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Preparation, crystal structures and properties of half-sandwich ruthenium complexes containing salicylbenzoxazole ligands

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ABSTRACT

Three half-sandwich ruthenium complexes [Ru(*p*-cymene)LCl] containing salicylbenzoxazole ligands [LH = 2-(5-methyl-benzoxazol-2-yl)-4-methyl-phenol (**2a**), LH = 2-(5-methyl-benzoxazol-2-yl)-4-chloro-phenol (**2b**), and LH = 2-(5-methyl-benzoxazol-2-yl)-4-bromo-phenol (**2c**)] were synthesized and characterized. All half-sandwich ruthenium complexes were fully characterized by ¹H and ¹³C NMR spectra, MS, elemental analyses, and UV-vis as well as cyclic voltammetry (CV). The molecular structures of **2a**, **2b**, and **2c** were confirmed by single-crystal X-ray diffraction. Single-crystal X-ray structures show that the synthesized ruthenium complexes are three-legged piano-stools with a six-membered metallocycle formed by coordination of the bidentate salicylbenzoxazole ligands to the metal centers. Data from CV and UV-vis absorption of the ruthenium complexes indicated that by changing the substituent on the para position of (donating or withdraw group) the salicylbenzoxazole ligands, minor changes in redox and electronic properties of the ruthenium complexes were observed.

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KEYWORDS

Half-sandwich; ruthenium; salicylbenzoxazole; cyclic voltammetry



1. Introduction

The coordination chemistry and reactivity of half-sandwich ruthenium complexes have been extensively studied due to the fact that these complexes have a wide range of potential applications in metallomacrocycles, host–guest, anticancer drugs, biological activities, electrochemical sensors, and catalysts in the past decades [1–7]. Various metal-organic frameworks including metallomacrocycles and cages have been obtained using Ru(*p*-cymene) as a building block [8–10]. Half-sandwich ruthenium complexes show high catalytic activities toward organic transformation, such as C–C bond formation via direct C–H bond activation [11, 12], addition of arylboronic acid [13, 14], acceptorless dehydrogenative coupling of alcohols [15], transfer hydrogenations of ketones [16] and water oxidation [17, 18]. Ruthenium complexes as anti-cancer drugs have entered clinical trials [19]. Thus, synthesis of half-sandwich ruthenium complexes and studying their chemical properties would be desirable.

In this work, the half-sandwich ruthenium complexes [Ru(*p*-cymene)LCI] bearing a chelating salicylbenzoxazole ligand [LH = 2-(5-methyl-benzoxazol-2-yl)-4-methyl-phenol (**2a**), LH = 2-(5-methyl-benzoxazol-2-yl)-4-chloro-phenol (**2b**) and LH = 2-(5-methyl-benzoxazol-2-yl)-4-bromo-phenol (**2c**)] have been synthesized and characterized. Solid state structures of the newly synthesized half-sandwich ruthenium complexes (**2a**-**2c**) were also elucidated by single-crystal X-ray diffraction. The results indicate that the ruthenium complexes are three-legged piano-stools with a six-membered metallocycle formed by coordination of the bidentate salicylbenzoxazole to ruthenium. The redox properties and UV-vis absorptions of ruthenium complexes were also investigated, indicating that the substituent (donating or withdraw group) on the salicylbenzoxazole ligands has minor influences on the ruthenium complexes.

2. Experimental

2.1. Materials and measurements

All manipulations were carried out under pure nitrogen using standard Schlenk techniques. All solvents were purified and degassed by standard procedures. The bidentate monoanionic [N,O] ligands were synthesized according to procedures described [20]. ¹H and ¹³C NMR spectra were recorded on 300 or 500 MHz NMR spectrometers at room temperature. Chemical shifts (δ) are in ppm relative to internal TMS and are referenced to residual ¹H and ¹³C solvent resonances. IR spectra were recorded on a Nicolet AVATAR-360IR spectrometer. Elemental analyses were performed on an Elementar III vario El Analyzer. Mass spectrometry was performed on a Bruker BIFLEX III MALDI-TOF-MS instrument. A CHI400c computerace instrument was employed to obtain cyclic voltammograms in acetonitrile solutions of the ruthenium complexes (2 mM) under nitrogen at room temperature (298 K) using 0.20 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. A glassy carbon working electrode, a platinum auxiliary electrode, and a Ag/AgCI reference electrode were used to obtain cyclic voltammograms. All $E_{1/2}$ values estimated from cyclic voltammetry (CV) were calculated as the average of the oxidative and reductive peak potentials ($E_{na} + E_{nc}$)/2 at a scan rate of 100 mV s⁻¹.

