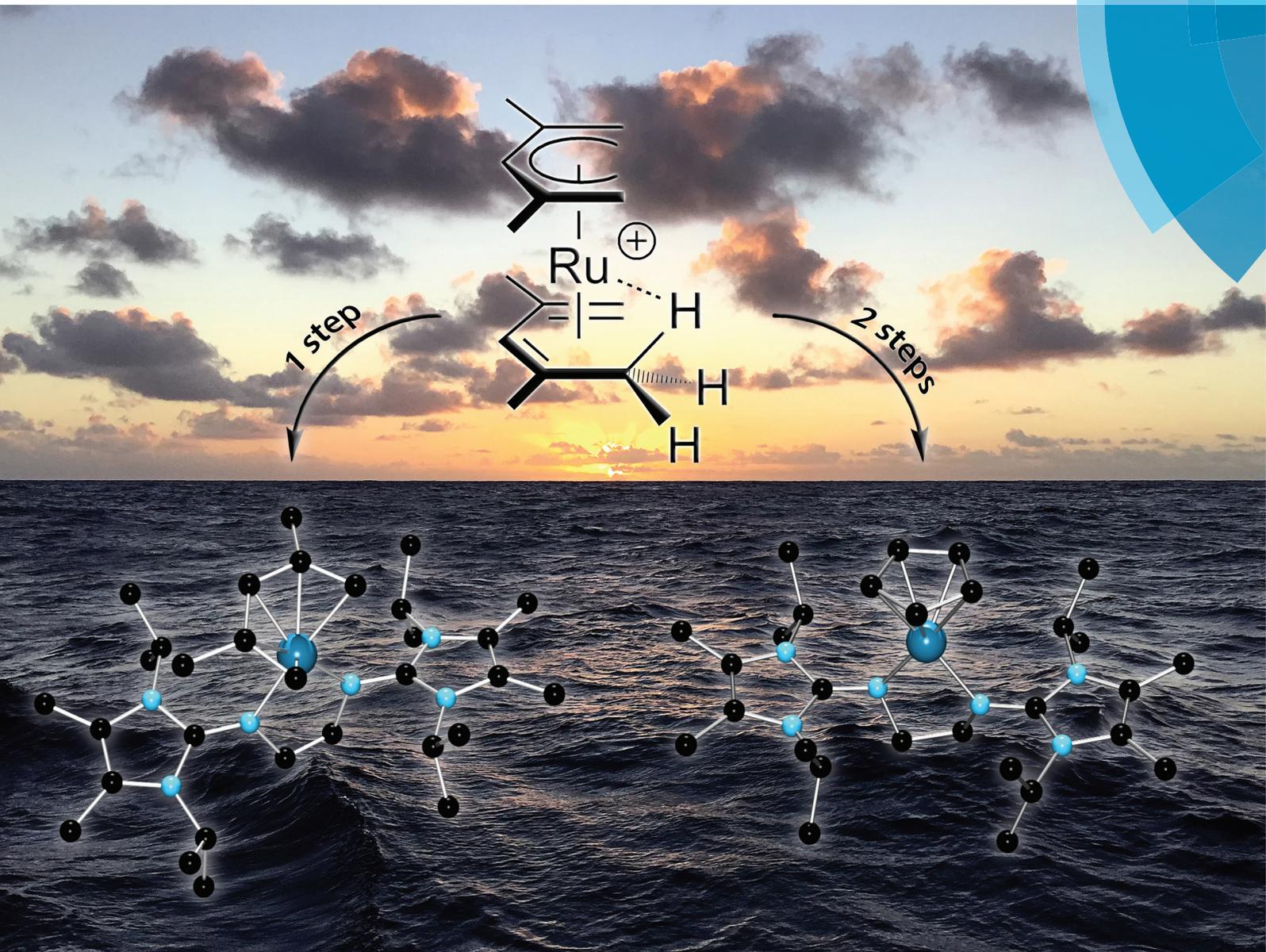


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PAPER

Matthias Tamm *et al.*

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# 16-Electron pentadienyl- and cyclopentadienyl-ruthenium half-sandwich complexes with bis(imidazol-2-imine) ligands and their use in catalytic transfer hydrogenation†

