Cluster Compounds

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A Triruthenium Complex Capped by a Triply Bridging Oxoboryl Ligand**

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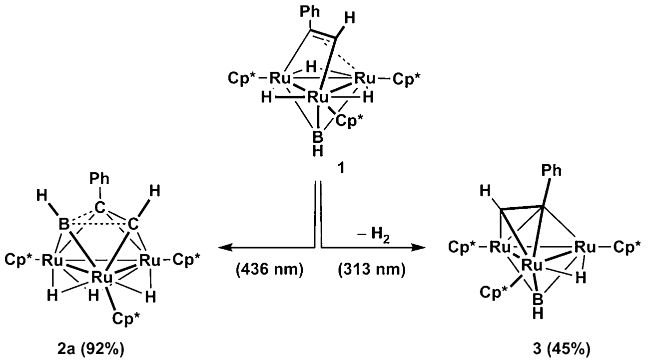
Since Mond et al. discovered [$Ni(CO)_4$] in 1890,[1] the carbonyl ligand has been widely used as a supporting ligand or substrate in organometallic chemistry. Besides common terminal coordination, it is well-known that the carbonyl group can bridge multiple metal nuclei: μ, μ_3, and μ_4 coordination modes have been recognized. For this reason, the CO ligand has a unique status, particularly in cluster chemistry.[2] Many complexes containing isoelectronic NO^+ ligands have also been prepared, and it has been demonstrated that NO^+ ligands can adopt various coordination modes similar to those observed for CO.[3] In contrast, although the properties of BO^-, another isoelectronic alternative to CO, have so far attracted considerable attention, a transition-metal complex containing a BO^- ligand was not been prepared until recently, probably as a result of the instability of free monomeric BO^-, in contrast to CO and NO.[4]

In 2010, Braunschweig et al. succeeded in the synthesis of the first platinum complex with a terminal oxoboryl ligand through the elimination of Me_3SiBr from a siloxyboryl ligand.[5] Not only did they elucidate the structural and spectroscopic properties of the BO^- ligand, but also its reactivity, and they demonstrated the Lewis basic nature of the BO^- ligand by the formation of a Lewis acid–base adduct with $B(C_6F_5)_3$.[6] They also showed that the abstraction of the bromide ligand from *trans*-[$(Cy_3P)_2BrPt(B{\equiv}O)$] (Cy = cyclohexyl) resulted in cyclodimerization, which led to the formation of a four-membered B_2O_2 skeleton.[7] The formation of the B_2O_2 linkage is most likely due to the highly polarized nature of the $B^+{\equiv}O^-$ bond. In contrast, CO ligands tend to dimerize by the formation of a μ-CO ligand.

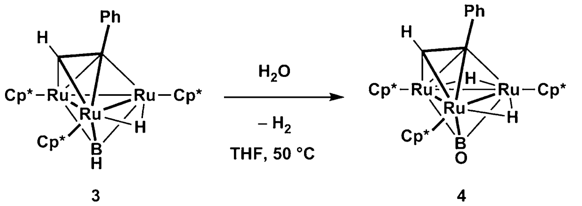
Although bridging coordination was elucidated for the isoelectronic BF ligand by Vidovic and Aldridge,[8] it has never been reported for the BO^- ligand, except in the case of a hypothetical dicobalt complex, [$Co_2(CO)_6(\mu\text{-}CO)(\mu\text{-}BO)_2$], by density functional theory (DFT) calculations.[9] Herein, we report the first synthesis and the properties of a triruthenium cluster capped by a μ_3-BO ligand.

We previously studied the reactivity of a triruthenium complex capped by a μ_3-BH ligand in terms of C–S bond scission[10a] and B–C bond formation[10b] on the Ru_3 plane. Recently, we showed the preferential formation of the triruthenium complex **2a**, which contains a μ_3-η^3-BC_2 ring, upon the irradiation of the alkyne complex **1** with visible light (Scheme 1).[10c] In contrast to irradiation with visible light, UV irradiation of **1** resulted in the formation of complex **3** with a perpendicularly coordinated alkyne through the elimination of dihydrogen. Since complex **3** adopts a coordinatively unsaturated 46-electron configuration, it was anticipated that **3** shows further reactivity similar to that of other (⊥)-alkyne complexes toward small molecules.[11,12]



Scheme 1. Transformation of **1** upon photoirradiation.

