Fluorinated Macrocycles

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Palladium Fluoro Complexes: Useful Tools To Access Organometallic Metallamacrocycles**

Andreas Steffen, Thomas Braun, Beate Neumann, and Hans-Georg Stammler*

The remarkable reactivity and exceptional properties of d^8 transition-metal fluoro complexes account for their role in the synthesis of highly fluorinated organic building blocks and provide novel synthetic pathways to unique coordination compounds.[1,2] It has been demonstrated that fluoro complexes can serve as fluorinating agents,[1,3] but they also appear as intermediates in catalytic conversions,[1,2] for instance in cross-coupling reactions. The fluoro ligand in an intermediate fluoro species often exhibits higher reactivity than a chloro or bromo ligand.[2] One striking example involves the activation of a C−F bond of 2,4,6-trifluoro-5-chloropyrimidine in the presence of a thermodynamically weaker C−Cl bond at $\{Ni(PPh_3)_2\}$.[2a] Only the resulting nickel fluoro complex shows catalytic activity towards C−C coupling reactions with aryl boronic acids, whereas the chloro analogue does not. Comparable behavior has been found for a C−Si coupling reaction at a palladium center.[2c] In this case, a disilane is employed to replace the fluoro ligand through the formation of a strong Si−F bond. V. V. Grushin and coworkers found that palladium halide complexes of the type *trans*-$[PdX(Ph)(PPh_3)_2]$ (X = Cl, Br, I) undergo CO insertion into the M−C bond, but no reductive elimination occurred. When *trans*-$[PdF(Ph)(PPh_3)_2]$ is used, *trans*-$[PdF(PhCO)(PPh_3)_2]$ forms under CO atmosphere. This complex is only stable up to 10 °C, and reductive elimination of benzoyl fluoride is reported.[4] Access to d^8 transition-metal fluoro complexes is provided by reaction of an appropriate precursor complex with a fluoride source, such as HF, AgF, XeF_2, Me_3SnF, or ClF, or by activation of a carbon–fluorine bond at a transition-metal center.[1a–e,2,4,5] Pd complexes bearing anionic ligands, such as chloro, nitrato, or triflato ligands, have been found to undergo self-assembly in the presence of ligands that can serve as bridging units.[6] For example, $[Pd(en)(NO_3)_2]$ (en = ethylenediamine) readily reacts with 4,4′-bipyridine (4,4′-bpy) under dissociation of NO_3^- to give the macrocyclic compound $[\{Pd(en)(\mu\text{-}4,4'\text{-bpy})\}_4][NO_3]_8$.[6a] Comparable behavior of Pd−F complexes has not yet been reported.

Herein, we demonstrate the applicability of fluoride exchange at palladium for the synthesis of organometallic macrocycles; the latter comprise heteroaromatic rings as spacer units between Pd centers. This approach provides new opportunities for the synthesis of neutral macrocycles, examples of which are scarce. We use this strategy to prepare square and triangular molecules, which are stabilized by tetrafluoropyridyl ligands. Comparable triangular compounds have been referred to as “metallacalixarenes”.[6a,7,8]

Treatment of a solution of palladium fluoro complex **1** (Scheme 1) in THF with 1-trimethylsilyl-imidazole at 203 K led to the formation of the imidazole derivative *trans*-$[Pd(1\text{-}C_3N_2H_3)(4\text{-}C_5NF_4)(P\textit{i}Pr_3)_2]$ (**2a**), which is only stable below 283 K. Above this temperature, free phosphine and macrocycle **3a** form. Palladacycle **3a** was characterized by NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray diffraction analysis. Single crystals of **3a** were obtained from a solution in benzene.[9] Both enantiomers of the chiral compound **3a** were found in the unit cell; one is shown in Figure 1.