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Bis( $\eta^5$ -2,4-dimethylpentadienyl)ruthenium(II), [ $(\eta^5$ -C<sub>7</sub>H<sub>11</sub>)<sub>2</sub>Ru] (**1**, “open ruthenocene”), which has become accessible in high yield and large quantities via an isoprene-derived diallyl ruthenium(IV) complex, can be converted into the protonated open ruthenocene **2** by treatment with HBF<sub>4</sub> and subsequently into the protonated half-open ruthenocene **3** by reaction with cyclopentadiene. The electronic structure of **3** was studied by DFT methods, revealing that the CH-agostic complex [ $(\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ru{(1-4 $\eta$ )-C<sub>7</sub>H<sub>12</sub>- $\eta^2$ -C<sup>5</sup>,H<sup>5</sup>}-BF<sub>4</sub>] (**A**) represents the global minimum, which is 3.7 kcal mol<sup>-1</sup> lower in energy than the hydride complex [ $(\eta^5$ -C<sub>5</sub>H<sub>5</sub>)RuH( $\eta^5$ -C<sub>7</sub>H<sub>11</sub>)]BF<sub>4</sub> (**B**). **2** and **3** were treated with the ligands *N,N'*-bis(1,3,4,5-tetramethylimidazolin-2-ylidene)-1,2-ethanediamine (BL<sup>Me</sup>) and *N,N'*-bis(1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene)-1,2-ethanediamine (BL<sup>iPr</sup>) to afford the cationic 16-electron pentadienyl and cyclopentadienyl complexes [ $(\eta^5$ -C<sub>7</sub>H<sub>11</sub>)Ru(BL<sup>R</sup>)]BF<sub>4</sub> (**4a**, R = Me; **4b**, R = *iPr*) and [ $(\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ru(BL<sup>R</sup>)]BF<sub>4</sub> (**5a**, R = Me; **5b**, R = *iPr*). All complexes catalyse the transfer hydrogenation of acetophenone in isopropanol, and the most active complex **4a** in this reaction was employed for the hydrogenation of a broader range of aliphatic and aromatic ketones.

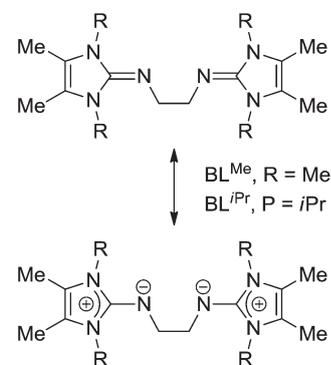
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## Introduction

Imidazolin-2-imine ligands such as BL<sup>Me</sup> and BL<sup>iPr</sup>,<sup>1,2</sup> and related guanidine-type ligands,<sup>3</sup> have found widespread use in organometallic and coordination chemistry and proved to be suitable ancillary ligands for applications in homogeneous catalysis.<sup>4</sup> Because the imidazole moiety can efficiently stabilise a positive charge (Scheme 1),<sup>5</sup> these diimine species are highly basic and may serve as strong N-donor ligands towards transition metals, as was demonstrated *e.g.* by the isolation of stable 16-electron half-sandwich complexes of the type [ $(\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ru(BL<sup>R</sup>)]<sup>+</sup>,<sup>6,7</sup> [ $(\eta^7$ -C<sub>7</sub>H<sub>7</sub>)Mo(BL<sup>R</sup>)]<sup>+</sup>,<sup>8</sup> and [ $(\eta^6$ -arene)-Ru(BL<sup>R</sup>)]<sup>2+</sup> (R = Me, *iPr*; arene = cymene, benzene).<sup>9</sup> The mono- and dicationic cyclopentadienyl- and arene-ruthenium complexes, which are isolable even in the presence of chloride



Scheme 1 Mesomeric structures for the bis(imidazolin-2-imine) ligands BL<sup>R</sup> (R = Me, *iPr*).

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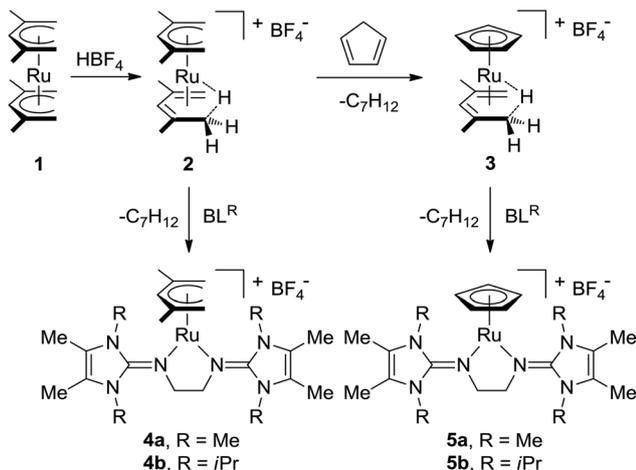
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† Electronic supplementary information (ESI) available: Selected NMR spectra and computational details. CCDC 1054781–1054784. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/C5DT01080B

counterions,<sup>6,9</sup> were employed as catalysts for the transfer hydrogenation of acetophenone, with isopropanol serving as the hydrogen source.<sup>9</sup>

To vary the half-sandwich ruthenium moiety in these coordinatively unsaturated and catalytically active complexes,<sup>10</sup> we chose bis( $\eta^5$ -2,4-dimethylpentadienyl)ruthenium(II), [ $(\eta^5$ -C<sub>7</sub>H<sub>11</sub>)<sub>2</sub>Ru] (**1**, “open ruthenocene”),<sup>11</sup> as a suitable starting material, since this compound has recently become con-





**Scheme 2** Preparation of pentadienyl and cyclopentadienyl ruthenium half-sandwich complexes from protonated open and half-open ruthenocenes.

