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Oxidative Metalation as a Route to Size-Mismatched Macrocyclic Complexes: Osmium Corroles**

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Abstract: *Heavy-element corroles are of great interest as optical sensors, near-IR dyes, phosphors, organic light-emitting diodes, and anticancer compounds. Insertion of 5d metals into corroles, however, is often a difficult and unpredictable process. Against this backdrop, oxidative metalation of meso triarylcorroles with [$Os_3(CO)_{12}$]/NaN_3 in refluxing 1:2 diethylene glycol monomethyl ether/glycol has provided a convenient and relatively high-yielding route to nitridoosmium(VI) corroles, three of which could be characterized with single-crystal X-ray structure analysis.*

Although corroles were discovered as long ago as 1964 by Johnson and Kay,[1] the chemistry of corroles started in earnest only some 15 years ago, with reports of convenient one-pot syntheses of meso triarylcorroles.[2,3] Since then, the field has grown exponentially and, in many ways, has begun to rival the breadth and excitement of porphyrin chemistry.[4] Yet porphyrins and corroles share only a superficial similarity. The small N_4 holes of corroles, coupled with their trianionic character as ligands, sustain a strikingly different coordination chemistry, relative to porphyrins. These differences are particularly pronounced for 4d and 5d transition metals,[5] whose ionic radii are about 0.1–0.2 Å longer than those of their 3d congeners. The size mismatch between the ionic radii of the lower oxidation states of the 4d/5d elements and the corrole N_4 hole results in unusual difficulties in the metalation process. These difficulties are compounded by the higher degree of covalence of metal–ligand bonds and the propensity to form metal–metal bonds,[6] relative to the 3d metals. To our knowledge, few metalations are more capricious than the insertion of platinum into corroles, and it was recently accomplished in low yields in our laboratories with tetranuclear [$Pt_4(OAc)_8$] as the platinum source and benzonitrile as the solvent under highly specific conditions.[7] Other platinum sources and solvents have so far failed to lead to platinum insertion. As of today, the synthesis of osmium corroles remains one of the outstanding synthetic challenges in comparison to that of the middle and late 5d metallocorroles.

Refluxing free-base triarylcorroles under an inert atmosphere with [$Os_3(CO)_{12}$] in a high-boiling solvent such as diethylene glycol monomethyl ether (DEGME) led to recovery of the unchanged corroles after 12–24 hours. We surmised that the presence of an anionic nucleophile might assist the reaction. We were particularly intrigued by azide, because of its ability to generate a nitrido ligand by loss of N_2. Repeating the above reaction with added NaN_3 led, after about 16 hours, to a red-shift of the Soret band from $\lambda = 417$ nm, characteristic of free-base corroles, to approximately $\lambda = 440$ nm. MALDI-TOF analysis of the product suggested the formation of OsN corroles, but only in yields of about 5%. Because of the difficulty of removing DEGME from the final products, we then investigated ethylene glycol as a solvent, which is conveniently removed by aqueous extraction. Unfortunately, free-base triarylcorroles proved to be poorly soluble in ethylene glycol, thus prompting us to add a certain proportion of DEGME to assist with solubilizing the corroles. To our delight, use of 1:2 v/v DEGME/glycol led to a nearly tenfold increase in the yield of the OsN corrole products, from about 5% to about 50%. The mixed solvent also proved to be easily removable with aqueous extraction. Overall, oxidative insertion in a suitable high-boiling solvent proved to be the key to the successful insertion of osmium into corroles.

As shown in Scheme 1, four different *meso*-tris(*p*-X-phenyl)corroles, $H_3\{T(p\text{-X-P})C\}$, where $X = CF_3$, H, CH_3, and OCH_3, led to the corresponding $Os^{VI}N$ complexes. As square-pyramidal complexes with a single strongly π-donating axial ligand, the complexes are expected to exhibit a diamagnetic ground state, with a d_{xy}^2 electronic configuration. This picture is consistent with the observed diamagnetic ^1H NMR spectra of the compounds, spectra which could be fully assigned with COSY and NOESY analyses.

