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# Dinitrogen Cleavage by a Heterometallic Cluster Featuring Multiple Uranium–Rhodium Bonds

Xiaoqing Xin,<sup>1</sup> Iskander Douair,<sup>2</sup> Yue Zhao,<sup>1</sup> Shuao Wang,<sup>3</sup> Laurent Maron,<sup>2\*</sup> and Congqing Zhu<sup>1\*</sup>

<sup>1</sup> State Key Laboratory of Coordination Chemistry, Jiangsu Key Laboratory of Advanced Organic Materials, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China

<sup>2</sup> LPCNO, CNRS & INSA, Université Paul Sabatier, 135 Avenue de Rangueil, 31077 Toulouse, France

<sup>3</sup> State Key Laboratory of Radiation Medicine and Protection, School for Radiological and interdisciplinary Sciences (RAD-X) and Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, Soochow

University, Suzhou, China

Supporting Information Placeholder

**ABSTRACT:** Reduction of dinitrogen  $(N_2)$  is a major challenge for chemists. Cooperation of multiple metal centers to break the strong  $N_2$  triple bond has been identified as a crucial step in both the industrial and the natural ammonia syntheses. However, reports of the cleavage of  $N_2$  by a multimetallic uranium complex remain extremely rare, although uranium species was used as catalyst in the early Harber-Bosch process. Here we report the cleavage of  $N_2$  to two nitrides by a multimetallic uranium–rhodium cluster at ambient temperature and pressure. The nitride product further reacts with acid to give substantial yields of ammonium. The presence of uranium-rhodium bonds in this multimetallic cluster was revealed by X-ray crystallographic and computational studies. This study demonstrates that the multimetallic clusters containing uranium and transition metals are promising materials for  $N_2$  fixation and reduction.

# INTRODUCTION

The cleavage and conversion of the strong N=N triple bond in dinitrogen (N<sub>2</sub>) has attracted considerable attention from both academia and industry.<sup>1-12</sup> The current industrial ammonia synthesis from N<sub>2</sub>, the Haber-Bosch process, uses an iron-based catalyst and requires high temperatures and pressures. Biologically, however, N<sub>2</sub> can be converted to ammonia by nitrogenases at ambient temperature and pressure. The most important active site in nitrogenases is a multimetallic ironmolybdenum cluster.<sup>13-16</sup> This has inspired chemists to explore the fixation and reduction of N<sub>2</sub> by Fe and Mo-based molecular catalysts, which have been investigated extensively in recent decades.<sup>17-28</sup>

Before an Fe-based catalyst was used for the industrial synthesis of ammonia, the early Haber-Bosch process utilized a uranium-based catalyst.<sup>29</sup> Since the first uranium  $N_2$  complex was reported in 1998,30 some examples of molecular uranium complexes capable of fixing or reducing N<sub>2</sub> have appeared.<sup>31-40</sup> However, only one example of N<sub>2</sub> cleavage achieved by a uranium species with [K(naphthalenide)] has been reported.33 Consequently, understanding the six-electron N<sub>2</sub> reduction by molecular uranium complexes remains a substantial challenge.<sup>41</sup> Previous investigations show that the multimetallic uranium complexes have great potential in N<sub>2</sub> reduction due to the synergistic effects from the different metals.<sup>31,36-38</sup> For instance, Cummins and co-workers showed that a trivalent uranium precursor can facilitate N2 reduction on an Mo center.31 Mazzanti and co-workers reported a four-electron reduction of N<sub>2</sub> by the multimetallic uranium-potassium complexes.<sup>36,37</sup> Very recently, Arnold and co-workers reported that thorium or uranium dinuclear metallacycles can mediate the four-electron reduction and conversion of  $N_2$  in the presence of  $KC_8$ .<sup>40</sup> These studies suggest that dinitrogen fixation or activation may be expected for highly active low-valent uranium compounds with N/O-donor-based ligand. However, the complete cleavage of  $N_2$ , a six-electron reduction, by multimetallic complexes containing uranium and transition metals has not been reported to date.

Here we describe the first example of a multimetallic uranium-rhodium cluster that reacts with  $N_2$  and a potassiumbased reducing agent to give a species with two nitrides through  $N\equiv N$  bond cleavage. Protonation of this product with an excess of acid leads to the formation of ammonium.