veniently accessible in high yield and large quantities *via* an isoprene-derived diallyl ruthenium(IV) complex.<sup>12–14</sup> Previously, a related protocol had directly furnished the protonated open ruthenocene **2**,<sup>15</sup> which was also obtained by treatment of **1** with HBF<sub>4</sub> (Scheme 2).<sup>16</sup> It was also briefly mentioned that the reaction of **2** with cyclopentadiene affords the corresponding cationic Cp complex **3**, but to the best of our knowledge, no experimental details were published.<sup>17</sup> Alternatively, **3** can be prepared by the reaction of the half-open ruthenocene ( $\eta^5$ -2,4-dimethylpentadienyl)( $\eta^5$ -cyclopentadienyl)ruthenium(II),  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta^5\text{-C}_7\text{H}_{11})]$ , with HBF<sub>4</sub>.<sup>18</sup> Complex **2** served as a versatile starting material for the preparation of numerous half-sandwich 2,4-dimethylpentadienyl-ruthenium complexes by displacement of the diene ligand,<sup>12,16,19,20</sup> and consequently we expected that both **2** and **3** would readily react with the diimine ligands BL<sup>R</sup> (R = Me, iPr) to afford complexes of type **4** and **5**, respectively (Scheme 2).<sup>21</sup> Thus, the preparation and characterisation of these complexes and their use in hydrogen transfer catalysis is described herein. In addition, an electronic structure calculation of **3** together with full experimental details for its preparation from **2** are reported.

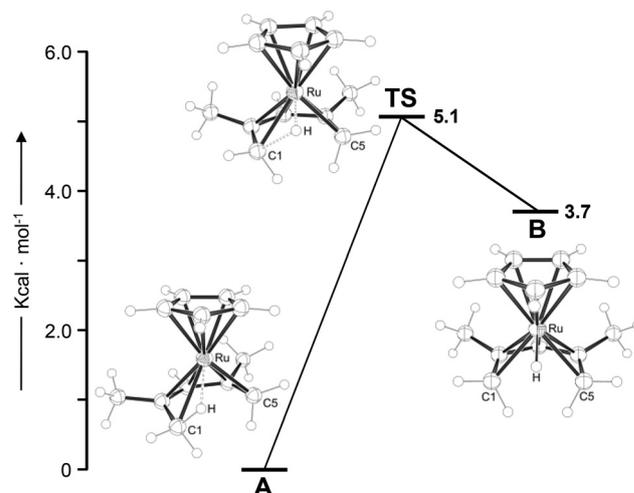
## Results and discussion

### Preparation and electronic structure of the half-open ruthenocene **3**

The open ruthenocene **1** was treated with HBF<sub>4</sub>·Et<sub>2</sub>O in diethyl ether solution as previously described to afford **2** as a yellow crystalline solid in quantitative yield.<sup>16</sup> Dropwise addition of freshly distilled cyclopentadiene to an acetone solution of **2** at  $-75$  to  $-80$  °C gave **3** as a pale yellow solid in 80% yield after stirring at room temperature and precipitation with diethyl ether (Scheme 2).<sup>17</sup> It should be noted that this method is generally applicable and provides *e.g.* the corresponding methyl-

and *tert*-butylcyclopentadienyl complexes by reaction with the corresponding cyclopentadiene derivatives.<sup>21</sup> The NMR spectroscopic data of **3** are identical to those reported previously, with the <sup>1</sup>H NMR spectrum displaying signals at *ca.*  $-10.1$ ,  $-0.3$  and  $3.0$  ppm in the temperature range between  $-10$  and  $-80$  °C,<sup>17,18</sup> which can be assigned to the RuH and to the *endo*- and *exo*-CH<sub>2</sub> hydrogen atoms of an agostic ruthenium species (see the ESI†). Accordingly, methyl rotation, *i.e.* H exchange within an agostic CH<sub>3</sub> group, is frozen out in this temperature range on the NMR time scale, and a detailed dynamic NMR study derived a barrier of  $\Delta G^\ddagger = 12.6$  kcal mol<sup>-1</sup> for this process. In contrast, 1,5-H transfer cannot be frozen out (*vide supra*), and an upper limit of *ca.*  $7.2$  kcal mol<sup>-1</sup> was estimated for the barrier of the latter process.<sup>17,22</sup>