In this initial report on osmium corroles, we have primarily focused on proof of composition and structure, as opposed to detailed spectroscopic and electronic-structural questions. Two properties of the complexes are nevertheless worth pointing out. First, the Soret maxima of the complexes are relatively insensitive to the *para*-substituent X, thus showing a red-shift of only 4 nm when going from $X = CF_3$ to $X = OCH_3$ (see Table S1 in the Supporting Information). Second, the electrochemical HOMO–LUMO gaps are large,

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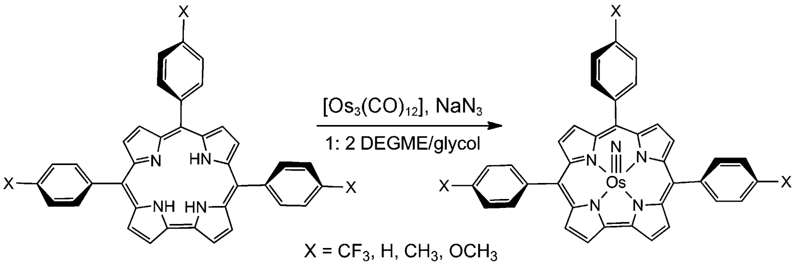

Scheme 1. Synthesis of $Os^{VI}N$ triarylcorroles.

approximately 2.2 eV (see Table S2). Over a lengthy series of studies,[8,9] we established that these two characteristics are indicative of an innocent $[corrole]^{3-}$ ligand, such as that found in a gold corrole, as opposed to a noninnocent $[corrole]^{\bullet 2-}$ ligand, for which copper corroles provide some of the best-studied examples. Thus, in contrast to the OsN corroles, the Soret maxima of copper triarylcorroles shift by some 27 nm when going from $X = CF_3$ ($\lambda = 407$ nm) to $X = OCH_3$ ($\lambda = 434$ nm).[8a] In the same vein, the electrochemical HOMO–LUMO gaps of copper triarylcorroles are only around 0.9 eV, less than half that for Au and OsN corroles.[8d]

All but one of the four OsN corroles proved amenable to single-crystal X-ray structure determination. The structures refined well, giving R_1 $[I > 2\,s(I)]$ values around 3-5%. Selected crystallographic data and metal–ligand distances are listed in Tables 1 and 2, respectively, and thermal ellipsoid plots are shown in Figure 1. The observed Os≡N distances of 1.643–1.648 Å are in essentially perfect agreement with the sum of Pyykkö's covalent radii for triply bonded osmium (1.09 Å) and triply bonded nitrogen (0.54 Å).[10] The Os–$N_{corrole}$ distances are in the range (1.990 ± 0.015) Å and are distinctly shorter than those in other N-coordinated osmium complexes. For example, the osmium porphyrins ($[Os^{II}(TPP)(PPh_3)_2]$, $[Os^{IV}(TPP)(OEt)_2]$) and $[Os^{VI}\{T(p\text{-}CH_3)C\}(O)_2]$ exhibit Os–N distances averaging 2.044, 2.042, and 2.066 Å.[11] In other words, the Os–N distances in the osmium corroles are some 0.05–0.08 Å shorter than those found for a variety of osmium porphyrins. Furthermore, as shown in Figure S13, for all three complexes, the corrole macrocycle is domed or folded in a taco-like manner, with the osmium displaced approximately 0.6 Å from the corrole N_4 plane. The overall tightness of the coordination environment may provide a partial explanation for the difficulties encountered in the insertion of osmium and other 5d transition metals into corroles.

Table 2: Crystallographic metal–ligand distances (Å).

	[Os{T(*p*-CF$_3$)C}(N)]	[Os(TPC)(N)]	[Os{T(*p*-OCH$_3$)C}(N)]
Os1–N1	1.979(2)	1.9797(11)	1.978(3)
Os1–N2	2.005(2)	1.9971(12)	1.996(3)
Os1–N3	1.994(2)	1.9971(11)	1.995(3)
Os1–N4	1.983(2)	1.9970(12)	1.975(3)
Os1–N5	1.643(2)	1.6473(12)	1.648(3)
ΔOs–N$_4$	0.6049(15)	0.6125(6)	0.6049(15)

Somewhat unusually, as shown in Figure 2 and Figure S12, resonance Raman measurements of the compounds revealed at least two ^{15}N-sensitive Os≡N vibrations. For the unlabeled compounds, they occur at approximately 1099 and 1079 cm^{-1}. Preliminary DFT (OLYP/STO-TZP) calculations indicate that these vibrations are best viewed as symmetric and antisymmetric combinations of the Os≡N and Os–$N_{corrole}$ stretching modes. The coupling of these two coordinates is presumably facilitated by the doming of the macrocycles.