## **RESULTS AND DISCUSSION**

Synthesis, characterization and reactivity. Complex  $\{U[N(CH_3)(CH_2CH_2NP'Pr_2)_2](Cl)_2(THF)\}$  (2) was synthesized by the reaction of uranium tetrachloride (UCl<sub>4</sub>) with  $[CH_3N(CH_2CH_2NHP'Pr_2)_2]$  (1) in the presence of "BuLi in tetrahydrofuran (THF). It can be isolated as a brown solid in 82% yield (Scheme 1). The structure of 2 was characterized by nuclear magnetic resonance (NMR) spectroscopy, elemental analysis, and single-crystal X-ray diffraction. The <sup>1</sup>H NMR spectrum of 2 shows a broad range of peaks from +88.49 to -81.53 ppm, which is consistent with the presence of paramagnetic tetravalent uranium complexes. Our previous studies implied that complexes with N-P ligand are the useful precursors for the construction of multimetallic clusters with fblock elements.<sup>42-45</sup> Therefore, we examined the reaction of **2** with monovalent transition metal species. Treatment of 4 equiv. of monomeric uranium complex 2 with 1 equiv. of  $[RhCl(COD)]_2$  (COD = cyclooctadiene) at 110 °C in toluene results formation of complex in the а  $[{U[N(CH_3)(CH_2CH_2NP^iPr_2)_2](Cl_2)}_2(\mu-Cl)(\mu-Rh)]$ (3) as brown crystals in 35% yield after recrystallization from toluene at -30 °C (Scheme 1).

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The reduction of 2 equiv. of complex **3** with 4 equiv. of potassium graphite (KC<sub>8</sub>) in THF under 1 atm of N<sub>2</sub> or argon leads to the formation of a multimetallic cluster  $[{U[N(CH_3)(CH_2CH_2NP'Pr_2)_2](Cl)}_2(\mu-Cl)(\mu-Rh)]$  (**4**), which can be isolated as red-brown crystals in 71% yield after a simple workup (Scheme 1). Further reduction of 2 equiv. of complex **4** with 6 equiv. of KC<sub>8</sub> under an N<sub>2</sub> atmosphere (1 atm) for 2 h followed by filtration and recrystallization furnished the N<sub>2</sub> cleavage complex  $[{U_2[N(CH_3)(CH_2CH_2NP'Pr_2)_2]_2(Rh)(\mu-N)}_2]$  (**5**) in 39% yield as dark brown crystals (Scheme 1). The deep colors of these multimetallic uranium clusters (**3**, **4**, and **5**) are consistent with the strong absorption of their THF solution in the ultraviolet-visible region (Figures S12-S14).

Complex 5 can be prepared directly by the reduction of 2 equiv. of complex 3 with excess (typically 10 equiv.) of  $KC_8$ under 1 atm N<sub>2</sub> at RT for 6 h. From *in situ* NMR experiments, we found that only complex 4 was generated in the first 2 h, and could further react with the residual KC<sub>8</sub> to form the final N<sub>2</sub> cleavage product 5 (Figure S8). In addition, the reaction of complex 2 with excess KC8 in THF under 1 atm N2 at RT for 2 days was performed and no reaction occurred, which suggests that this tetravalent uranium complex 2 was not liable to be reduced by KC<sub>8</sub> affording low-valent uranium species and then to reduce the N<sub>2</sub>. Therefore, the cluster 4 with U-Rh bonds is the species which undergoes the N2 cleavage in the presence of KC8. Only a mixture of unidentified products was observed when reduction of 2 equiv. of complexes 3 or 4 with 10 or 6 equiv. of  $KC_8$  under an atmosphere of argon rather than  $N_2$ . These results demonstrate that the two nitride ligands in 5 originate from N<sub>2</sub>.