To support the experimental findings and to further characterise the electronic structure of the protonated half-open ruthenocene, DFT calculations were carried out for the cation in **3** at the B3LYP/6-311G(d,p) level of theory. Two minimum structures **A** and **B** were located, which are connected by a low-energy transition state TS (Fig. 1). The global minimum **A** represents an agostic ruthenium complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{(\eta^5\text{-C}_7\text{H}_{12}\text{-}\eta^2\text{-C}^5\text{H}^5)\}]\text{BF}_4^{23}$  with Ru–C5 and Ru–H5 distances of 2.38 and 1.85 Å.<sup>24</sup> The agostic C–H bond is elongated (1.18 Å), and the C4–C5 bond is significantly longer than the other C–C bonds (1.49 vs. 1.42, 1.44 and 1.41 Å) within the pentadienyl ligand. Structure **B** is 3.7 kcal mol<sup>-1</sup> higher in energy and represents the hydride complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{RuH}(\eta^5\text{-C}_7\text{H}_{11})]$  with a Ru–H bond of 1.57 Å. The pentadienyl ligand is symmetrically bound, with long C1–H and C5–H distances of *ca.* 2.20 Å. **A** and **B** are connected by a transition state (TS) that is 5.1 and 1.4 kcal mol<sup>-1</sup> higher in energy than **A** and **B**, respectively. Naturally, **B** can be regarded as an intermediate in the intraligand 1,5-H transfer from C1 to C5, and the low calculated barrier for this process is in agreement with the observation



**Fig. 1** Potential-energy profile for 1,5-intraligand H transfer in the protonated half-open ruthenocene **3**. Values correspond to  $\Delta G_{298\text{ K}}$  = B3LYP/6-311G(d,p) Gibbs free energies at 298 K. For values derived with the B97-D and M06 functionals, see ESI.† TS = transition state.



that this process is not frozen out in an accessible temperature range on the NMR time scale.<sup>17</sup>

### Preparation of pentadienyl and cyclopentadienyl ruthenium bis(imidazolin-2-imine) complexes

The reaction of the protonated open and half-open ruthenocenes **2** and **3** with the ligands BL<sup>Me</sup> and BL<sup>iPr</sup> in acetonitrile afforded the half-sandwich pentadienyl and cyclopentadienyl complexes  $[(\eta^5\text{-C}_7\text{H}_{11})\text{Ru}(\text{BL}^{\text{R}})]\text{BF}_4$  (**4a**, R = Me; **4b**, R = iPr) and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{BL}^{\text{R}})]\text{BF}_4$  (**5a**, R = Me; **5b**, R = iPr) as purple solids in good yield (ca. 80%, Scheme 2). These reactions are likely to proceed *via* the cationic tris(acetonitrile) complexes  $[(\eta^5\text{-C}_7\text{H}_{11})\text{Ru}(\text{CH}_3\text{CN})_3]^+$  and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CH}_3\text{CN})_3]^+$ ,<sup>19,25</sup> which are conveniently accessible from **2** and **3**.<sup>21</sup> NMR spectra recorded in acetone-*d*<sub>6</sub> gave no indication for the formation of stable solvate complexes with tightly bound acetonitrile or acetone ligands. The <sup>1</sup>H NMR spectra of complexes **4** show the expected signals for the 2,4-dimethylpentadienyl ligand, with a singlet at ca. 4.9 ppm for the 3-CH and doublets at ca. 2.0 and -0.9 ppm (*J*<sub>H,H</sub> = 2.5 Hz) for the *exo*- and *endo*-1,5-CH hydrogen atoms. The <sup>1</sup>H NMR spectra of complexes **5** display a singlet at ca. 3.52 ppm for the C<sub>5</sub>H<sub>5</sub> moieties, which is at higher field than usually observed for cyclopentadienyl-ruthenium half-sandwich complexes and could be ascribed to shielding by the imidazole rings.<sup>24</sup> Resonances assigned to the BL<sup>Me</sup> and BL<sup>iPr</sup> ligands in **4** and **5** are similar to those reported for the corresponding  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{BL}^{\text{R}})]^+$  ions.<sup>6</sup>

The crystal structures of **4a**·THF, **4b** and **5b** were determined by X-ray diffraction analyses, confirming in all cases the formation of 16-electron half-sandwich complexes with two-legged piano-stool (pseudo-trigonal planar) geometries around the ruthenium atoms (Fig. 2–4). Interestingly, two different

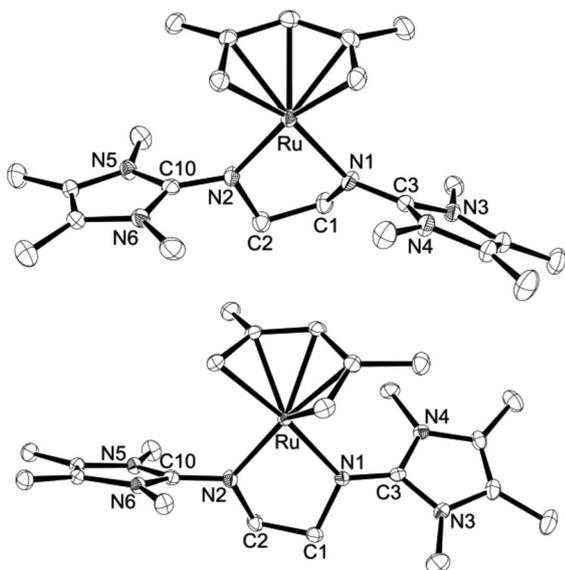


Fig. 2 ORTEP diagram of the cation in **4a**·THF in polymorphs A (top) and B (bottom) with thermal displacement parameters drawn at 50% probability (see Table 1 for bond lengths and angles).