When **3** was heated in the presence of H_2O at 50 °C, complex **4**, whose Ru_3 plane was capped by both μ_3-alkyne and μ_3-BO ligands, was obtained exclusively [Eq. (1)]. Unlike free BO, which was only detected at low temperature in an argon matrix,[4] the μ_3-BO ligand in **4** was robust toward moisture and heat. In fact, **4** was readily purified by column chromatography on alumina. Braunschweig et al. also noted that the terminal oxoboryl group was stable toward heating at 100 °C and irradiation with a Hg/Xe arc lamp.[5]



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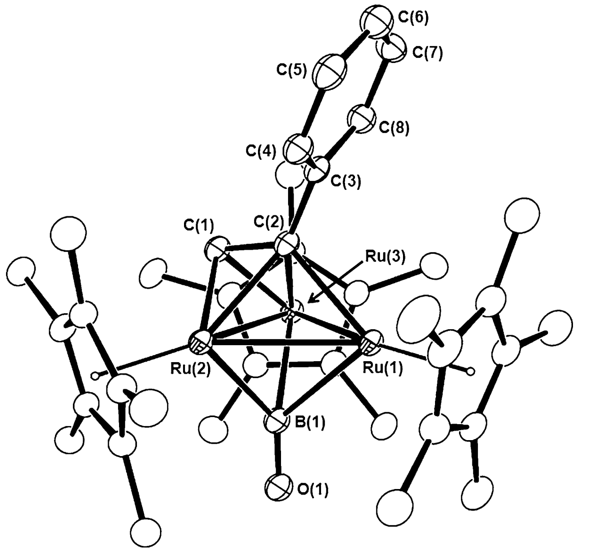


Figure 1. Molecular structure of **4** with thermal ellipsoids at the 30% probability level. Selected bond lengths [Å] and angles [°]: Ru(1)–Ru(2) 2.7464(7), Ru(1)–Ru(3) 2.7450(7), Ru(2)–Ru(3) 2.8220(7), Ru(1)–B(1) 2.415(8), Ru(2)–B(1) 2.234(8), Ru(3)–B(1) 2.273(8), Ru(1)–C(2) 2.233(6), Ru(2)–C(1) 2.035(6), Ru(2)–C(2) 2.246(7), Ru(3)–C(1) 2.021(6), Ru(3)–C(2) 2.242(6), B(1)–O(1) 1.239(9), C(1)–C(2) 1.391(9); Ru(2)-Ru(1)-Ru(3) 61.846(17), Ru(1)-Ru(2)-Ru(3) 59.053(17), Ru(1)-Ru(3)-Ru(2) 59.101(17).

The molecular structure of **4** was determined by an X-ray diffraction study (Figure 1).[13] Although the positions of the hydrido ligands were not determined during the Fourier synthesis, we could infer from the ^{1}H NMR spectrum that they are located at the Ru(1)–Ru(2) and Ru(1)–Ru(3) edges, as described below. The three ruthenium nuclei form an isosceles triangle with sides of 2.7467(7), 2.7450(7), and 2.8220(7) Å. The Ru−B bond lengths (2.415(8), 2.234(8), and 2.273(8) Å) are noticeably larger than the M–B distances reported for μ- and μ_3-borylene complexes (1.90–2.19 Å).[14] In particular, the Ru(1)–B(1) length of 2.415(8) Å implies that the interaction between Ru(1) and B(1) is considerably weak. This value is comparable with the W−B bond lengths in the distorted μ-borylene complexes [CpM(CO){μ-B=N-(SiMe$_3$)$_2$}W(CO)$_5$] (Cp = η^5-C_5H_5; M = Co, 2.433 Å; M = Rh, 2.423 Å).[15]

Although the B(1)–O(1) distance (1.239(9) Å) is slightly longer than the values reported for terminal BO ligands (1.210(3), 1.197(6) Å),[5,6] it is significantly shorter than the B−O bond length in the μ_3-ethoxyborylene complex [{Cp*Ru-(μ-H)}$_3$(μ_3-BOEt)] (Cp* = η^5-C_5Me_5; 1.374(13) Å).[10a] These values strongly indicate a multiple-bonding interaction between the B(1) and O(1) atoms.

