tridentate ligands ($\text{L}^{\text{SA}}=$ short amide ligand = *N,N′,N″*-tris(2-pyridinylethyl)-1,3,5-benzenetricarboxamide;[7] $\text{L}^{\text{LE}}=$ long ester ligand = *N,N′,N″*-tris(3-pyridinylpropyl)-1,3,5-benzenetricarboxylate;[5b] $\text{L}^{\text{LA}}=$ long amide ligand = *N,N′,N″*-tris(1-(3-imidazolylpropyl))-1,3,5-benzenetricarboxamide) affords various unprecedented four-layered tripalladium(II) cyclophanes. First, the reaction of K_2PdCl_4 with L^{SA} in a 3:2 mole ratio produces $[(\text{L}^{\text{SA}})(\text{PdCl}_2)_3(\text{L}^{\text{SA}})]$,[5b] and subsequent treatment with silver nitrate (6 equiv) gives $[(\text{L}^{\text{SA}})(\text{Pd}(\text{NO}_3)_2)_3(\text{L}^{\text{SA}})]$. The L^{SA} serves as an inner tridentate ligand capable of forming two-layered trimetallacyclophanes. Further in situ reaction of $[(\text{L}^{\text{SA}})(\text{Pd}(\text{NO}_3)_2)_3(\text{L}^{\text{SA}})]$ with L^{LE} and L^{LA} affords four-layered $[(\text{L}^{\text{LE}})(\text{L}^{\text{SA}})\text{Pd}_3(\text{L}^{\text{SA}})(\text{L}^{\text{LE}})](\text{NO}_3)_6$ ($\mathbf{4_0}$) and $[(\text{L}^{\text{LA}})(\text{L}^{\text{SA}})\text{Pd}_3(\text{L}^{\text{SA}})(\text{L}^{\text{LA}})](\text{NO}_3)_6$ ($\mathbf{4_2}$), respectively, indicating that L^{LE} and L^{LA} act as efficient outer-long building tectonics for the four-layered tripalladium(II)cyclophanes. A partial substitution reaction of $\mathbf{4_0}$ and $\mathbf{4_2}$ with L^{LA} in the 1:1 mole ratio can be achieved in *N,N*-dimethylformamide (DMF) or dimethyl sulfoxide (Me_2SO) to form $[(\text{L}^{\text{LA}})(\text{L}^{\text{SA}})\text{Pd}_3(\text{L}^{\text{SA}})(\text{L}^{\text{LE}})](\text{NO}_3)_6$ ($\mathbf{4_1}$) and $[(\text{L}^{\text{LA}})(\text{L}^{\text{SA}})\text{Pd}_3(\text{L}^{\text{LA}})(\text{L}^{\text{LA}})](\text{NO}_3)_6$ ($\mathbf{4_3}$), respectively ($\mathbf{4_n}$: four-layer, with *n* the number of L^{LA}). Thus, all of the four-layered tripalladium(II) cyclophanes can be efficiently synthesized, as depicted in Scheme 1. In particular, construction of $\mathbf{4_3}$ is a striking result in which one long L^{LA} acts as an inner ligand. $\mathbf{4_0}$, $\mathbf{4_2}$, and $\mathbf{4_3}$ can be synthesized by the direct reaction of $\text{Pd}(\text{NO}_3)_2$ (3 equiv) with the mole ratios of L^{SA}:L^{LE} (2:2), L^{SA}:L^{LA} (2:2), and L^{SA}:L^{LA} (1:3), respectively. Thus, the driving force behind such facile formations is their innate transannular π···π interactions which effects thermodynamic stability. However, the direct reaction of $\text{Pd}(\text{NO}_3)_2$ with L^{SA}:L^{LA}:L^{LE} (3:2:1:1) gives rise to a mixture of $\mathbf{4_1}$ and $\mathbf{4_2}$ in the 3:2 ratio (Supporting Information, Figure S1). At the initial stage, the reaction produces a statistical mixture, but after 5 h, it gives rise to the 3:2 mixture, owing presumably to

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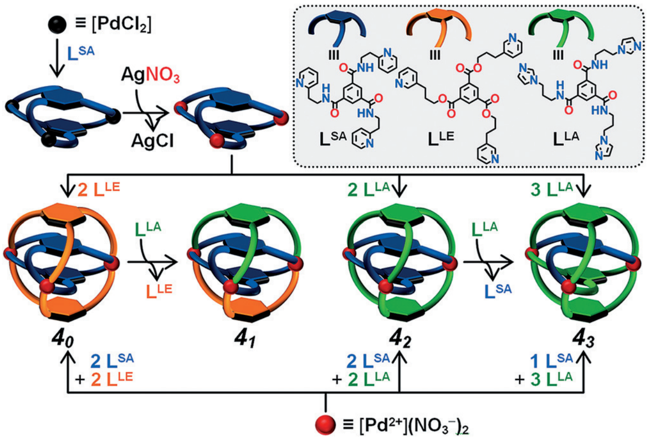

Scheme 1. Construction of hetero-four-layered tripalladium(II) cyclophanes through consecutive, substitution, and direct reactions.