To further verify the source of the nitride in complex 5, the <sup>15</sup>N-labeled product, 5-<sup>15</sup>N, was synthesized by the reduction of 3 with KC<sub>8</sub> under 1 atm of <sup>15</sup>N<sub>2</sub>. The production of the ammonium ion, NH<sub>4</sub><sup>+</sup> was observed by the acidification of these N<sub>2</sub> cleavage products, 5 and 5-<sup>15</sup>N (Figures S9-S11). For

instance, treatment of a THF solution of 5 with 50 equiv. of pyridine hydrochloride (PyHCl) gives NH<sub>4</sub>Cl in 82% yield, which shows a triplet resonance ( $\delta = 7.32$  ppm,  $J_{\rm NH} = 52$  Hz) in its <sup>1</sup>H NMR spectrum in deuterated dimethyl sulfoxide. Under the same procedure, a doublet resonance ( $\delta = 7.32$  ppm,  $J_{\rm NH} =$ 72 Hz) was observed in the <sup>1</sup>H NMR spectrum for the acidified product, <sup>15</sup>NH<sub>4</sub>Cl, formed from 5-<sup>15</sup>N. These results are consistent with previous studies for N<sub>2</sub> reduction and hydrogenation to ammonia.<sup>22,36</sup> These <sup>15</sup>N-labeled studies demonstrate that the two nitride ligands in 5 originate from N<sub>2</sub> and that both the nitrides are nucleophilic and react with acid to form ammonium salts. Therefore, the formation of 5 from 3 or 4 involves the binding, activation, and complete six-electron reductive cleavage of N<sub>2</sub> by multimetallic uranium-rhodium cluster and KC<sub>8</sub> under conditions of ambient temperature and pressure. Encouraged by the achievements of uranium nitrides functionalization, <sup>36,41,46-50</sup> the attempt to synthesis N-containing organic compounds from complex 5 was unsuccessful thus far.

The variable-temperature magnetic data of complexes 2, 3, 4, and 5 were measured in the solid state with a superconducting quantum interference device (SQUID). The magnetic moments for these complexes exhibit a strong temperature dependency and approach to zero at low temperatures (Figures S16-S19). These results show that the formal oxidation state of U ions in these clusters is +IV. Due to the unique electronic structure in our system, the NIR data for complexes 3, 4, and 5 (Figure S15) do not resemble typical U(IV) complexes,51-53 but are more similar to electronically non-innocent systems.54,55 Therefore, the reduction of 2 equiv. of complex 3 with 4 equiv. of  $KC_8$  has the effect of reducing Rh(I) to Rh(-I), whereas the six reducing electrons were used to cleavage the N≡N triple bond in the formation of 5 from the reaction of 2 equiv. of complex 4 with 6 equiv. of KC8. Thus the formal oxidation states of U and Rh (+IV for U and -I for Rh) in both clusters 4 and 5 are identical. To the best of our knowledge, this is the first example of six-

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electron reduction of  $N_2$  by a multimetallic cluster with uranium-metal bond and a reducing agent (KC<sub>8</sub>).

Solid-state structures. The solid-state structures of complexes 2, 3, 4, and 5 were determined by X-ray crystallography (Figure 1). The structural features of complex 2 were very similar to the uranium species employing a dianionic N-P ligand, {O[(CH<sub>2</sub>)<sub>2</sub>NP(<sup>i</sup>Pr)<sub>2</sub>]<sub>2</sub>UCl<sub>2</sub>(THF)}.<sup>45</sup> The U–Rh distances of 3.3177(5) Å and 3.2609(5) Å in complex 3 are larger than the sum of the covalent single bond radii for uranium and rhodium (2.95 Å),<sup>56</sup> which suggests that weak bonding interactions between Rh and U exist in complex 3 (Figure 1B).

However, the U-Rh distances in complex 4 (2.6555(6) Å) are significantly shorter than those found in complex 3 (Figure 1C). This U-Rh bond length is also shorter than the previously reported U-Rh dative bonds (2.7601(5) and 2.7630(5) Å), but slightly longer than the U-Rh double dative bond (2.5835(3) Å).<sup>57,58</sup> The U1…U1' separation of 4.0397(6) Å suggests that there is no significant U-U bonding interaction - the sum of the covalent single bond radii for U is 3.40 Å. With the formal oxidation states of U(IV) and Rh(-I) in complex 4, the bonding of the U-Rh-U unit probably has two resonance structures, U1– Rh1→U1' and U1←Rh1–U1', both of which contain a U-Rh  $\sigma$ bond and a Rh-to-U dative bond (Figure S20).