The alkyne ligand in **4** is located above the Ru(2)–Ru(3) edge in a perpendicular manner as in the parent alkyne complex **3**. This coordination mode is characteristic for a trinuclear alkyne complex that adopts a 46-electron configuration.[16] Thus, the perpendicular coordination geometry of the alkyne ligand suggests that the oxoboryl ligand formally acts as a one-electron donor in **4**. The C(1)−C(2) bond (1.391(9) Å) is slightly elongated by 0.04 Å from that of **3**.[10c] The ^{13}C NMR spectroscopic signals of the alkyne ligand in **4** (C^{in}, $\delta = 55.9$ ppm; C^{out}, $\delta = 174.9$ ppm) showed a remarkable upfield shift by approximately 25 ppm in comparison with those of **3** (C^{in}, $\delta = 82.7$ ppm; C^{out}, $\delta = 199.0$ ppm). These observations suggest that the alkyne ligand receives enhanced back donation from the metal centers, probably because of strong donation from the μ_3-BO ligand. This behavior is consistent with the nature of the terminal BO$^-$ ligand, which has extremely strong σ-donation but very weak π-accepting ability, as revealed by DFT calculations.[17]

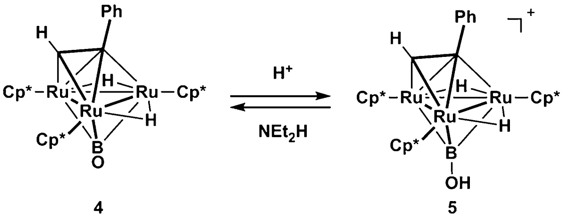
The alkyne ligand in **3** moves around the trinuclear site in the same way as in other (⊥)-alkyne complexes synthesized by us.[18] Owing to this motion, one broad signal was observed for the Cp* groups of **3** in the ^{1}H NMR spectrum at ambient temperature. This signal decoalesced into two sharp signals with an intensity ratio of 2:1 at −80 °C. In contrast, the ^{1}H NMR spectrum of **4** displayed two sharp signals for the Cp* groups at $\delta = 2.00$ and 1.62 ppm with an intensity ratio of 2:1 even at 100 °C. These results show that the mobility of the alkyne ligand in **4** is considerably lower than that of the alkyne ligand in **3**. The decreased mobility of the alkyne ligand in **4** is also probably due to the strong σ-donating nature of the μ_3-BO ligand.

In the IR spectrum, two sharp absorptions were observed at 1672 and 1623 cm^{-1}, which were assignable to ν(^{10}BO) and ν(^{11}BO), respectively. They underwent a bathochromic shift to 1639 and 1588 cm^{-1} upon the incorporation of ^{18}O through the reaction of **3** with $H_2{}^{18}O$ (see Figure S6 in the Supporting Information). The ν(BO) frequencies are considerably smaller than the ν(BO) values reported for [(Cy$_3$P)$_2$BrPt(B≡O)] (1853, 1797 cm^{-1})[5] and the computed values for the hypothetical μ-BO ligand in [Co$_2$(CO)$_6$(μ-CO)(μ-BO)$_2$] (1771, 1779 cm^{-1}).[9] The shift to a lower frequency upon bridging coordination is common for CO groups, and the frequencies of 1672 and 1623 cm^{-1} are comparable to those reported for μ_3-CO ligands, which range from 1600 to 1730 cm^{-1}.

A broad ^{11}B signal for the μ_3-BO group was observed at $\delta = 42.7$ ppm in the ^{11}B NMR spectrum. Thus, a significant upfield shift of the ^{11}B signal was observed relative to that of the μ_3-BH group in **3** ($\delta = 138.9$ ppm). A similar trend was also observed for [(Cy$_3$P)$_2$BrPt(B≡O)]: the ^{11}B signal of the BO$^-$ group was observed at $\delta = 17$ ppm, whereas the ^{11}B resonance for the parent siloxyboryl group occurred at $\delta = 32$ ppm.[5] The hydrido signal of **4** was observed at $\delta = -3.25$ ppm as a sharp singlet. This chemical shift indicates that the bonding interaction between the hydrido ligands and the B atom is negligible.