The palladium centers exhibit square-planar coordination geometry, thus leading to a square macrocycle with C_4 symmetry. The dihedral angle between the coordination planes at the transition-metal centers is 31.1°, whereas the imidazole units are arranged almost perpendicular to the Pd coordination planes. The diagonal Pd···Pd distance is 8.763 Å, and the separation of two Pd atoms on the same edge is 6.197 Å. The stacking of the molecules leads to a channel arrangement in the solid state (see the Supporting Information). The C−N bond lengths of the imidazole units are all in the same range. The equal N2−C17 and N3−C17 bond lengths and the angle N2-C17-N3 of 112.9°, which is widened compared to the free heterocycle, suggest that, to a degree, electron density is delocalized through the ring.[10] Although the $[\{Pd\}_4(1\text{-}C_3N_2H_3)_4]$ ($\{Pd\} = Pd(4\text{-}C_5NF_4)(P\textit{i}Pr_3)$) species **3a** is stable in the solid state as well as in solution, it undergoes fragmentation in MALDI-TOF experiments even at low laser intensities, giving a signal at m/z 1868.1, which corresponds to $[\mathbf{3a}-C_3N_2H_3]^+$ according to the isotope pattern.[11] Further fragments have been found at m/z 1384.6 $[\{Pd\}_3(C_3N_2H_3)_2]^+$ and m/z 900.4 $[\{Pd\}_2(C_3N_2H_3)]^+$.

The same synthetic strategy as for the preparation of **2a** can be employed to obtain *trans*-$[Pd(1\text{-}C_2N_3H_2)(4\text{-}C_5NF_4)(P\textit{i}Pr_3)_2]$ (**2b**) by addition of trimethylsilyltriazole to **1** (Scheme 1). Compound **2b** shows a similar behavior as **2a**, and conversion to the tetrameric triazole species **3b** and free

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[*] A. Steffen, Prof. Dr. T. Braun
Institut für Chemie
Humboldt-Universität zu Berlin
Brook-Taylor-Strasse 2, 12489 Berlin (Germany)
Fax: (+49) 30-2093-6939
E-mail: thomas.braun@chemie.hu-berlin.de

B. Neumann, Dr. H.-G. Stammler
Fakultät für Chemie
Universität Bielefeld
Postfach 100131, 33501 Bielefeld (Germany)

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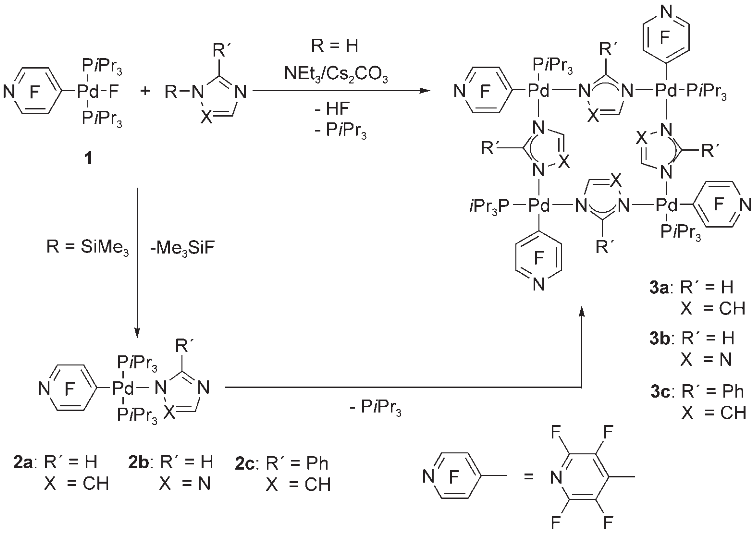


Scheme 1. Synthesis of **2a–c** and formation of the macrocycles **3a–c**.

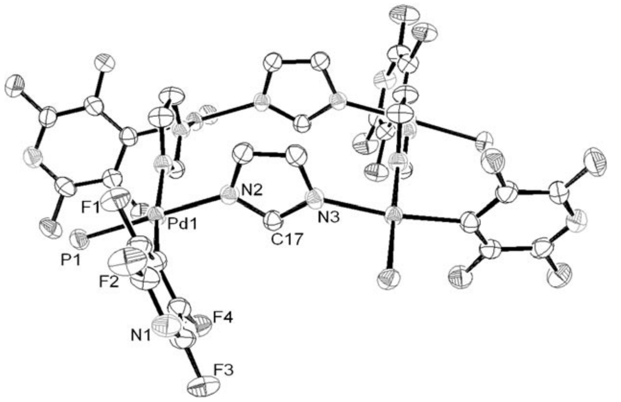


Figure 1. Crystal structure of **3a**. Thermal ellipsoids are set at the 50% probability level. H atoms and *i*Pr groups have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–N2 2.078(2), N2–C17 1.340(3), N3–C17 1.338(3); N2-C17-N3 112.9(2).