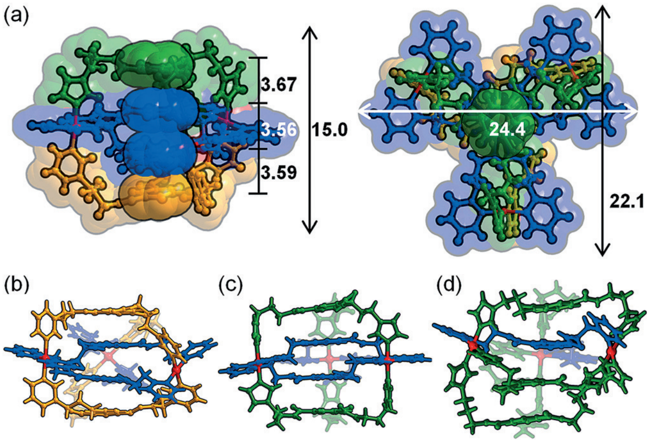

Figure 1. Crystal structures consisting of four ligands distinguished by different colors (Pd^{2+} red, L^{SA} blue, L^{LE} yellow, L^{LA} green). a) Side and top views of ***4$_1$*** in space-filling/ball-and-stick representations along with the relevant molecular dimensions [Å]. b)–d) Side views of ***4$_0$***, ***4$_2$***, and ***4$_3$*** in ball-and-stick representations. Nitrate anions and solvate molecules were omitted for clarity.[11]

the basicity difference between the pyridyl and imidazolyl moieties. All of the products are very air-stable crystalline solids that are soluble in Me$_2$SO, DMF, and a mixed solution of H$_2$O/Me$_2$CO. However, they are insoluble in common organic solvents, such as acetone, chloroform, ethyl acetate, and tetrahydrofuran. Their thermogravimetric analyses indicate that ***4$_0$***, ***4$_1$***, ***4$_2$***, and ***4$_3$*** are thermally stable up to 381, 460, 449, and 433 °C, respectively, and the solvate molecules evaporate in the 50–210 °C temperature range. The high-temperature collapse of the tripalladium(II) cyclophane skeletal structures seems to be attributable to the stable, long-range π···π interaction-based arrangement.

All of the crystal structures in the present study were four-layered tripalladium(II) cyclophanes consisting of three palladium(II) ions, two inner ligands, two outer ligands, six nitrate anions, and solvate molecules (Figure 1). The relevant crystallographic data on the four crystal structures are listed in Table 1. The local geometry around Pd^{II} centers is a typical square-planar arrangement (Pd–N 1.897(8)–2.105(8) Å) of the four nitrogen donors of four ligands. The four pyridyl/imidazolyl groups around the Pd^{II} ions are twisted from the palladium(II) plane to form a propeller-type conformation (dihedral angles 18.6(2)–90.0(5)°; Supporting Information, Figure S2). The inner ligands are coordinated to the central palladium(II) in a *trans* fashion, as are the outer ligands. Helicity is induced by means of the tridentate conformational restrictions involved in coordination with palladium(II) ions. All of the ***4$_0$***, ***4$_1$***, ***4$_2$***, and ***4$_3$*** crystals consist of racemic helices, but the ***4$_0$*** crystals can be obtained in the conglomerate in a different solvent system. Conglomerate crystals of ***4$_0$***, [(M-L^{LE})(P-L^{SA})Pd$_3$(P-L^{SA})(M-L^{LE})](NO$_3$)$_6$ and its enantiomers [(P-L^{LE})(M-L^{SA})Pd$_3$(M-L^{SA})(P-L^{LE})](NO$_3$)$_6$ (chiral $R3$ space group) are formed from a mixture of Me$_2$SO/CH$_3$COOC$_2$H$_5$ (M = left-handed helix, P = right-handed helix; Supporting Information, Figure S3). In particular, the crystal structure of

Table 1: Crystallographic summary of four-layered tripalladium(II)cyclophanes.