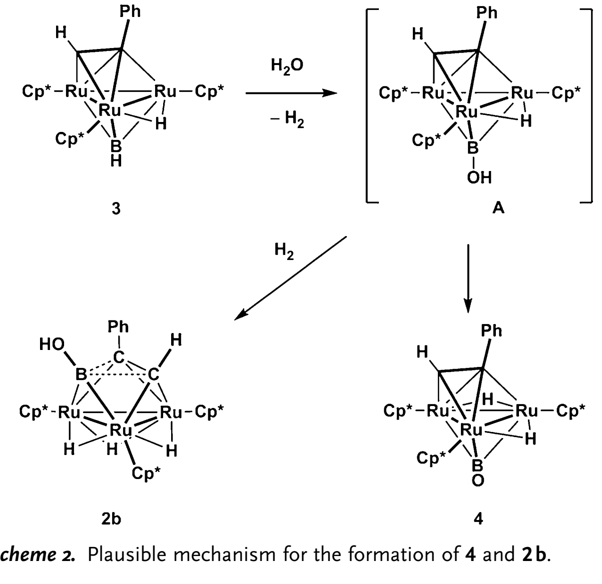
To gain deeper insight into the μ_3-BO group, we carried out a DFT study. The B−O bond was estimated to be slightly longer by 0.03 Å, and the optimized structure exhibited reasonable agreement with the molecular structure (see Figure S3 in the Supporting Information). Natural bond orbital (NBO) analysis revealed that the Wiberg bond index for the B−O bond is 1.5570, which clearly shows the multiple-bonding interaction between the B(1) and O(1) atoms. The DFT calculation also showed remarkable polarization between the B(1) and O(1) atoms: whereas the O(1) atom was negatively charged (−0.88144), the natural charge at the B(1) atom was largely positive (0.93811).

This polarized structure was confirmed by the protonation of **4**, which led to the exclusive formation of the cationic μ$_3$-hydroxyborylene complex **5** [Eq. (2)]. The ^{11}B NMR signal of **5** at $\delta = 66.8$ ppm was substantially shifted downfield as compared to that of **4**. The chemical shift was comparable to that of a neutral μ$_3$-methoxyborylene complex ($\delta = 77.7$ ppm).[10a] On the other hand, the chemical shifts of the ^{13}C NMR signals of the alkyne ligand in **5** were similar to those observed for the μ$_3$-BO complex **4** in spite of the cationic nature of **5** (C^{in}, $\delta = 54.7$ ppm; C^{out}, $\delta = 177.6$ ppm), probably because of the localization of the cationic charge at the boron atom. A similar trend was observed in the protonation of a face-capping pyridine complex to yield the corresponding cationic pyridinium complex.[19]



(2)

The treatment of **5** with NEt$_2$H at 80 °C resulted in the regeneration of **4**. This transformation shows that the μ$_3$-BOH$^+$ group in **5** is substantially protic, and that μ$_3$-BO can be regarded as a stable conjugate base. Thus, the reversible formation of **5** implies that proton migration from the μ$_3$-BOH group of the hydroxyborylene intermediate **A** to the metal center could be a key step for the formation of **4** (Scheme 2). We have already reported the facile conversion of a μ$_3$-BH group into a μ$_3$-BOMe group upon the treatment of [{Cp*Ru(μ-H)}$_3$(μ$_3$-BH)] with methanol.[10a] Thus, it would be reasonable that the hydroxyborylene intermediate **A** is initially formed by the reaction of **3** with H$_2$O, accompanied by the elimination of dihydrogen.



Scheme 2. Plausible mechanism for the formation of **4** and **2b**.

When the reaction was carried out in a closed flask, hardly any of the oxoboryl complex **4** was obtained. Instead, complex **2b** with a μ$_3$-η^3-BC$_2$ ring containing a B(OH) moiety was the preferential product. Complex **2b** was isolated and fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy. Because of the presence of the OH group on the boron atom, the positions of the B(1) and C(2) atoms in the BC$_2$ ring could be unambiguously determined by X-ray diffraction analysis, unlike for the previously published disordered structure of **2a**. The structural parameters of **2b** (Figure 2), notably the long B–C bond distances of approximately 1.67 Å, are similar to those calculated for **2a**.