2.2. Synthesis

2.2.1. Synthesis of 2-(5-methyl-benzoxazol-2-yl)-4-methyl-phenol (1a)

A solution of 5-methylsalicylaldehyde (1.36 g, 10 mmol), 2-amino-4-methylphenol (1.23 g, 10 mmol), and 3–5 drops of acetic acid in 50 mL of methanol was refluxed with stirring for 3 h after bulk orange precipitate formation under nitrogen. When the resulting mixture was cooled to room temperature, Phl(OAc)₂ (3.54 g, 11 mmol) was added and the mixture immediately turned black. After the mixture was refluxed again for 1 h in open air, the solvent was evaporated to dryness and the black crude product was chromatographed on silica gel with petroleum ether to give white powder (1.63 g, 68%). Anal. Calcd for C₁₅H₁₃NO₂ (239.09) : C, 75.30; H, 5.48; N, 5.85. Found : C, 75.40; H, 5.25; N, 5.60. ¹H NMR (500 MHz, CDCl₃, ppm) : δ 11.33 (s, 1H, Ph-OH), 7.79 (s, 1H, Ph-H), 7.50 (t, 2H, Ph-H), 7.25 (s, 2H, Ph-H),

7.02 (d, 1H, Ph-H), 2.48 (s, 3H, –CH₃), 2.36 (s, 3H, –CH₃). ¹³C NMR (125 MHz, CDCl₃, ppm) : 163.04, 156.55, 147.31 140.23, 134.83, 134.33, 128.66, 126.83, 126.32, 119.12, 117.12, 110.24, 109.90, 21.48, 20.48.

2.2.2. Synthesis of 2-(5-methyl-benzoxazol-2-yl)-4-chloro-phenol (1b)

A procedure similar to that used for preparation of **1a** was employed. White powder, yield: 1.82 g (70%). Anal. Calcd for $C_{14}H_{10}CINO_2$ (259.04) : C, 64.75; H, 3.88; N, 5.39. Found: C, 64.60; H, 4.05; N, 5.20. ¹H NMR (500 MHz, CDCl₃, ppm): δ 11.50 (s, 1H, Ph-OH), 7.98 (d, 1H, Ph-H), 7.52 (t, 2H, Ph-H), 7.38 (d, 1H, Ph-H), 7.22 (d, 1H, Ph-H), 7.07 (d, 1H, Ph-H), 2.50 (s, 3H, $-CH_3$). ¹³C NMR (125 MHz, CDCl₃, ppm): 162.09, 157.53, 147.75, 140.30, 135.60, 133.55, 127.31, 126.67, 124.75, 119.70, 119.25, 112.07, 110.49, 21.87.

2.2.3. Synthesis of 2-(5-methyl-benzoxazol-2-yl)-4-bromo-phenol (1c) [21]

A procedure similar to that used for preparation of **1a** was employed. White powder, yield: 2.19 g (72%). Anal. Calcd for $C_{14}H_{10}BrNO_2$ (302.99): C, 55.29; H, 3.31; N, 4.61. Found: C, 55.41; H, 3.35; N, 4.53. ¹H NMR (500 MHz, CDCl₃, ppm): δ 11.50 (s, 1H, Ph-OH), 8.08 (d, 1H, Ph-H), 7.48 (m, 3H, Ph-H), 7.19 (d, 1H, Ph-H), 7.00 (t, 1H, Ph-H), 2.48 (s, 3H, -CH₃). ¹³C NMR (125 MHz, CDCl₃, ppm): 161.57, 157.58, 147.35, 139.88, 135.96, 135.21, 129.23, 126.92, 119.30, 119.25, 112.28, 111.23, 110.10, 21.49.