The centrosymmetric structure of **5** reveals the presence of two bridged nitride groups ( $N^{3-}$ ) in a U<sub>4</sub>Rh<sub>2</sub>N<sub>2</sub> core (Figure 1D).

Each of the nitride atoms is bonded to three U atoms, with one U–N bond (U2'-N7: 2.302(6) Å) significantly longer than the other two almost equivalent U–N bonds (U1-N7: 2.158(7), U2-N7: 2.154(7) Å). These three U–N bond distances in complex 5 are comparable to those found in a hydrazido-bridged uranium complex (2.163(13)–2.311(13) Å),<sup>36</sup> and are consistent with the presence of U–N single bonds. The N7…N7' distance of 2.780 Å in complex 5 suggests that there is no N–N bond. Thus, the N=N triple bond in N<sub>2</sub> has been broken via a six-electron reduction to form two nitrides. Previously studies show that the four-electron reductive cleavage of N=N double bond in azobenzene to form bisphenylimido derivatives has been established by electron-rich uranium species with redox-active ligands.<sup>59,60</sup>

The U2'–Rh1 bond length of 2.5139(7) Å in complex **5** is slightly shorter than that found in complex **4**, which is consistent with a direct U-Rh  $\sigma$  bond. However, the bond length of U1-Rh1 (3.2160(7) Å) is much longer than the sum of the covalent single bond radii for U and Rh (2.95 Å),<sup>56</sup> suggesting a weak dative bond interaction between Rh1 and U1. In addition, the distances of U1…U2' (3.4677(4) Å) and U2…U2' (3.4730(6) Å) are shorter than that in **4**, indicating a weak interaction between these U atoms. Despite a series of species with U-M bonds reported previously,<sup>61-68</sup> the formation of complex **5** is the first example of N<sub>2</sub> fixation, reduction and cleavage by a complex containing U-M bonds.



Figure 1. Solid-state structures of 2 (A), 3 (B), 4 (C) and 5 (D) by X-ray crystallography with 50% probability ellipsoids. Solvent molecules, hydrogen atoms, and isopropyl moieties in  $P^{i}Pr_{2}$  are omitted for clarity. The U-Rh bonds in 3 and 4 and the core of 5 (U<sub>4</sub>Rh<sub>2</sub>N<sub>2</sub>) are red. Uranium, green; rhodium, red; phosphorus, violet red; nitrogen, blue; chlorine, yellow green; oxygen, pink; and carbon, grey.

Computational analysis. To gain further insight into the nature of this unprecedented full reduction of N<sub>2</sub>, DFT (B3PW91 with and without inclusion of the dispersion corrections) calculations were carried out to describe the bonding in complexes 3, 4 and 5 as this computational approach has proven its accuracy to describe U-M systems.42,43 The optimized geometry of complex 3 with dispersion correction included is in excellent agreement with the experimental one (see Supporting Information). Among other the U-Rh bond distances are reproduced with an accuracy of 0.01 Å (3.28 and 3.31 Å) as well as the U-Cl and Rh-Cl bond lengths, illustrating the correctness of this method. The square planar geometry around the rhodium center is consistent with a Rh(I) d<sup>8</sup> center, implying the presence of two U(IV) moieties. The latter is ensured by the unpaired density plot (see Supporting Information). Even though the U-Rh distance is long, a bonding interaction is observed in the molecular orbital spectrum. Indeed, the HOMO-6 (Figure 2) shows a bonding interaction between the two uranium centers and the rhodium. This orbital is strongly polarized toward Rh (95%) and can be viewed as a donation from a filled d orbital of Rh to the empty df hybrid orbitals on U (5%). On the other hand, no U-U interaction could be found.

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**Figure 2.** Selected molecular orbitals of complex **3**. The HOMO-6 displaying the U-Rh bonding interaction is on the top and the LUMO on the bottom.