phosphine has been observed. X-ray diffraction analysis[9] indicates an N1,N4 bridging mode for the triazole units (Figure 2). Judging from the geometric data, delocalization of electron density seems to be feasible. The Pd···Pd separations of atoms located on the same edge are 6.132 and 6.305 Å, while the separations along the diagonals are 8.729 and 8.860 Å. Unlike the situation in **3a**, the 1,2-alternating triazole moieties deviate about 25° from a perpendicular conformation relative to the metal coordination plane. The identity of **3b** was also confirmed by mass spectrometry with signals in the MALDI-TOF mass spectrum at m/z 1874.2 ([**3b**−$C_2N_3H_2$]$^+$) and 1792.3 ([**3b**−C_5NF_4]$^+$).

Encouraged by these results, we tried to extend our reaction route to the preparation of macrocycles that exhibit bowl-like structures.[7,12] Suitable heterocyclic spacer units can be provided by silylated compounds such as 1-trimethylsilylated 2-phenylimidazole, benzimidazole, or purine. Addition of these heterocycles to a solution of **1** at room temperature led to the slow formation of **2c** and **4a,b** (Schemes 1 and 2).

We were not able to isolate **2c**, **4a**, or **4b**, because the subsequent reactions to the macrocyclic compounds with concomitant dissociation of a phosphine ligand proceeded while the starting compound **1** was still present. Upon heating a solution of **2c**, macrocycle **3c** is formed (Scheme 1). Single crystals suitable for X-ray diffraction analysis[9] were obtained from a solution in fluorobenzene. The molecular structure shown in Figure 3 clearly demonstrates the presence of a tetranuclear macrocyclic compound in which the 2-phenylimidazole units each connect two Pd atoms. The phenylimidazole moieties are arranged in an alternating up

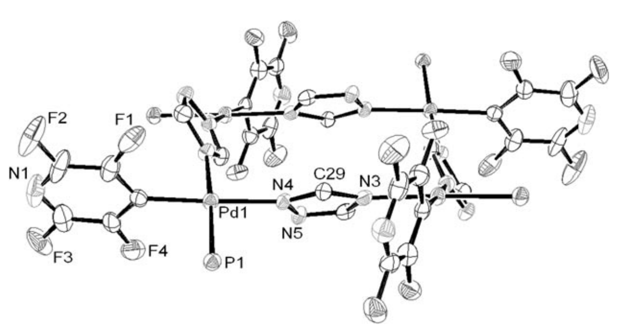
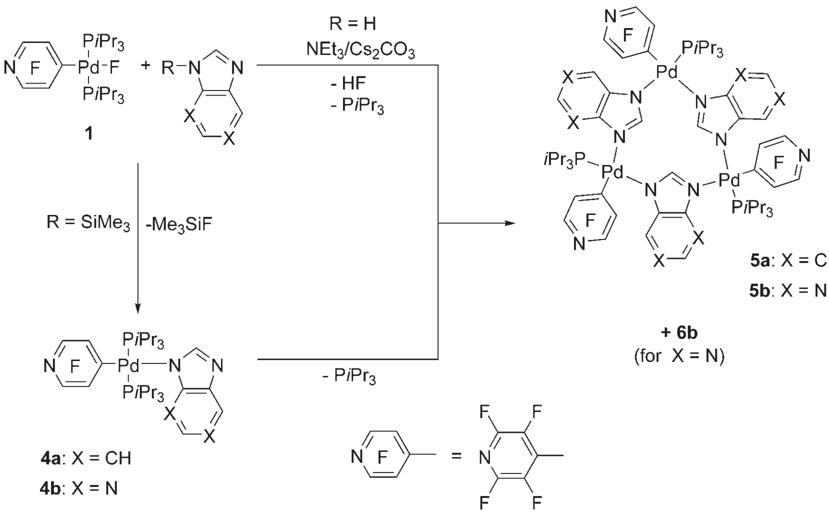


Figure 2. Crystal structure of **3b**. Thermal ellipsoids are set at the 50% probability level. H atoms and *i*Pr groups have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–N4 2.057(6), N4–C29 1.341(11), N3–C29 1.347(10); N3-C29-N4 112.8(7).