In conclusion, it is worth reflecting on the significance of oxidative metalation for corrole chemistry, where it is far from new. Quite a number of metals, including Cr, Fe, Cu, Mo, and Ag, undergo oxidative insertion into corroles without any added oxidants other than ambient O_2.[8,12] The recent, rather serendipitous insertion of platinum into corroles with $[Pt_4(OAc)_8]$/benzonitrile also involved aerial oxidation, as well as C–H activation of benzonitrile. The present syntheses involved a rational application of oxidative metalation to corrole chemistry. Oxidative metalation and reductive demetalation[13] are indeed two sides of the same coin, both manifestations of the sterically constrained, highly charged nature of corrole ligands. This work affords facile access to reasonable quantities of $Os^{VI}N$ corroles (hundreds of

Table 1: Crystallographic data for the complexes analyzed.

Sample	[Os{T(*p*-CF$_3$)C}(N)]	[Os{T(*p*-H)C}(N)]	[Os{T(*p*-OCH$_3$)C}(N)]
Chemical formula	$C_{40}H_{20}F_9N_5Os$	$C_{37}H_{23}N_5Os$	$C_{40}H_{29}O_3N_5Os$
Formula mass	931.81	727.80	817.88
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
λ (Å)	0.7749	0.5904	0.5635
a (Å)	16.4459(15)	10.3439(4)	13.3068(6)
b (Å)	14.1502(13)	8.0654(3)	8.1147(4)
c (Å)	14.1923(13)	32.4759(13)	30.1311(14)
β (deg.)	93.6600(14)	96.9208(16)	101.604(3)
Z	4	4	4
V (Å^3)	3296.0(5)	2689.65(18)	3187.1(3)
Temperature (K)	100(2)	100(2)	100(2)
Density (g cm^{-3})	1.878	1.797	1.705
Measured reflections	36129	903013	63715
Unique reflections	9981	22525	9713
Parameters	496	388	445
Restraints	0	0	0
R_{int}	0.0399	0.0763	0.0592
θ range (deg.)	2.650–33.607	3.149–36.184	2.958–23.735
R_1, wR_2 all data	0.0281, 0.0622	0.0285, 0.0647	0.0361, 0.0816
S (GooF) all data	1.062	1.157	1.323
Max/min res. Dens. (e Å^{-3})	0.767/−1.493	4.464/−3.169	2.077/−2.869

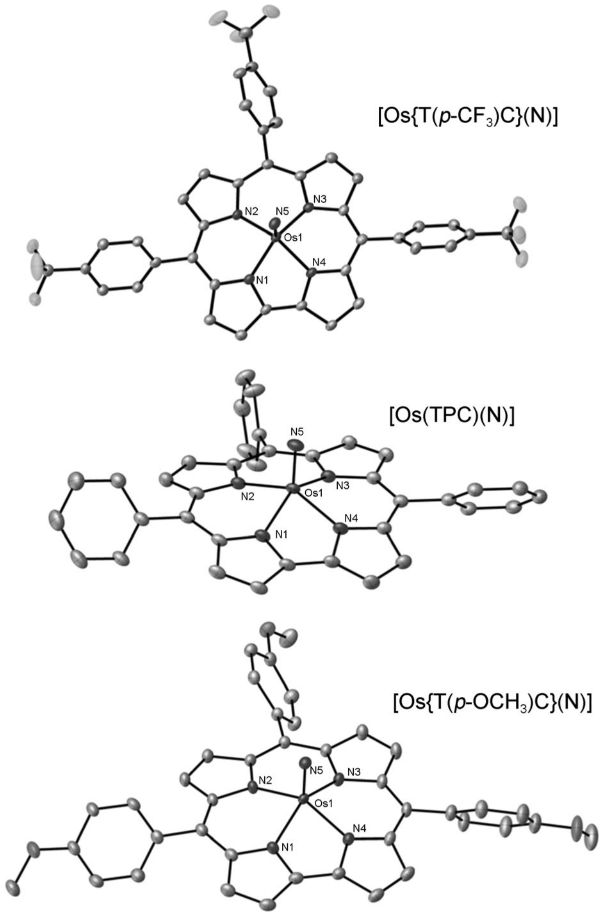

Figure 1. Thermal ellipsoid (40 % probability) plots for OsN corroles.