Compounds			Dimensions [Å^3]	Intramolecular π···π interactions		Helicity
Formula		Structure		Distance [Å]	Dihedral angles [°]	
[(L^{LE})(L^{SA})Pd$_3$(L^{SA})(L^{LE})](NO$_3$)$_6$	***4$_0$***[a]		23.6×21.7×15.2	3.49(3) 3.51(3) 3.51(3)	5.8(8) 4.6(8) 5.8(8)	racemic[b]
[(L^{LA})(L^{SA})Pd$_3$(L^{SA})(L^{LE})](NO$_3$)$_6$	***4$_1$***		24.4×22.1×15.0	3.67(1) 3.56(1) 3.59(1)	4.1(6) 2.5(5) 4.2(6)	racemic
[(L^{LA})(L^{SA})Pd$_3$(L^{SA})(L^{LA})](NO$_3$)$_6$	***4$_2$***		22.8×20.3×16.3	4.08(5) 3.68(4) 3.62(4)	13.2(5) 3.9(5) 5.4(5)	racemic
[(L^{LA})(L^{SA})Pd$_3$(L^{LA})$_2$](NO$_3$)$_6$	***4$_3$***		21.5×20.6×16.4	3.84(5) 4.10(4) 3.60(5)	10.30(7) 14.1(1) 10.2(1)	racemic

[a] The number ***4*** indicates four-layered metallacyclophanes and the subscripts denote the number of L^{LA}. [b] ***4$_0$*** could also be obtained in conglomerate crystals: the detailed synthetic conditions are provided in the Supporting Information.

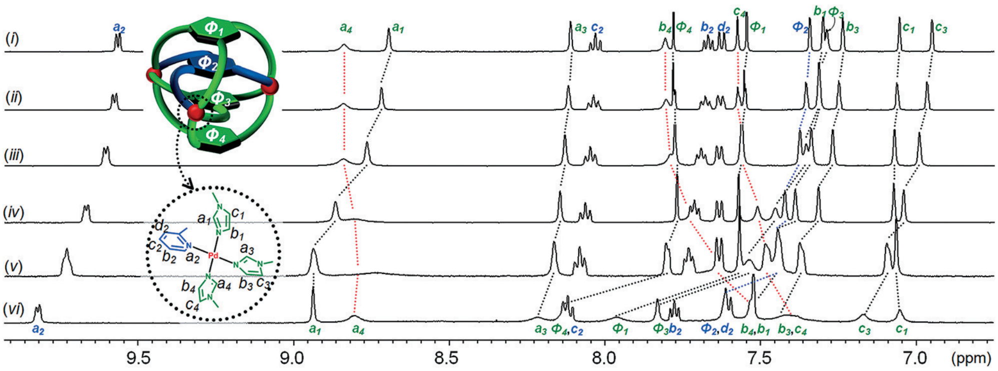

Figure 2. Partial ^1H NMR (500 MHz) spectra along with detailed assignment of $\mathbf{4_3}$ upon addition of $[D_6]Me_2SO$ to mixture of $D_2O/[D_6]Me_2CO$ at room temperature, reflecting solvent dependence of intramolecular π···π interactions. The volume ratios of D_2O:$[D_6]Me_2CO$:$[D_6]Me_2SO$ are (i) 5:5:0, (ii) 5:5:1, (iii) 5:5:2, (iv) 5:5:6, and (v) 5:5:10. vi) The spectrum of $\mathbf{4_3}$ in $[D_6]Me_2SO$.