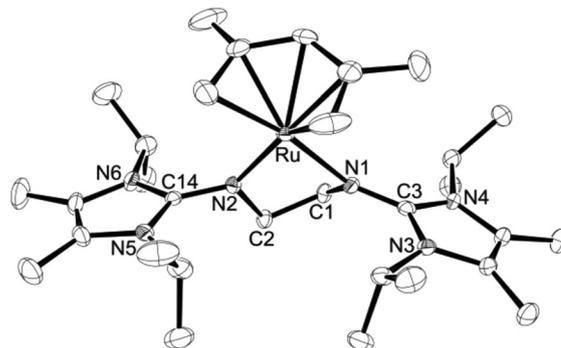


Fig. 3 ORTEP diagram of the cation in **4b** (only one of the two independent cations is shown) with thermal displacement parameters drawn at 50% probability (see Table 1 for bond lengths and angles).

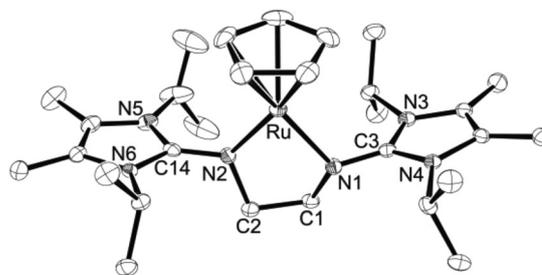


Fig. 4 ORTEP diagram of the cation in **5b** with thermal displacement parameters drawn at 50% probability (see Table 1 for bond lengths and angles).

polymorphs of **4a**·THF (**A** and **B**) were characterised, which both crystallise in the triclinic space group *P* $\bar{1}$ . While the metal-carbon and metal-nitrogen bond lengths are similar (Table 1), the structures differ in the orientation of the pentadienyl ligand, which renders the molecules either almost *C*<sub>s</sub>- (**A**, Fig. 2, top) or *C*<sub>1</sub>-symmetric (**B**, Fig. 2, bottom). These conformations are similar to those found in bis(pentadienyl) complexes, which may exhibit symmetric *syn*- and *anti*-eclipsed or asymmetric *gauche*-eclipsed conformations.<sup>26</sup> The latter orientation is also found for the two independent molecules in **4b** (Fig. 3, only one cation shown). It should be noted that **4a** and **4b** represent, to the best of our knowledge, the first structurally characterised half-sandwich pentadienyl ruthenium complexes with a (formal) electron count of 16, and previously described pentadienyl species are usually 18-electron complexes with common three-legged piano-stool (pseudo-tetrahedral) geometries.<sup>16,19,27,28</sup> **5a** and **5b** are also very rare examples of 16-electron half-sandwich ruthenium complexes bearing the  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}$  unit, with  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{tmeda})][\text{BAr}^{\text{F}}_4]$  and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{dppe})][\text{GaI}_4]$  representing the only previously characterised systems (tmeda = Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>, dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>).<sup>29,30</sup> In contrast, a significantly larger number of 16-electron complexes are known that contain the sterically more demanding  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}$  fragment.<sup>31–33</sup>



**Table 1** Selected bond lengths (Å) and angles (°) for pentadienyl and cyclopentadienyl ruthenium bis(imidazolin-2-imine) complexes

	4a·THF (polymorph A)	4a·THF (polymorph B)	4b <sup>a</sup>	5b
Ru–N1	2.0529(17)	2.1262(12)	2.123(2)	2.0601(15)
Ru–N2	2.0627(17)	2.0155(12)	2.009(2)	2.0423(15)
Ru–C	2.128(2)– 2.159(2)	2.0928(14)– 2.1850(14)	2.104(3)– 2.153(3)	2.1135(19)– 2.1569(19)
C3–N1	1.344(3)	1.3266(18)	1.336(3)	1.348(2)
C3–N3	1.358(3)	1.3620(18)	1.360(3)	1.362(2)
C3–N4	1.351(3)	1.3554(18)	1.360(3)	1.355(2)
C10/C14–N2	1.359(3)	1.3530(18)	1.362(3)	1.353(2)
C10/C14–N5	1.345(3)	1.3472(18)	1.348(3)	1.351(2)
C10/C14–N6	1.351(3)	1.3528(18)	1.355(3)	1.362(2)
N1–Ru–N2	78.52(7)	77.79(5)	78.85(8)	77.31(6)
(N–Ru–N)/ (C <sub>3</sub> N <sub>2</sub> ) <sup>b</sup>	69.5; 86.7	62.8; 69.9	79.1; 78.4	83.9; 82.6
ρ <sup>c</sup>	0.992; 1.008	0.976; 1.002	0.982; 1.008	0.992; 0.997

<sup>a</sup> The asymmetric unit contains two independent molecules with very similar structural parameters; the values of molecule 1 are shown.