Scheme 2. Formation of the metallamacrocycles **5a**, **5b**, and **6b**.

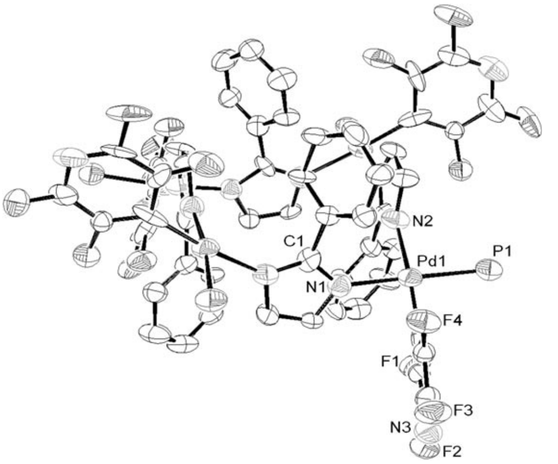


Figure 3. Crystal structure of **3c**. Thermal ellipsoids are set at the 50% probability level. H atoms and *i*Pr groups have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–N1 2.098(13), N1–C1 1.339(18), N2–C1 1.302(18); N1-C1-N2 116.28(16).

and down mode with respect to the square plane defined by the four Pd atoms.[12] A MALDI-TOF mass spectrum with signals at *m*/*z* 2096.3 [**3c**−$C_9N_2H_7$]$^+$ and 2046.5 [**3c**−(C_3H_7)C_5NF_4]$^+$ confirms the identity of the tetramer **3c**.[11]

At 343 K, the transformation of the monomers **4a** and **4b** into the metallacalix[3]arenes **5a** and **5b** is completed (Scheme 2). With purine as the spacer unit, the generation of a second macrocycle, **6b**, was also observed (ratio **5b**/**6b** 1:1, Scheme 2). On the basis of mass spectra, we believe that the latter consists of a pentanuclear macrocycle. ^{31}P NMR spectroscopic investigations revealed that **5b** and **6b** do not interconvert upon heating a solution of the two in toluene or THF.[6a, 13] Signals at *m*/*z* 1601.6 and 1484.4 in the MALDI-TOF spectra of **5a** correspond to the parent ion [**5a**]$^+$ and to [**5a**−$C_7N_2H_5$]$^+$. The palladacycles **5b** and **6b** give rise to fragmentation signals at $m/z = 1491.4$ [**5b**−$C_5N_4H_3$]$^+$ and 2561.1 [**6b**−$C_5N_4H_3$]$^+$, respectively. Single crystals of **5b** suitable for X-ray diffraction analysis[9] were obtained. The data reveal a bowl-shaped conformation with C_3 symmetry (Figure 4). To our knowledge, such an arrangement is unprecedented for an organometallic compound.[6,7,8e,12,14,15] The purine units in **5b** exhibit a N1,N3 bridging mode and are oriented to the same face of the Pd_3 triangle, unlike in other Pd^{II}-based macrocycles.[8a,e,12e] The distance between a palladium atom and the opposite heterocyclic spacer unit is about 5.9 Å. Lippert and co-workers have reported the synthesis of cationic metallacalix[4]- and metallacalix[6]arenes of the type $[a_2PdL]_n^{n+}$ ($a_2 = 1,2$-diaminocyclohexane, L = hydroxypyrimidine derivatives, $n = 4,6$).[12] Furthermore, **5b** represents a rare example of a coordination compound with a triangular geometry with metal atoms at the vertices.[6a,8,13,15c,d]