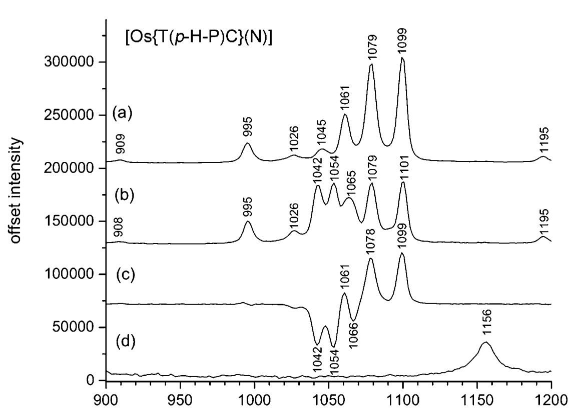

Figure 2. Resonance Raman spectra ($\lambda_{ex} = 413.1$ nm) of [Os(TPC)(N)] in CH_2Cl_2: a) unlabeled; b) 50 % ^{15}N-labeled on Os≡N; c) ^{14}N–^{15}N difference spectrum; d) solvent spectrum.

mg), thus opening up many opportunities for further studies. Ongoing research in our laboratory include detailed spectroscopic studies, experiments aimed at activating the osmium-bound nitrido ligand,[14] and explorations of the potential biological, especially anticancer, activity of these complexes.[14d,15]

Experimental Section

General procedure for the synthesis of [Os{T(*p*-X-Ph)C}(N)]: A free-base corrole, H_3[T(*p*-X-P)C (0.189 mmol), [$Os_3(CO)_{12}$] (0.134 mmol), and sodium azide (6 equiv) were added to a 50 mL three-necked round bottom flask fitted with a reflux condenser and charged with ethylene glycol (6 mL) and DEGME (3 mL) and a magnetic stirring bar. The contents were degassed with a flow of argon and then refluxed under Ar with constant stirring for 16 h. Completion of the reaction was indicated by the disappearance of the Soret absorption of the free-base corrole and appearance of a new Soret maximum at approximately $\lambda = 440$ nm. After cooling, distilled water (300 mL) was added and the resulting mixture was extracted with dichloromethane (200 mL). The organic phase was repeatedly (at least 3 times) washed with distilled water and extracted with dichloromethane to ensure full removal of the high-boiling solvents used in the reaction. The organic phase was then dried with anhydrous sodium sulfate and filtered and the filtrate evaporated to dryness in a rotary evaporator. The crude material obtained was chromatographed on a silica gel column with 1:1 *n*-hexane/dichloromethane. All fractions with λ_{max} around 440 nm were collected and dried. The products were further purified with a second column chromatography and finally with preparative thin-layer chromatography with the same solvent as eluent.