<sup>b</sup> Angle between the RuN<sub>2</sub> and imidazole ring planes. <sup>c</sup>  $\rho = 2a/(b + c)$ , with *a*, *b*, and *c* representing the exo- (*a*) and endocyclic (*b*, *c*) bonds within the CN<sub>3</sub> guanidine moiety.

Similarly to the previously reported complexes  $[(\eta^5\text{-C}_5\text{Me}_5)\text{-Ru}(\text{BL}^{\text{R}})]^+$  and  $[(\eta^6\text{-arene})\text{Ru}(\text{BL}^{\text{R}})]^{2+}$ ,<sup>6,9</sup> the stability of **4** and **5** can be ascribed to the strong  $\pi$ -electron-releasing ability of the BL<sup>R</sup> ligands as illustrated by the ylidic mesomeric structure in Scheme 1, which consistently affords short Ru–N bond lengths in the range 2.01–2.13 Å (Table 1). Charge separation and delocalisation can also be clearly deduced from the observation of large dihedral angles between the imidazole and N–Ru–N planes, which rules out the possibility of any substantial  $\pi$ -interaction between the imidazole rings and the nitrogen atoms. As a consequence, the three C–N bond lengths within the imidazolin-2-imine (or guanidine) CN<sub>3</sub> unit are almost equal, and this structural feature can be illustrated by the parameter  $\rho = 2a/(b + c)$ , with *a*, *b*, and *c* representing the exo- (*a*) and endocyclic (*b*, *c*) bonds.<sup>34</sup> In agreement with efficient charge delocalisation,  $\rho$  values between 0.98 and 1.01 are found (Table 1).

### Catalytic transfer hydrogenation of ketones

Catalytic transfer hydrogenation has become a standard method for the reduction of ketones to secondary alcohols,<sup>35</sup> with half-sandwich ruthenium complexes representing the most widely studied catalyst systems.<sup>36</sup> Coordinatively unsaturated species are considered as important reaction intermediates, and therefore, the complexes **4** and **5** can be expected to serve as hydrogen transfer catalysts. The hydrogenation of acetophenone was chosen as a test reaction, and the activity of the complexes **4a**, **4b**, **5a** and **5b** was studied in boiling 2-propanol (b.p. = 82 °C) with 1 mol% catalyst loading and potassium hydroxide (10 mol%) as the base. The reaction progress was monitored by gas chromatography (GC), and the results are summarized in Table 2. The cyclopentadienyl complexes

**Table 2** Catalytic transfer hydrogenation of acetophenone<sup>a</sup>

Substrate	Catalyst	Time [h]	Conversion [%]	TOF [h <sup>-1</sup> ]
Acetophenone	<b>4a</b>	0.5	99	198
Acetophenone	<b>4b</b>	0.75	98	131
Acetophenone	<b>5a</b>	3	86	29
Acetophenone	<b>5b</b>	4	100	25

<sup>a</sup> Conditions: 0.02 mmol cat., 0.2 mmol KOH, 10 mL iPrOH, 2 mmol acetophenone, temperature: 82 °C, the formation of 2-phenylethanol is monitored by gas chromatography.

**Table 3** Catalytic transfer hydrogenation of various ketones with **4a**<sup>a</sup>

Substrate	Catalyst	Time [min]	Conversion [%]	TOF [h <sup>-1</sup> ]
3-Pentanone	<b>4a</b>	40	100	150
2-Methylbutanone	<b>4a</b>	60	99	99
Cyclohexanone	<b>4a</b>	10	100	600
Cycloheptanone	<b>4a</b>	40	97	146
4-Heptanone	<b>4a</b>	60	96	96
<i>p</i> -Chloroacetophenone	<b>4a</b>	30	100	200
Benzophenone	<b>4a</b>	60	98	98
1-Acetonaphthone	<b>4a</b>	20	96	288

<sup>a</sup> Conditions: 0.02 mmol cat., 0.2 mmol KOH, 10 mL iPrOH, 2 mmol ketone, temperature: 82 °C, the formation of the respective secondary alcohol is monitored by gas chromatography.

**5a** and **5b** display activities similar to those previously reported for the related complexes  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{BL}^{\text{R}})]\text{X}$  and  $[(\eta^6\text{-arene})\text{Ru}(\text{BL}^{\text{R}})]\text{X}_2$  (*X* = Cl or weakly-coordinating counterion),<sup>9</sup> whereas the pentadienyl complexes **4a** and **4b** show higher activities. The most active complex **4a** was further employed as a catalyst under the same conditions for the reduction of a range of aliphatic and aromatic ketones to the corresponding secondary alcohols. In all cases, full conversion was achieved in less than one hour (Table 3).