2.2.4. Synthesis of half-sandwich ruthenium complex 2a

[Ru(*p*-cymene)(*μ*-Cl)Cl]₂ (306 mg, 0.5 mmol), **1a** (287 mg, 1.2 mmol), 193 mg (1.4 mmol) K₂CO₃ and 30 mL CH₃CN as solvent were placed in a 100 mL Schlenk tube. The mixture was stirred and refluxed for 3 h and then cooled to room temperature. The solvent was removed with a rotary evaporator; the resulting solid was washed with Et₂O. The product was recrystallized from Et₂O/MeOH to give orange **2a** (265 mg, 52%). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.51 (d, 2H, Ph-H), 7.42 (s, 1H, Ph-H), 7.17 (d, 1H, Ph-H), 7.07 (d, 2H, Ph-H), 5.54 (d, 1H, Ph-H), 5.47 (d, 1H, Ph-H), 5.42 (d, 1H, Ph-H), 5.35 (d, 1H, Ph-H), 2.77 (m, 1H, -*CH*(CH₃)₂), 2.52 (s, 3H, -CH₃), 2.25 (s, 6H, -CH₃), 1.19 (d, 3H, -CH(*CH*₃)₂), 1.10 (d, 3H, -CH(*CH*₃)₂). ¹³C NMR (125 MHz, CDCl₃, ppm): 168.23, 160.64, 148.24, 141.34, 135.70, 135.33, 126.85, 126.25, 123.89, 123.81, 118.86, 110.37, 110.26, 102.63, 97.54, 83.54, 81.95, 80.10, 79.78, 30.78, 22.71, 21.84, 21.77, 20.31, 18.90. MS (MALDI-TOF): Calcd for C₂₅H₂₆NO₂Ru⁺ 474.1007 (M⁺), found 474.4827 (M⁺). IR (KBr cm⁻¹): 3052(w), 2969(w), 2912(w), 2861(w), 1626(m), 1556(s), 1485(m), 1339(m), 1250(w), 830(w).

2.2.5. Synthesis of half-sandwich ruthenium complex 2b

Complex **2b** was prepared by the same procedure as described above for **2a** using [Ru(*p*-cymene)(μ -Cl) Cl]₂ (306 mg, 0.5 mmol), **1b** (311 mg, 1.2 mmol) and 193 mg (1.4 mmol) K₂CO₃. Yield: (291 mg, 55%). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.70 (d, 1H, Ph-H), 7.47 (t, 2H, Ph-H), 7.21 (t, 2H, Ph-H), 7.03 (d, 1H, Ph-H), 5.54 (d, 1H, Ph-H), 5.50 (d, 1H, Ph-H), 5.42 (d, 1H, Ph-H), 5.36 (d, 1H, Ph-H), 2.77 (m, 1H, $-CH(CH_3)_2$), 2.53 (s, 3H, $-CH_3$), 2.28 (s, 3H, $-CH_3$), 1.20 (d, 3H, $-CH(CH_3)_2$), 1.11 (d, 3H, $-CH(CH_3)_2$). ¹³C NMR (125 MHz, CDCl₃, ppm): 168.51, 159.49, 148.19, 141.17, 135.70, 134.08, 126.86, 126.45, 125.64, 119.11, 118.94, 111.46, 110.52, 102.89, 97.85, 83.74 (MALDI-TOF): Calcd for C₂₄H₂₃CINO₂Ru⁺ 494.0461 (M⁺), found 494.2528 (M⁺). IR (KBr cm⁻¹): 3041(w), 2971(w), 2915(w), 2869(w), 1600(m), 1551(m), 1518(m), 1458(s), 1396(m), 1334(m), 1235(m), 1186(m), 1098(w), 1052(w), 819(m), 724(m), 658(w), 592(w), 533(w).