$\mathbf{4_3}$ indicates that a long ligand, L^{LA}, coordinates to Pd^{II} as an inner ligand, and thus, the side view structure is severely distorted. Concomitantly, its intramolecular π···π interactions (3.60(5)–4.10(4) Å) between the central aromatic rings are relatively weak. The Pd–N bond lengths (2.014(5)–2.049(5) Å) of the outer ligand L^{LA} next to the inner ligand L^{LA} are slightly longer than those (1.990(4)–2.017(5) Å) of the other L^{LA} ligands. For the present four-layered tripalladium(II) cyclophanes, the Pd–N bond distances from the inner ligands are inversely proportional to the central intramolecular π···π interactions between the inner ligands (Supporting Information, Figure S4). The conglomerate-$\mathbf{4_0}$ crystals consist of *abcabc*··· layers (*ccp*) along the *c*-axis, showing suprachannels (Supporting Information, Figure S5) that are occupied with nitrate anions and solvate molecules. The suprachannel volumes of the conglomerate crystals in the unit cells were detected as 47.8 % (6979.3 Å^3/ 14613.2 Å^3) and 47.0 % (6705.5 Å^3/ 14261.4 Å^3) using the PLATON/SOLV utility.[8] By contrast, racemic crystals of $\mathbf{4_0}$ are packed in a columnar fashion in the (111) direction, and each column consists of two enantiomers alternately (Supporting Information, Figure S6). The void volume of racemate-$\mathbf{4_0}$ including nitrate anions and solvate molecules was determined to be 29.4 % (2215.6 Å^3/ 7531.6 Å^3). The distances of intermolecular π···π interactions are 3.39(1) and 3.35(1) Å. $\mathbf{4_2}$ and $\mathbf{4_3}$ molecules align in a columnar fashion in the (101) direction and on the *b*-axis, respectively, thereby exhibiting the intermolecular π···π interactions (3.68(1) and 3.47(1) Å, respectively). Each column of $\mathbf{4_2}$ consists of two enantiomers alternately, whereas that of $\mathbf{4_3}$ is composed of one enantiomer. The structure of $\mathbf{4_1}$ shows a non-closed packing system. The nitrate anions and solvate molecules exist in the unit-cell vacancy.

^1H NMR spectra of the present four-layered tripalladium(II) cyclophanes show that the chemical shifts corresponding to the central phenyl moieties are significantly upfield-shifted relative to their free ligands, indicating that the intramolecular π···π interactions exist in solution which is consistent with their X-ray crystal structures. Their resonance signals in a mixture of D_2O and $[D_6]Me_2CO$ could be assigned according to ^1H–^1H COSY measurement (Supporting Information, Figures S7–S9). To elucidate the behavior of the hetero-four-layered tripalladium(II) cyclophanes along with the ligands in solution, their temperature- and solvent-dependent ^1H NMR spectra were scrutinized (Supporting Information, Figures S10–S12). All metallacyclophanes have diastereotopic protons in the methylene groups even in solution, which is due to the strong molecular rigidity resulting from the intramolecular π···π interactions. The ^1H NMR spectra of $\mathbf{4_3}$ in solution are complicated owing to the three non-equivalent L^{LA}, as depicted in Figure 2. In a mixed $D_2O/[D_6]Me_2CO$ solution, the proton signals of the imidazolyl moiety (a_4 and b_4) in L^{LA} containing $Φ_4$ are broad relative to those of ligands containing $Φ_1$ and $Φ_3$, indicating that the imidazolyl moiety is fluxional owing to the weak coordination bonds (2.014(5)–2.049(5) Å) relative to those of the other two L^{LA} (1.990(4)–2.017(4) Å) arising from the conformational distortion, which is consistent with its crystal structure. The resonances of the phenyl moieties corresponding to $Φ_2$ and $Φ_3$ exhibit an upfield shift relative to those corresponding to $Φ_1$ and $Φ_4$, resulting from the relatively weak anisotropic effect. The addition of $[D_6]Me_2SO$ to a mixture of $D_2O/[D_6]Me_2CO$ solution at room-temperature changes to contrastingly downfield-shifts and peak-broadening, owing presumably to the Me_2SO solvent effects. It is noteworthy that the proton signals of a_4, b_4, and c_4 corresponding to the above-noted imidazolyl moiety show, upon the addition of $[D_6]Me_2SO$, a weaker anisotropy effect than those of the other imidazolyl and pyridyl moieties, due to the fluxional behavior in solution (Figure 2).

According to ESI-TOF-mass data, the tripalladium(II) cyclophane skeletons along with the respective ligand species were detected (Figure 3; Supporting Information, Fig-

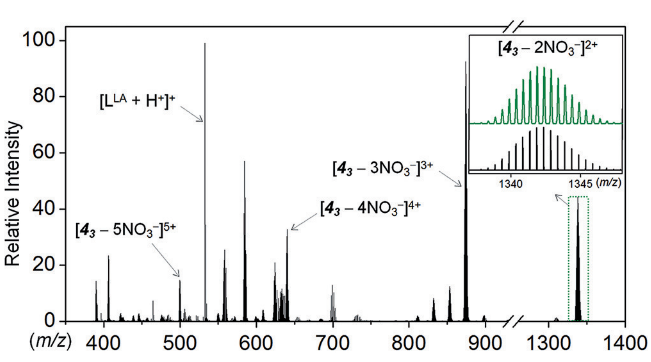

Figure 3. HR-ESI-TOF-MS main peaks of $\mathbf{4_3}$. Inset: the magnified data of experimental (green) and calculated (black) mass peaks corresponding to $[\mathbf{4_3}\text{-}2\,NO_3^-]^{2+}$ (see the Experimental Section in the Supporting Information for the assignments).

ures S13–S15). The mass peaks were isotopically resolved and shown to be in good agreement with their calculated theoretical distributions.