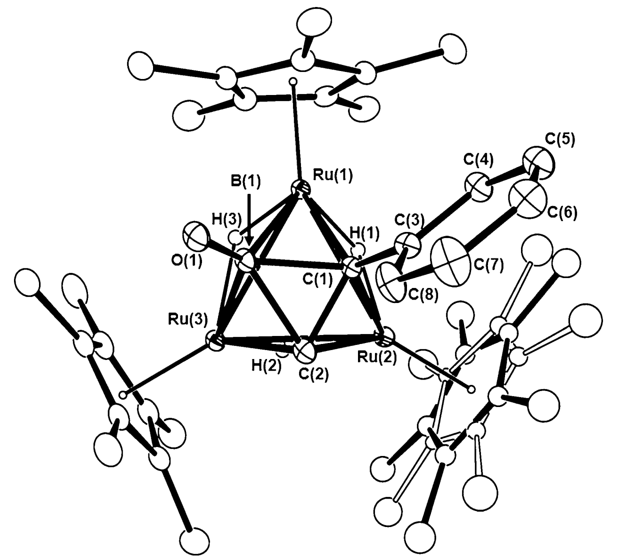


Figure 2. Molecular structure of **2b** with thermal ellipsoids at the 30% probability level. Selected bond lengths [Å] and angles [°]: Ru(1)–Ru(2) 2.8026(5), Ru(1)–Ru(3) 2.8603(5), Ru(2)–Ru(3) 2.8293(5), Ru(1)–B(1) 2.132(5), Ru(1)–C(1) 2.126(4), Ru(2)–C(1) 2.132(4), Ru(2)–C(2) 2.090(5), Ru(3)–B(1) 2.125(5), Ru(3)–C(2) 2.070(4), B(1)–C(1) 1.679(6), B(1)–C(2) 1.705(6), B(1)–O(1) 1.425(6), C(1)–C(2) 1.513(6); Ru(2)-Ru(1)-Ru(3) 59.938(12), Ru(1)-Ru(2)-Ru(3) 61.043(10), Ru(1)-Ru(3)-Ru(2) 59.019(12), C(1)-B(1)-C(2) 53.1(2), B(1)-C(1)-C(2) 64.3(3), B(1)-C(2)-C(1) 62.6(3).

The formation of **2b** in the reaction carried out in a closed vessel implies that the uptake of eliminated dihydrogen occurred effectively. Whereas **4** does not react with H$_2$, **3** reacts readily with H$_2$ (1 atm) to yield **2a** through the formation of the coordinatively saturated (||)-alkyne complex **1** (see Figure S13 in the Supporting Information). Thus, the formation of **2b** strongly indicates that the hydroxyborylene intermediate **A** is produced initially and can be trapped by the accumulated hydrogen.

In conclusion, the first trinuclear complex capped by a μ$_3$-BO ligand was synthesized by the reaction of a μ$_3$-borylene complex with water. The unusual μ$_3$-BO ligand was clearly established by X-ray diffraction analysis as well as by ^{11}B NMR and IR spectroscopy. The Lewis basic nature of the μ$_3$-BO ligand was shown by protonation at the oxygen atom to form the cationic complex **5**. The results described herein provide a possibility for extending BO chemistry to the field of transition-metal clusters, as already seen for the isoelectronic CO and NO ligands. We are currently studying the detailed mechanisms of these transformations and further exploring the reactivity of the μ_3-oxoboryl ligand.

Experimental Section

General considerations regarding the experimental procedures, the X-ray diffraction study, and the DFT calculation are provided in the Supporting Information.