This description is corroborated by the Natural Bonding Orbital (NBO) analysis in which donations from Rh to U are found at the second order donor-acceptor level (donation around 40 kcal mol<sup>-1</sup>). Interestingly, some back-donation U-Rh was also found (20 kcal mol<sup>-1</sup> in average), enhancing the presence of an Rh(I) d<sup>8</sup>. The LUMO of the system (Figure 2) involves the empty *d* orbital on Rh as well as *f* orbitals on the two uranium centers. Consequently, the reduction of complex **3** can involve both the uranium and rhodium centers. To investigate this, calculations were carried out on complex **4**, which was obtained by reacting **3** with 2 equiv. of KC<sub>8</sub>. Similar to complex **3**, the optimized geometry of **4** with dispersion correction included is in agreement with the experimental geometry. The shortening of the U-Rh distance is observed and the distance is reproduced with a precision of 0.05 Å. The short distance is in line with a more covalent interaction as found both in the molecular orbital diagram and at the NBO level.

Two  $\sigma$  U-Rh interactions strongly polarized toward Rh (91%) are found and involve a pure d orbital on Rh (97%) and a pdf hybrid orbital on U (12% p, 35% d, 49% f). The associated WBI are 0.85 in line with mainly covalent interactions (donoracceptor interaction with overlap). On the other hand, some U-U interaction is observed as indicated by a WBI of 0.17 (equivalent to hydrogen bonding). The geometry around Rh is no longer square-planar but rather a distorted tetrahedron that may indicate that the reduction mainly occurred at the rhodium center having a d10 configuration. This is confirmed by analysis of the unpaired spin density (Figure 3). Indeed, the unpaired spin density is only located on the two uranium centers, consistent with a closed-shell configuration at the Rh center, and the values that were found are similar to that of complex 3, in line with two U(IV). Thus, the reduction occurred at the Rh center. This is further highlighted by a large core calculation where the oxidation state of uranium was fixed to +IV (the optimized geometry in this case compares well with the small core one, see table in the theoretical calculations section in the SI). Interestingly, although the U-Rh distances are far less precise without dispersion corrections, the bonding analysis is quite similar in terms of interactions but not in strength.



Figure 3. Unpaired spin density plot of complex 4.

Finally, the unprecedented reduction of  $N_2$  by complex 4 was investigated computationally, even though locating transition states for a heterometallic cluster electron transfer reaction is not possible as it occurs through tunneling effects. It should be noticed that experimentally, in the absence of Rh the reduction of  $N_2$  does not occur, and this is consistent with a cooperative effect between the two metals. As the Rh centers in complex 4 are already fully reduced, the subsequent reduction of  $N_2$  should involve the uranium center. This is highlighted by the nature of the LUMO of complex 4 (Figure 4), that is involving the two uranium centers but also the rhodium. Therefore, the coordination of an incoming molecule such as  $N_2$  has to occur at the uranium center and the electron rich rhodium ensures electronic stabilization through electronic communication with the uranium centers. Page 5 of 8

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Figure 4. LUMO of complex 4.

Accordingly, a possible reaction sequence is proposed in which  $N_2$  is sequentially reduced with 6 equiv. of  $KC_8$  to abstract the chlorine ions (Figure 5). The overall reduction of  $N_2$  from 4 to 5 is exothermic by 40.0 kcal mol<sup>-1</sup> and each step of this reduction is computed to be favored (23.4 kcal mol<sup>-1</sup> for the formation of A from 4 and 6.3 kcal mol<sup>-1</sup> for the formation of 5 from A and finally 10.3 kcal mol<sup>-1</sup> for the formation of 5

from **B**). This process is similar to that observed in the formation of 4 from 3 which is exothermic by 17.6 kcal mol<sup>-1</sup>. The reduction of  $N_2$  is effective through the coordination to the uranium centers in the proposed intermediates as highlighted by the increase of the N-N bond distance (1.23 Å in A in line with a double bond character and 1.43 Å in **B** in line with a single bond). Moreover, the disruption of the N-N bond is evidenced by the nature of the HOMO of intermediate A and B (see Supporting Information). For intermediate A, the HOMO is clearly the N-N  $\pi^*$  in line with the disruption of one N-N  $\pi$  bond. The LUMO is the second  $\pi^*$  that overlaps with f orbitals on uranium and involves a d from Rh. Thus, this indicates that a second reduction of the N-N bond would be possible by populating this LUMO and this reduction will involves both uranium and rhodium centers. This second reduction is therefore found in the molecular orbital diagram of intermediate **B** as the HOMO is the second N-N  $\pi^*$  in line with a sequential disruption of the N-N bond. The HOMO is clearly involving both uranium and rhodium center in line with a synergistic effect of the two metal for this reduction. The LUMO of intermediate **B** is involving the  $\sigma^*$  of N<sub>2</sub> but also the rhodium and uranium centers so that a further reduction of N<sub>2</sub> is possible and implies U and Rh. This is achieved in complex 5 for which the HOMO in this time only involving the rhodium center, that further highlights the importance of the rhodium center in this reduction process.