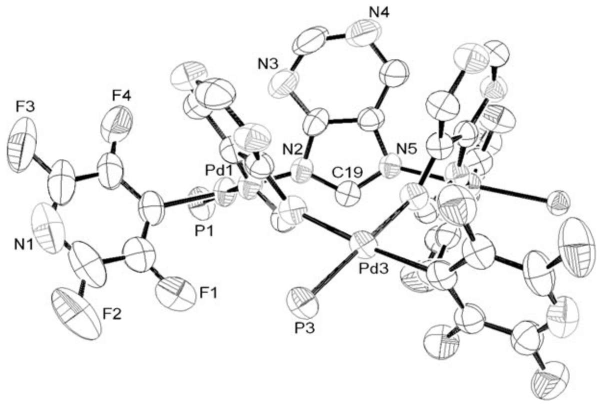


Figure 4. Crystal structure of **5b**. Thermal ellipsoids are set at the 50% probability level. H atoms and *i*Pr groups have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–N2 2.091(3), N2–C19 1.344(5), N5–C19 1.331(5); N2-C19-N5 115.3(3).

The transformations presented above can also be carried out at elevated temperatures when non-silylated heterocycles are employed together with the bases NEt_3 and Cs_2CO_3 to give the macrocycles **3a–c**, **5a**,**b**, and **6b**. However, under these conditions no isolation or spectroscopic detection of **2a–c** or **4a**,**b** has been successful, and several unidentified byproducts are formed (12–50%).

The fluoro ligand in *trans*-[PdF(4-C_5NF_4)(P*i*Pr_3)$_2$] (**1**) is evidently crucial for the formation of the monomeric building blocks, because the corresponding chloro complex *trans*-[PdCl(4-C_5NF_4)(P*i*Pr_3)$_2$][2c] cannot be used for the transformations presented above, neither on employing silylated heterocycles nor on using non-silylated heterocycles in the presence of bases (e.g. NEt_3 and Cs_2CO_3), even at elevated temperatures.

The metal atoms of Pt^{II}- and Pd^{II}-based macrocycles are often stabilized by *cis*-coordinating chelating ligands to avoid dissociation and scrambling of the monomers to cycles of different sizes.[8,12d,e,14,15] Complexes **3a–c** and **5a**,**b** are not stabilized in such a way. Instead, it is more likely that a stabilizing influence of the tetrafluoropyridyl ligands[16] plays a key role not only for the stability but also in the formation of the tetrameric or trimeric species. Even at elevated temperatures, no reductive elimination of a 4-(N-heterocycle)tetrafluoropyridine compound is observed, neither from **2a–c**, **3a–c**, nor from **4–6**.[2]

Some of the Pd macrocycles synthesized could potentially be used for host–guest chemistry.[12,15d,17,18] Most of the known palladacycles are cationic with multiple charges[7,8,12–15] and thus restricted to the recognition of anions or electron-rich systems. The fact that the metallamacrocycles **3a–c**, **5a**, **5b**, and **6b** are neutral compounds is therefore of particular interest. They might be capable of coordinating neutral, anionic, and cationic guests through π interactions, depending on the substitution pattern of the heterocyclic spacer units.[12,15d,17]

In conclusion, we presented a new strategy to access organometallic macrocycles. In this approach, fluoro ligands are replaced by heterocyclic building blocks, leading to molecular squares and triangles. We believe that it will be possible to expand this reaction route to other transition-metal fluorides. Our work also reveals that other organometallic macrocycles bearing electron-withdrawing anionic carbon ligands such as C_5F_4N should be accessible.[8e]