## Conclusions

This paper provides further evidence for the ability of the bis-(imidazolin-2-imine) ligands BL<sup>Me</sup> and BL<sup>iPr</sup> to stabilise coordinatively unsaturated transition metal complexes, furnishing the complexes  $[(\eta^5\text{-C}_7\text{H}_{11})\text{Ru}(\text{BL}^{\text{R}})]\text{BF}_4$  (**4a**, R = Me; **4b**, R = iPr) and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{BL}^{\text{R}})]\text{BF}_4$  (**5a**, R = Me; **5b**, R = iPr) as rare examples of 16-electron ruthenium complexes containing pentadienyl- or cyclopentadienyl (C<sub>5</sub>H<sub>5</sub>) ligands. These complexes were prepared from bis( $\eta^5$ -2,4-dimethylpentadienyl)-ruthenium(II),  $[(\eta^5\text{-C}_7\text{H}_{11})_2\text{Ru}]$  (**1**, “open ruthenocene”) via the protonated open or half-open ruthenocenes **2** and **3**, and this route provides a general and convenient pathway to the important class of pentadienyl and cyclopentadienyl ruthenium half-sandwich complexes.



## Experimental

### General

All operations were performed in an atmosphere of dry argon using Schlenk and vacuum techniques. All solvents were purified by standard methods and distilled prior to use.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX 400 device. The chemical shifts are given in ppm relative to tetramethylsilane (TMS) as internal standard. The spin coupling patterns are indicated as s (singlet), d (doublet), m (multiplet), sept (septet) and br (broad, for unresolved signals). Elemental analyses (C, H, N) were measured on an Elementar Vario EL III CHNS elemental analyser. **1**,<sup>13</sup> **2**,<sup>14,16</sup>  $\text{BL}^{\text{Me}}$ ,<sup>6</sup> and  $\text{BL}^{\text{iPr}}$ ,<sup>6</sup> were prepared according to published procedures.

$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{\text{(1-}\eta\text{)-C}_7\text{H}_{12}\text{-}\eta^2\text{-C}^5\text{H}^5\}]\text{BF}_4$  (**3**, “protonated half-open ruthenocene”). A solution of the protonated open ruthenocene **2** (190 mg, 0.50 mmol) in acetone (7.5 mL) was cooled to  $-80\text{ }^\circ\text{C}$ . A solution of freshly distilled cyclopentadiene (42  $\mu\text{L}$ , 0.50 mmol) in acetone (7.5 mL) was added dropwise at  $-75$  to  $-80\text{ }^\circ\text{C}$  over a period of 20 min. The solution was allowed to warm to room temperature, concentrated to ca. 3 mL, and the product was precipitated with diethyl ether (15 mL). The supernatant solution was removed *via* syringe, and the precipitate was washed with diethyl ether ( $3 \times 5$  mL). The precipitate was dried *in vacuo* to yield the product as a pale yellow solid (138 mg, 0.40 mmol, 80%). The spectroscopic data are identical to those previously published.<sup>17,18</sup> A variable-temperature NMR study is shown in the ESI.†

$[(\eta^5\text{-C}_7\text{H}_{11})\text{Ru}(\text{BL}^{\text{Me}})]\text{BF}_4$  (**4a**). A solution of  $\text{BL}^{\text{Me}}$  (82.2 mg, 0.27 mmol) in acetonitrile (5 mL) was added dropwise to an orange suspension of **2** (100.0 mg, 0.26 mmol) in acetonitrile (10 mL) at room temperature. During the addition of the ligand, the reaction mixture turned purple and the solution was stirred overnight. The solvent was removed under reduced pressure. The residue was dissolved in 5 mL THF and the product precipitated with *n*-hexane (30 mL). Filtration, washing with *n*-hexane ( $2 \times 10$  mL) and drying *in vacuo* afforded the product as a purple solid (123.2 mg, 81%). Anal. Calcd for  $\text{C}_{23}\text{H}_{39}\text{BF}_4\text{N}_6\text{Ru}$ : C, 47.02; H, 6.69; N, 14.31. Found: C, 46.92; H, 6.80; N, 13.70.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $25\text{ }^\circ\text{C}$ ):  $\delta = 4.92$  (s, 1 H, CH), 3.57 (s, 12 H, NCH<sub>3</sub>), 2.81 (s, 4 H, C<sub>2</sub>H<sub>4</sub>), 2.19 (s, 12 H,  $\text{BL}^{\text{Me}}$ -CCH<sub>3</sub>), 2.00 (d,  $J_{\text{H,H}} = 2.5$  Hz, 2 H, CH<sub>2</sub>-*exo*), 1.49 (s, 6 H, C<sub>7</sub>H<sub>11</sub>-CH<sub>3</sub>),  $-0.86$  (d,  $J_{\text{H,H}} = 2.5$  Hz, 2 H, CH<sub>2</sub>-*endo*) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $25\text{ }^\circ\text{C}$ ):  $\delta = 155.9$  (NCN), 119.6 (NCCH<sub>3</sub>), 87.0 (C<sub>7</sub>H<sub>11</sub>-CCH<sub>3</sub>), 83.7 (CH), 56.3 (C<sub>2</sub>H<sub>4</sub>), 38.8 (CH<sub>2</sub>), 31.2 (NCH<sub>3</sub>), 24.8 (C<sub>7</sub>H<sub>11</sub>-CH<sub>3</sub>), 9.0 ( $\text{BL}^{\text{Me}}$ -CCH<sub>3</sub>) ppm.