Figure 5. Proposed reaction sequence for the N<sub>2</sub> reduction.

Due to the number of metal centers, calculations of complex 5 were conducted using f-in-core RECPs to describe the uranium centers adapted to the +IV oxidation state. The optimized geometry using this methodology is in agreement with the experimental geometry (see Supporting Information). The U-U distance is well reproduced within 2.0% and the U-Rh bond length is reproduced with a maximum deviation of 9.0%. The latter is well-known when large RECPs are used as it corresponds to the lack of correlation of the core-valences. Thus, these results are in line with an oxidation state +IV of the uranium centers and -I of the rhodium in complex 5. This is further corroborated by small core calculations of unpaired spin densities (2.0 on each U, see Supporting Information). The bonding analysis in complex 5 indicates that the U-Rh bonds are mainly described as dative bonds from filled d orbitals on Rh into an empty df hybrid orbital on the U. This is further highlighted by the WBI which are 0.52 and 0.35 in line with a less covalent interaction than in complex 4 (for comparison the U-Rh WBI is 0.83 in complex 4). A weak U-U interaction is also found with an associated WBI of 0.25 whereas no N-N interaction is observed and the LUMO of the system is a  $\pi$ -type interaction between the two nitrogen centers, in line with a fully cleaved N-N bond.

# CONCLUSION

In summary, we have shown that the multimetallic uraniumrhodium cluster can be used to cause the cleavage of N<sub>2</sub> in the presence of KC<sub>8</sub>. Although uranium complexes exhibit great potential in N<sub>2</sub> reduction, the complete cleavage of N<sub>2</sub> by a multimetallic uranium complex remains extremely rare. Therefore, the formation of N<sub>2</sub> cleavage product 5 from 3 or 4 represents the first example of N2 fixation and six-electron reduction by a multimetallic cluster with uranium and transition metals. The <sup>15</sup>N-labeled product (5-<sup>15</sup>N) was synthesized from  $^{15}N_2$ , further confirms the two nitride ligands in complex 5 originated from N<sub>2</sub>. The nitride products 5 and 5-<sup>15</sup>N could be protonated by excess acid, leading to the formation of substantial yields of ammonia. Computational analysis indicates that the cooperation of uranium and rhodium is important in this process of N<sub>2</sub> cleavage as after the reduction of the rhodium center, the  $N_2$  molecule can be reduced by  $KC_8$ with the help of the uranium center. This study demonstrates that a multimetallic uranium cluster can serve as an efficient platform for N<sub>2</sub> fixation and reduction. Further studies on the mechanism of  $N_2$  reduction by 4 and the functionalization of 5 are in progress.

## ASSOCIATED CONTENT

#### Supporting Information

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The Supporting Information is available free of charge at <u>https://pubs.acs.org</u>.

Complete experimental details, NMR and electronic absorption spectrum, SQUID, and computational details including Cartesian coordinates, and crystallographic data (PDF)

Crystallographic data for  ${\bf 2}~({\rm CIF})$ 

- Crystallographic data for 3 (CIF)
- Crystallographic data for 4 (CIF)
- Crystallographic data for 5 (CIF)

# AUTHOR INFORMATION

## Corresponding Author

\* L.M. (E-mail: laurent.maron@irsamc.ups-tlse.fr)

\* C.Z. (E-mail: zcq@nju.edu.cn)

# Notes

The authors declare no competing financial interests.

Crystal data of **2**, **3**, **4**, and **5** have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under reference numbers CCDC-1974258 (**2**), 1974259 (**3**), 1974260 (**4**), and 1974261 (**5**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (https://www.ccdc.cam.ac.uk/structures/).

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