Our key strategy for construction of the four-layered trimetallacyclophanes reflecting the combined concept of inner-short/outer-long C_3-symmetric tridentate ligands and transannular π⋯π interactions is depicted in Scheme 1. How are the original four-layered tripalladium(II)cyclophanes efficiently formed, and why are they not palladium(II) coordin-ation cages instead? The first reaction of square planar palladium(II) ions with the short C_3-symmetric tridentate L^{SA} in the 3:2 mole ratio affords the two-layered tripalladium(II) cyclophane, $[(L^{SA})(PdCl_2)_3(L^{SA})]$. The length and conformation of the tridentate L^{SA} ligand are significant tectonic elements for self-assembly of the two-layered metallacyclophane system by square planar coordination to the palladium(II) ions. Formation of the metallacyclophane system can be ascribed to the presence of the transannular π⋯π interactions along with the above-noted square-planar coordination. Reaction of $[(L^{SA})(PdCl_2)_3(L^{SA})]$ with $AgNO_3$ smoothly yields its anion-exchanged species, $[(L^{SA})(Pd(NO_3)_2)_3(L^{SA})]$. Consecutive reaction of $[(L^{SA})(Pd(NO_3)_2)_3(L^{SA})]$ with a long C_3-symmetric tridentate ligand, L^{LE} or L^{LA}, in the 1:2 mole ratio produces the four-layered tripalladium(II) cyclophanes with the transannular π⋯π interactions, which are comparable to that (3.3–3.4 Å) of graphite.[9] Formation of the final metallacyclophanes seems to be related to a minimum in the energy profile of the molecular system based on a combination of enthalpic and entropic factors. Thus, $\boldsymbol{4_0}$, $\boldsymbol{4_2}$, and $\boldsymbol{4_3}$ can also be synthesized by the direct reaction of $Pd(NO_3)_2$ with L^{SA}, L^{LE}, and L^{LA} in appropriate mole ratios. Furthermore, formation of $\boldsymbol{4_1}$ and $\boldsymbol{4_3}$ by substitution reactions using L^{LA} can be explained by the slightly stronger Lewis basicity of the imidazolyl moiety relative to that of the pyridyl group.[10] The substitution reaction occurs more effectively at low temperature rather than direct reaction (Supporting Information, Figures S16, S17). At high temperature, dissociation of the metal complexes occurs instead of the substitution reaction. The reverse substitution reaction of $\boldsymbol{4_3}$ with L^{SA} cannot occur. Formation of the final products provides strong evidence that the present coordination-driven self-assembly by direct reaction, stepwise reaction, or substitution reaction is an efficient method for construction of hetero tripalladium(II) cyclophanes. Both the transannular π⋯π interactions and the space-length associated with a high degree of structural rigidity in the four-layered tripalladium(II) cyclophanes serve as good proof-of-concept experiments for $\boldsymbol{4_0}$, $\boldsymbol{4_1}$, $\boldsymbol{4_2}$, and $\boldsymbol{4_3}$. In the case of $\boldsymbol{4_0}$, formation of both racemate and conglomerate crystals induced by the crystallization media indicates that solvent choice is a pivotal factor in the molecular packing of the four-layered metallacyclophane system.

In conclusion, the direct reaction, stepwise reaction, and substitution reaction of Pd^{II} centers with the appropriate inner-short/outer-long C_3-symmetric tridentate ligands containing a central aromatic ring efficiently allow for the construction of unprecedented hetero-four-layered trimetallacyclophanes. The present study stands as typical proof-of-concept experiment for fine-tuning of an original molecular system via the transannular π⋯π interactions and inner-short/outer-long spacer lengths of the cyclophanes. The structural information including molecular rigidity and anisotropic effects in solution were clearly elucidated. The synthetic method showcased herein can be helpful in enhancing understanding of new topological constructions and in altering the electronic and optical properties of the skeleton, including relevant structural thermodynamics and stability.

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Keywords: crystal engineering · palladium · π⋯π interactions · supramolecular chemistry · trimetallacyclophanes

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[11] CCDC 1423637–1423642 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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