2.2.6. Synthesis of half-sandwich ruthenium complex 2c

Complex **2c** was prepared by the same procedure as described above for **2a** using $[Ru(p-cymene)(\mu-Cl)Cl]_2$ (306 mg, 0.5 mmol), **1c** (193 mg, 1.2 mmol) and 193 mg (1.4 mmol) K₂CO₃. Yield: (332 mg 58%). ¹H NMR (500 MHz, CDCl₃, ppm): δ 7.84 (d, 1H, Ph-H), 7.47 (s, 1H, Ph-H), 7.43 (d, 1H, Ph-H), 7.26 (m, 1H, Ph-H), 7.19 (d, 1H, Ph-H), 6.97 (d, 1H, Ph-H), 5.55 (d, 1H, Ph-H), 5.49 (d, 1H, Ph-H), 5.43 (d, 1H, Ph-H), 5.35 (d, 1H, Ph-H), 2.75 (m, 1H, $-CH(CH_3)_3$), 2.52 (s, 3H, $-CH_3$), 2.27 (s, 3H, $-CH_3$), 1.20 (d 3H, $-CH(CH_3)_2$), 1.11 (d, 3H, $-CH(CH_3)_2$). ¹³C NMR (125 MHz, CDCl₃, ppm): 168.85, 159.32, 148.15, 141.12, 136.65, 135.69, 129.50, 126.86, 126.08, 118.91, 112.28, 110.51, 105.74, 102.86, 97.82, 83.72, 81.99, 80.21, 79.55, 30.82, 22.67, 21.85, 21.80, 18.93. MS (MALDI-TOF): Calcd for C₂₄H₂₃BrNO₂Ru⁺ 537.9956 (M⁺), found 538.1400 (M⁺). IR (KBr cm⁻¹): 3070(w), 3041(w), 2968(w), 2959(w), 2919(w), 2866(w), 1597(m), 1511(m), 1521(m), 1462(s),

Table 1. Crystallographic data and structure refinement parameters for 2a-2c.

	2a	2b	2c
Empirical formula	C ₂₅ H ₂₆ CINO ₂ Ru	C ₂₄ H ₂₃ Cl ₂ NO ₂ Ru	C ₂₄ H ₂₃ BrCINO ₂ Ru
Formula weight	508.99	529.40	573.86
Crystal system, space group	Monoclinic, P21/c	Monoclinic, P21/c	Triclinic, P-1
a (Å)	18.263(4)	18.103(4)	7.3429(5)
b (Å)	17.428(4)	17.336(4)	10.3625(7)
c (Å)	7.5956(18)	7.5709(17)	14.5662(10)
a (°)	90.00	90.00	90.1710(10)
β (°)	97.296(4)	96.794(3)	98.2340(10)
γ (°)	90.00	90.00	93.9370(10)
Volume (ų), Z	2398.0(9), 4	2359.3(9), 4	1094.25(13), 2
$D_{c} (mg m^{-3})$	1.410	1.490	1.742
μ (Mo-K α) (mm ⁻¹)	0.785	0.911	2.685
F(0 0 0)	1040	1072	572
heta range (°)	1.62-25.00	1.63-25.00	1.97-25.00
Limiting indices	-21, 21; -20, 20; -8, 9	-21, 21; -19, 20; -8, 8	-8, 8, -12, 10, -16, 17
Reflections/unique [R(int)]	4191/1887 [0.1775]	4132/2697 [0.0865]	3837/3634 [0.0186]
Completeness to θ (°)	25.00 (99.3%)	25.00 (99.4%)	25.00 (99.1%)
Data/restraints/parameters	4191/0/268	4132/0/271	3837/0/319
Goodness of fit on F ²	0.938	1.023	1.058
$R_{1}, WR_{2} [l > 2\sigma(l)]^{a}$	$R_1 = 0.0823, wR_2 = 0.1810$	$R_1 = 0.0669, wR_2 = 0.1550$	$R_1 = 0.0247, wR_2 = 0.0649$
R_1, wR_2 (all data)	$R_1 = 0.1734, wR_2 = 0.2107$	$R_1 = 0.1074, wR_2 = 0.1697$	$R_1 = 0.0262, wR_2 = 0.0660$

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|; wR_{2} = [\Sigma w (|F_{o}^{2}| - |F_{c}^{2}|)^{2} / \Sigma w |F_{o}^{2}|^{2}]^{1/2}.$

Table 2. Selected bond lengths (Å) and angles (°) for 2a-2c.