[Os{T(*p*-CF_3-Ph)C}(N)]. Yield 90 mg (50.8 %). UV/Vis (CH_2Cl_2) λ_{max} [nm, $\varepsilon \times 10^{-4}$ ($M^{-1}cm^{-1}$)]: 441 (10.75), 553 (1.52), 590 (2.39). ^1H NMR (400 MHz, CD_2Cl_2, 253 K): $\delta = 9.63$ (d, 2H, $^3J_{HH} = 4$ Hz, β-H); 9.30 (d, 2H, $^3J_{HH} = 4$ Hz, β-H); 9.23 (d, 2H, $^3J_{HH} = 4$ Hz, β-H); 9.07 (d, 2H, $^3J_{HH} = 4$ Hz, β-H); 8.69 (d, 2H, $^3J_{HH} = 8$ Hz, 5,15-*o*1-Ph); 8.61 (d, 1H, $^3J_{HH} = 8$ Hz, 10-*o*1-Ph); 8.25 (d, 2H, $^3J_{HH} = 8$ Hz, 5,15-*m*1-Ph); 8.17 (d, 2H, $^3J_{HH} = 8$ Hz, 5,15-*o*2-Ph); 8.15 (d, 1H, $^3J_{HH} = 8$ Hz, 10-*o*2-Ph); 8.11 (d, 1H, $^3J_{HH} = 8$ Hz, 10-*m*1-Ph); 8.07 (d, 2H, $^3J_{HH} =$ 8 Hz, 5,15-*m*2-Ph); 8.02 ppm (d, 1H, $^3J_{HH} = 8$ Hz, 10-*m*2-Ph). C,H,N analysis (%): found: C 51.40, H 2.31, N 7.40; calcd: C 51.56, H 2.16, N 7.52. MS (MALDI-TOF, major isotopomer): $M^+ = 933.20$ (expt), 933.12 (calcd for $C_{40}H_{20}N_5F_9Os$).

[Os(TPC)(N)]. Yield 83 mg (60 %). UV/Vis (CH_2Cl_2): λ_{max} (nm), [$\varepsilon \times 10^{-4}$ ($M^{-1}cm^{-1}$)]: 442 (8.65, Soret), 555 (1.23), 594 (2.09). ^1H NMR (400 MHz, CD_2Cl_2, 253 K): $\delta = 9.57$ (d, 2H, $^3J_{HH} = 4$ Hz, β-H); 9.32 (d, 2H, $^3J_{HH} = 4$ Hz, β-H); 9.23 (d, 2H, $^3J_{HH} = 4$ Hz, β-H); 9.07 (d, 2H, $^3J_{HH} = 4$ Hz, β-H); 8.55 (d, 2H, $^3J_{HH} = 8$ Hz, 5,15-*o*1-Ph); 8.46 (d, 1H, $^3J_{HH} = 8$ Hz, 10-*o*1-Ph); 8.12 (d, 2H, $^3J_{HH} = 8$ Hz, 5,15-*o*2-Ph); 7.97 (d, 1H, $^3J_{HH} = 8$ Hz, 10-*m*1-Ph); 7.83–7.93 (m, 4H, 5,15-*m*1-Ph, 10-*m*1-Ph and 10-*p*-Ph, overlapping); 8.83–7.72 (m, 5H, 5,15-*m*2-Ph 10-o2-Ph); 8.07 ppm (d, 2H, $^3J_{HH} = 8$ Hz, 5,15-*m*2-Ph, 5,15-*p*-Ph and 10-*m*2-Ph, overlapping). C,H,N analysis (%): found: C 61.34, H 3.34, N 9.58; calcd: C 61.06, H 3.19, N 9.62. MS (MALDI-TOF, major isotopomer): $M^+ = 729.10$ (expt), 729.16 (calcd for $C_{37}H_{23}N_5Os$).

[Os{T(*p*-CH_3-Ph)C}(N)]. Yield 80 mg (55.7 %) UV/Vis (CH_2Cl_2): λ_{max} (nm), [$\varepsilon \times 10^{-4}$ ($M^{-1}cm^{-1}$)]: 443 (9.53), 556 (1.38), 596 (2.37). ^1H NMR (400 MHz, CD_2Cl_2, 253 K): $\delta = 9.55$ (d, 2H, $^3J_{HH} = 4$ Hz, β-H); 9.31 (d, 2H, $^3J_{HH} = 4$ Hz, β-H); 9.21 (d, 2H, $^3J_{HH} = 4$ Hz, β-H); 9.06 (d, 2H, $^3J_{HH} = 4$ Hz, β-H); 8.42 (d, 2H, $^3J_{HH} = 8$ Hz, 5,15-*o*1-Ph); 8.32 (d, 1H, $^3J_{HH} = 8$ Hz, 10-*o*1-Ph); 7.99 (d, 2H, $^3J_{HH} = 8$ Hz, 5,15-*o*2-Ph); 7.83 (d, 1H, $^3J_{HH} = 8$ Hz, 10-*o*2-Ph); 7.70 (d, 2H, $^3J_{HH} = 8$ Hz, 5,15-*m*1-Ph); 7.66 (d, 1H, $^3J_{HH} = 8$ Hz, 10-*m*1-Ph); 7.60 (d, 2H, $^3J_{HH} =$ 8 Hz, 5,15-*m*2-Ph); 7.54 (d, 1H, $^3J_{HH} = 8$ Hz, 10-*m*2-Ph); 2.68 (s, 6H, 5,15-*p*-CH_3); 2.66 ppm (s, 3H, 10-*p*-CH_3). C,H,N analysis (%): found: C 61.69, H 3.98, N 8.95; calcd: C 62.40, H 3.80, N 9.10. MS (MALDI-TOF, major isotopomer): $M^+ = 771.08$ (expt), 771.20 (calcd for $C_{40}H_{29}N_5Os$).