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[9] Data for the X-ray structure analyses. All structures were solved by direct methods and refined with full-matrix least-square methods on F^2 (SHELX-97).[19,20] **3a**: $C_{68}H_{96}F_{16}N_{12}P_4Pd_4$, $M_r = 1935.05$, $0.28 \times 0.20 \times 0.10$ mm^3, tetragonal, space group $P4/n$, $a = 17.4280(3)$, $c = 14.8970(3)$ Å, $Z = 2$, $V = 4524.74(14)$ Å^3, $\rho_{calcd} = 1.420$ g cm^{-3}, $2\theta_{max} = 54.94°$, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 100(2)$ K, 55351 reflections collected, 5175 were unique ($R_{int} = 0.049$), Nonius KappaCCD diffractometer, multiscan absorption correction (min/max transmission 0.7813/0.9130), $\mu = 0.927$ mm^{-1}, final $R_1 = 0.0452$, $wR_2 = 0.0879$ (all data), $R_1 = 0.0352$, $wR_2 = 0.0839$ [4241 reflections $I_0 > 2\sigma(I_0)$], residual electron density $+0.703/-0.908$ e Å^{-3}. **3b**: $C_{88}H_{116}F_{16}N_{16}P_4Pd_4$, $M_r = 2251.45$, $0.17 \times 0.14 \times 0.10$ mm^3, triclinic, space group $P\bar{1}$, $a = 10.4617(7)$, $b = 14.9170(12)$, $c = 17.3570(8)$ Å, $\alpha = 67.107(4)$, $\beta = 80.368(4)$, $\gamma = 87.575(4)°$, $Z = 1$, $V = 2459.2(3)$ Å^3, $\rho_{calcd} = 1.520$ g cm^{-3}, $2\theta_{max} = 50°$, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 100(2)$ K, 46456 reflections collected, 8567 were unique ($R_{int} = 0.1131$), Nonius KappaCCD diffractometer, multiscan absorption correction (min/max transmission 0.8667/0.9184), $\mu = 0.866$ mm^{-1}, final $R_1 = 0.1331$, $wR_2 = 0.1565$ (all data), $R_1 = 0.0678$, $wR_2 = 0.1281$ [5089 reflections $I_0 > 2\sigma(I_0)$], residual electron density $+0.842/-0.952$ e Å^{-3}. **3c**: $C_{116}H_{132}F_{20}N_{12}P_4Pd_4$, $M_r = 2623.82$, $0.30 \times 0.08 \times 0.06$ mm^3, tetragonal, space group $I4_1/a$, $a = 33.001(2)$, $c = 11.0402(6)$ Å, $Z = 4$, $V = 12023.4(13)$ Å^3, $\rho_{calcd} = 1.449$ g cm^{-3}, $2\theta_{max} = 50.5°$, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 100(2)$ K, 86185 reflections collected, 5412 were unique ($R_{int} = 0.3991$), STOE IPDS 2T diffractometer, numerical absorption correction (min/max transmission 0.8121/0.9578), $\mu = 0.724$ mm^{-1}, final $R_1 = 0.2689$, $wR_2 = 0.2066$ (all data), $R_1 = 0.0857$, $wR_2 = 0.1482$ [5412 reflections with $I_0 > 2\sigma(I_0)$], residual electron density $+1.270/-0.473$ e Å^{-3}. **5b**: $C_{64}H_{90}F_{12}N_{15}OP_3Pd_3$, $M_r = 1725.62$, $0.16 \times 0.14 \times 0.02$ mm^3, triclinic, space group $P\bar{1}$, $a = 10.6090(2)$, $b = 15.3420(3)$, $c = 24.7640(4)$ Å, $\alpha = 77.3280(11)$, $\beta = 77.7970(10)$, $\gamma = 81.8330(9)°$, $Z = 2$, $V = 3824.24(12)$ Å^3, $\rho_{calcd} = 1.499$ g cm^{-3}, $2\theta_{max} = 50°$, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 220(2)$ K, 75989 reflections collected, 13450 were unique ($R_{int.} = 0.058$), Nonius KappaCCD diffractometer, multiscan absorption correction (min/max transmission 0.8774/0.9834), $\mu = 0.839$ mm^{-1}, final $R_1 = 0.0616$, $wR_2 = 0.0940$ (all data), $R_1 = 0.0379$, $wR_2 = 0.0839$ [9998 reflections with $I_0 > 2\sigma(I_0)$], residual electron density $+0.655/-0.445$ e Å^{-3}. CCDC-653977 (**3a**), CCDC-653978 (**3b**), CCDC-653716 (**3c**), and CCDC-653979 (**5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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