	2a	2b	2c
Ru1–N1	2.121(9)	2.103(8)	2.0981(19)
Ru1–O1	2.052(7)	2.065(6)	2.0794(17)
Ru1–Cl1	2.411(3)	2.411(3)	2.4079(7)
N1-Ru1-O1	86.2(3)	85.6(3)	85.74(7)
N1-Ru1–Cl1	86.0(2)	85.1(2)	82.73(6)
O1-Ru1–Cl1	85.8(2)	86.0(2)	87.06(6)

1393(m), 1311(m), 1256(m), 1232(m), 1186(m), 1085(w), 947(w), 895(w), 872(w), 849(w), 816(m), 708(m), 648(m), 589(w), 530(w).

2.3. X-ray structure determination

Diffraction data of **2a**, **2b**, and **2c** were collected on a Bruker AXS SMART APEX diffractometer equipped with a CCD area detector using Mo K α radiation ($\lambda = 0.71073$ Å). All the data were collected at 298 K and the structures were solved by direct methods and subsequently refined on F^2 using full-matrix least squares techniques (SHELXL) [22]. SADABS [23] absorption corrections were applied to the data, all non-hydrogen atoms were refined anisotropically, and hydrogens were located at calculated positions. All calculations were performed using the Bruker Smart program. A summary of the crystallographic data and selected experimental information is given in Table 1 with selected bond distances and angles given in Table 2.

3. Results and discussion

3.1. Synthesis of ligands and half-sandwich ruthenium complexes

As outlined in Scheme 1, the salicylbenzoxazoles (**1a-1c**) were readily accessible from salicylaldehyde in two steps [20], condensation of the corresponding salicylaldehyde with *o*-aminophenol and then



Scheme 1. Synthesis of salicylbenzoxazole ligands (1a-1c).



Scheme 2. Synthesis of 2a-2c with salicylbenzoxazole ligands.

oxidation with PhI(OAc)₂ in refluxing CH₃CN. The desired products were separated through column chromatography on silica gel as white powders in moderate to good yields. A general synthetic route for half-sandwich ruthenium complexes is shown in Scheme 2. The complexes **2a–2c** were obtained by the treatment of two equiv of the salicylbenzoxazole ligands with [Ru(*p*-cymene)(μ -Cl)Cl]₂ in the presence of K₂CO₃ in CH₃CN under reflux for 3 h, affording orange crystals of **2a–2c** in yields of 52–58%. These complexes are stable toward air and moisture in the solid state.

These ruthenium complexes were characterized by IR and NMR spectroscopy and MS. These half-sandwich ruthenium complexes have similar NMR spectra, so we use **2c** for an example. The ¹H NMR spectrum of **2c** show signals at δ 1.11, 1.20, and 2.75 ppm, which can be assigned to the isopropyl groups, which exhibited signals at δ 5.35–5.55 ppm for the arene of *p*-cymene ring, respectively. Mass spectra also provided further evidence for the formation of the half-sandwich ruthenium complexes, with peaks at *m*/*z* = 474.1007 (for **2a**), 494.2528 (for **2b**), and 537.9956 (for **2c**), corresponding to the loss of the Cl anion [M–Cl]⁺.

Crystals of **2a**, **2b**, and **2c** suitable for X-ray crystallographic diffraction were obtained by slow diffusion of diethyl ether into a concentrated solution of the ruthenium complexes in dichloromethane or methanol solution. The crystallographic data for **2a**, **2b**, and **2c** are summarized in Table 1, and selected bond lengths and angles are given in Table 2. The molecular structures of **2a–2c** are shown in Figures 1–3.

As shown in Figures 1–3, the half-sandwich ruthenium complexes have remarkably similar structures. Each Ru is surrounded by one chloride, one nitrogen, and one oxygen from the ligand and one of the *p*-cymene rings. All of the ruthenium centers have six-coordinate geometry, assuming that the *p*-cymene ring is a three-coordinate ligand. Ruthenium of **2a**, **2b**, and **2c** has a three-legged piano-stool conformation with a six-membered metallocycle formed by coordination of the bidentate salicylbenzoxazole ligands to the metal centers. The Ru–N distances (2.121(9) Å in **2a**, 2.103(8) Å in **2b**, and 2.0981(19) Å in **2c**) are in the range of typical distances of reported ruthenium complexes containing pyridine or [N,O] anionic bidentate ligands [9, 24, 25].



Figure 1. Complex 2a with thermal ellipsoids drawn at the 30% level. All hydrogens are omitted for clarity.