[Os{T(*p*-OCH_3-Ph)C}(N)]. Yield 68 mg (43 %). UV/Vis (CH_2Cl_2): λ_{max} (nm), [$\varepsilon \times 10^{-4}$ ($M^{-1}cm^{-1}$)]: 445 (9.65), 557 (1.35), 600 (2.44). ^1H NMR (400 MHz, CD_2Cl_2, 253 K): $\delta = 9.54$ (d, 2H, $^3J_{HH} =$ 4 Hz, β-H); 9.33 (d, 2H, $^3J_{HH} = 4$ Hz, β-H); 9.21 (d, 2H, $^3J_{HH} = 4$ Hz, β-H); 9.07 (d, 2H, $^3J_{HH} = 4$ Hz, β-H); 8.45 (d, 2H, $^3J_{HH} = 8$ Hz, 5,15-*o*1-Ph); 8.35 (d, 1H, $^3J_{HH} = 8$ Hz, 10-*o*1-Ph); 8.03 (d, 2H, $^3J_{HH} = 8$ Hz, 5,15-*o*2-Ph); 7.88 (d, 1H, $^3J_{HH} = 8$ Hz, 10-*o*2-Ph); 7.42 (d, 2H, $^3J_{HH} =$

8 Hz, 5,15-*m*1-Ph); 7.37 (d, 1 H, $^3J_{HH} = 8$ Hz, 10-*m*1-Ph); 7.32 (d, 2 H, $^3J_{HH} = 8$ Hz, 5,15-*m*2-Ph); 7.25 (d, 1 H, $^3J_{HH} = 8$ Hz, 10-*m*2-Ph); 4.06 (s, 6 H, 5,15-*p*-OCH$_3$); 4.04 ppm (s, 3 H, 10-*p*-OCH$_3$). C,H,N analysis (%): found: C 58.27, H 3.69, N 8.37; calcd: C 58.74, H 3.57, N 8.56. MS (MALDI-TOF, major isotopomer): $M^+ = 819.05$ (expt), 819.19 (calcd for $C_{40}H_{29}O_3N_5Os$).

Crystallization and crystallography: Approximately 5–10 mg of each OsN corrole was dissolved in a minimum quantity of dichloromethane in a vial and carefully layered with *n*-hexane. The vial was covered with Parafilm and aluminum foil and left to stand for two weeks, during which X-ray quality crystals formed for three of the OsN corroles. X-ray data were collected on beamline 11.3.1 at the Advanced Light Source of Lawrence Berkeley National Laboratory, Berkeley, California. The samples were mounted on MiTeGen kapton loops and placed in a 100(2) K nitrogen cold stream provided by an Oxford Cryostream 700 Plus low temperature apparatus on the goniometer head of a Bruker D8 diffractometer equipped with an APEXII CCD detector. Diffraction data were collected using synchrotron radiation monochromated with silicon(111) to wavelengths of 0.7749(1), 0.5904(1), and 0.5635(1) Å for Os{T(p-CF$_3$-Ph)C}(N), Os(TPC)(N) and Os{T(p-OCH$_3$-Ph)C}(N), respectively. In each case, an approximate full-sphere of data was collected using 0.3° ω scans. The structures were solved by direct methods (SHELXT) and refined by full-matrix least squares on F^2 (SHELXL-2013). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically calculated and refined as riding atoms. The crystallographic information files have been deposited at the Cambridge Crystallographic Data Centre. CCDC 1002320, 1002321, and 1002322 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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