Preparation of **4**: Complex **3** (36.8 mg, 44.7 μmol), THF (10 mL), and H_2O (1 mL) were placed in a 50 mL Schlenk tube equipped with a reflux condenser connected to an argon line and sealed with a paraffin bubbler, and the solution was heated at 50°C for 24 h with vigorous stirring. The solvent was then removed under reduced pressure, and the residual solid was extracted with toluene (2 mL) and purified by column chromatography on alumina (Merck, Art. No. 1097). After the first brown band (containing complex **3**) in the column had been removed with toluene, the second green band (containing **4**) was collected with THF as the eluent. Drying under reduced pressure afforded **4** as a dark-green solid (30.0 mg, 80% yield). ^{1}H NMR (400 MHz, [D$_8$]THF, 25°C): $\delta = -3.25$ (s, 2H, RuH), 1.62 (s, 15H, C_5Me_5), 2.00 (s, 30H, C_5Me_5), 5.48 (d, $J_{H,H} = 7.6$ Hz, 2H, *o*-Ph), 6.49 (t, $J_{H,H} = 7.6$ Hz, 1H, *p*-Ph), 6.72 (dd, $J_{H,H} = 7.6$, 7.6 Hz, 2H, *m*-Ph), 9.56 ppm (s, 1H, PhCC*H*); ^{11}B{^{1}H} NMR (128.7 MHz, [D$_6$]benzene, 25°C): $\delta = 42.7$ ppm; IR (KBr): $\tilde{\nu} = 1672$ (ν(^{10}BO)), 1623 cm^{-1} (ν(^{11}BO)).

Preparation of **2b**: Complex **3** (38.5 mg, 46.7 μmol), THF (10 mL), and H_2O (1 mL) were placed in a 50 mL Schlenk tube equipped with a J. Young valve, and the solution was heated at 50°C for 24 h with vigorous stirring. The solution was then removed under reduced pressure, and the residual solid was extracted with toluene (2 mL) and purified by column chromatography on alumina (Merck, Art. No. 1097). After the first brown band (containing **3**) in the column had been removed with toluene, the second orange band containing **2b** was collected with THF as the eluent. Drying under reduced pressure afforded **2b** as an orange solid (16.1 mg, 41% yield). ^{1}H NMR (400 MHz, [D$_8$]THF, 25°C): $\delta = -23.44$ (dd, $J_{H,H} = 4.4$, 4.4 Hz, 1H, RuH), −19.71 (dd, $J_{H,H} = 4.4$, 4.4 Hz, 1H, RuH), −18.77 (dd, $J_{H,H} = 4.4$, 4.4 Hz, 1H, RuH), 1.59 (s, 15H, C_5Me_5), 1.73 (s, 15H, C_5Me_5), 1.87 (s, 15H, C_5Me_5), 3.39 (s, 1H, OH), 6.97 (t, $J_{H,H} = 7.6$ Hz, 1H, *p*-Ph), 7.09 (dd, $J_{H,H} = 7.6$, 7.6 Hz, 2H, *m*-Ph), 7.17 (d, $J_{H,H} = 4.4$ Hz, 2H, *o*-Ph), 7.25 ppm (s, 1H, PhCC*H*); ^{11}B{^{1}H} NMR (128.7 MHz, [D$_6$]benzene, 25°C): $\delta = 57.6$ ppm.

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[13] Crystal data for **4**: space group $P2_1/n$ (No. 14), $a = 10.8663(8)$, $b = 20.3379(17)$, $c = 16.4440(12)$ Å, $\beta = 101.3660(17)°$, $V = 3562.8(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.566$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 1.283$ mm^{-1}; of the 38009 reflections that were collected, 8111 were unique ($R_{int} = 0.1356$), $R_1 = 0.0661$ [$I > 2\sigma(I)$], $wR_2 = 0.1597$ [$I > 2\sigma(I)$]. Crystal data for **2b**: space group $P\bar{1}$ (No. 2), $a = 11.0295(7)$, $b = 12.2613(8)$, $c = 17.4055(9)$ Å, $\alpha = 105.5120(18)$, $\beta = 91.3900(18)$, $\gamma = 107.090(2)°$, $V = 2154.4(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.440$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 1.069$ mm^{-1}; of the 21608 reflections that were collected, 21536 were unique ($R_{int} = 0.0393$), $R_1 = 0.0451$ [$I > 2\sigma(I)$], $wR_2 = 0.1172$ [$I > 2\sigma(I)$]. CCDC 951625 (**4**) and 951626 (**2b**) 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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