Figure 2. Complex 2b with thermal ellipsoids drawn at the 30% level. All hydrogens are omitted for clarity.

3.2. The CV and UV-vis absorbance of 2a-2c

The electrochemical properties of **2a–2c** have been studied by CV in degassed CH₃CN solution under nitrogen using 0.2 M TBAP as supporting electrolyte. A glassy carbon working electrode, a platinum auxiliary electrode, and a Ag/AgCl reference electrode were used to obtain cyclic voltammograms. The data for **2a–2c** are collected in Table 3, and the cyclic voltammograms of the complexes are shown in Figure 4. Complexes **2a–2c** displayed a one-electron oxidation process Ru(II)/Ru(III) with *quasi*-reversible half-potentials and similar to those of other half-sandwich ruthenium complexes [26]. The *quasi*-reversible reduction couples ($E_{1/2}$) for **2a–2c** were –0.782, –0.796, and –0.783 V, respectively. On modifying



Figure 3. Complex 2c with thermal ellipsoids drawn at the 30% level. All hydrogens are omitted for clarity.

Complex	$E_{\rm pc}/V$	$E_{\rm pa}/V$	E _{1/2} /V	Absorption $\lambda_{\max}(nm) \epsilon_{\max} (dm^3 mol^{-1} cm^{-1})$
2a	-0.903	-0.660	-0.782	299 (11,812), 400 (5660)
2b	-0.911	-0.680	-0.796	298 (9950), 400 (5125)
2c	-0.875	-0.691	-0.783	299 (12,420), 400 (6254)

Notes: Measured with a glassy carbon electrode at 100 mV s⁻¹ in CH₃CN containing 0.2 M NBu₄ClO₄ and $E_{1/2} = (E_{pa} + E_{pc})/2$ in volts using Ag/AgCl as reference. $E_{1/2} = (E_{pa} + E_{pc})/2$ for the quasi-reversible reduction couples; E_{pa} and E_{pc} are peak anodic and peak cathodic potentials, respectively.



Figure 4. Cyclic voltammograms of 2a-2c.



Figure 5. The UV-vis absorption of 2a-2c (1 × 10⁻⁵ mol L⁻¹) in CH₃CN.

the para substituent on the ligand from –Me to –Br on the ligands, the oxidation potential increases from –0.660 V (**2a**) to –0.691 V (**2c**). This slight variation is attributed to the electron-rich (–Me) and electron-deficient (Cl⁻ and Br⁻) substituents on the salicylbenzoxazole ligands. It is apparent from the cyclic voltammograms that the $E_{1/2}$ values are sensitive to substituents on the salicylbenzoxazole ligands.

The absorption spectra of **2a–2c** were measured at room temperature in CH₃CN. The UV/Vis absorption data are summarized in Table 3, and the corresponding electronic absorption spectra of ruthenium complexes are depicted in Figure 5. All ruthenium complexes show intense absorptions at 299 and 400 nm with molar extinction coefficients (ε) in the order of 10⁴ dm³ mol⁻¹ cm⁻¹, which can be assigned to charge transfer between salicylbenzoxazole ligands and ruthenium (MLCT). The salicylbenzoxazole compounds have a strong absorption between 220 and 280 nm due to the π - π * transition. When complexed to ruthenium, this absorption band was slightly red shifted for **2a–2c**, as observed in ruthenium complexes with [3] radialene ligands [27].

4. Conclusion

We have synthesized and characterized three half-sandwich salicylbenzoxazole ruthenium complexes. A combination of spectroscopic studies and X-ray crystallographic confirmed the molecular structures of **2a–2c**. The redox properties and electronic absorptions of **2a–2c** showed that the electron-rich or electron-deficient substituents on the salicylbenzoxazole ligands have minor influences to the redox and spectroscopic properties of the ruthenium complexes.

Supplementary material

The crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC–1063395 (**2a**), CCDC–1063396 (**2b**) and CCDC–1063397 (**2c**) (Fax: +44–1223-336–033; E-mail: deposit@ccdc.cam. ac.uk; http://www.ccdc.cam.ac.uk).

Disclosure statement

No potential conflict of interest was reported by the authors.

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