$[(\eta^5\text{-C}_7\text{H}_{11})\text{Ru}(\text{BL}^{\text{iPr}})]\text{BF}_4$  (**4b**). A solution of  $\text{BL}^{\text{iPr}}$  (112.5 mg, 0.27 mmol) in acetonitrile (5 mL) was added dropwise to an orange suspension of **2** (100.0 mg, 0.26 mmol) in acetonitrile (10 mL) at room temperature. During the addition of the ligand the reaction mixture turned purple and the solution was stirred overnight. The solvent was removed under reduced pressure. The residue was dissolved in 5 mL THF and the product precipitated with *n*-hexane (30 mL). Filtration, washing with *n*-hexane ( $2 \times 10$  mL) and drying *in vacuo*

afforded the product as a purple solid (144.6 mg, 81%). Anal. Calc. for  $\text{C}_{31}\text{H}_{55}\text{BF}_4\text{N}_6\text{Ru}$ : C, 53.22; H, 7.92; N, 12.01. Found: C, 53.26; H, 8.12; N, 12.28.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $25\text{ }^\circ\text{C}$ )  $\delta = 5.35$  (sept,  $^3J_{\text{H,H}} = 7.1$  Hz, 4 H, NCH<sub>3</sub>), 5.01 (s, 1 H, CH), 2.78 (s, 4 H, C<sub>2</sub>H<sub>4</sub>), 2.29 (s, 12 H,  $\text{BL}^{\text{iPr}}$ -CCH<sub>3</sub>), 2.01 (d,  $J_{\text{H,H}} = 2.5$  Hz, 2 H, CH<sub>2</sub>-*exo*), 1.60 (d, 12 H, CHCH<sub>3</sub>,  $^3J_{\text{H,H}} = 7.1$  Hz), 1.60 (s, 6 H, C<sub>7</sub>H<sub>11</sub>-CH<sub>3</sub>), 1.43 (d, 12 H, CHCH<sub>3</sub>,  $^3J_{\text{H,H}} = 7.1$  Hz),  $-0.95$  (d,  $J_{\text{H,H}} = 2.5$  Hz, 2 H, CH<sub>2</sub>-*endo*) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $25\text{ }^\circ\text{C}$ )  $\delta = 155.7$  (NCN), 120.6 (NCCH<sub>3</sub>), 87.2 (C<sub>7</sub>H<sub>11</sub>-CCH<sub>3</sub>), 85.6 (CH), 58.9 (C<sub>2</sub>H<sub>4</sub>), 48.9 (NCH), 36.6 (CH<sub>2</sub>), 24.7 (C<sub>7</sub>H<sub>11</sub>-CCH<sub>3</sub>), 22.7 (CHCH<sub>3</sub>), 21.8 (CHCH<sub>3</sub>), 10.4 ( $\text{BL}^{\text{iPr}}$ -CCH<sub>3</sub>) ppm.

$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{BL}^{\text{Me}})]\text{BF}_4$  (**5a**). A solution of  $\text{BL}^{\text{Me}}$  (54.8 mg, 0.18 mmol) in acetonitrile (5 mL) was added dropwise to an orange suspension of **3** (59.6 mg, 0.17 mmol) in acetonitrile (10 mL) at room temperature. During the addition of the ligand, the reaction mixture turned purple and the solution was stirred overnight. The solvent was removed under reduced pressure. The residue was dissolved in 5 mL THF and the product precipitated with *n*-hexane (30 mL). Filtration, washing with *n*-hexane ( $2 \times 10$  mL) and drying *in vacuo* afforded the product as a purple solid (63.0 mg, 65%). Anal. Calcd for  $\text{C}_{25}\text{H}_{35}\text{BF}_4\text{N}_6\text{Ru}$ : C, 45.25; H, 5.97; N, 15.08. Found: C, 45.15; H, 6.13; N, 14.44.  $^1\text{H}$  NMR (400 MHz, acetone-*d*<sub>6</sub>,  $25\text{ }^\circ\text{C}$ ):  $\delta = 3.71$  (s, 12 H, NCH<sub>3</sub>), 3.53 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 2.74 (s, 4 H, C<sub>2</sub>H<sub>4</sub>), 2.28 (s, 12 H, CCH<sub>3</sub>) ppm.  $^{13}\text{C}$  NMR (100 MHz, acetone-*d*<sub>6</sub>,  $25\text{ }^\circ\text{C}$ ):  $\delta = 158.0$  (NCN), 120.0 (NCCH<sub>3</sub>), 58.3 (C<sub>5</sub>H<sub>5</sub>), 55.6 (C<sub>2</sub>H<sub>4</sub>), 31.6 (NCH<sub>3</sub>), 8.7 (CCH<sub>3</sub>) ppm.

$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{BL}^{\text{iPr}})]\text{BF}_4$  (**5b**). A solution of  $\text{BL}^{\text{iPr}}$  (100.0 mg, 0.24 mmol) in acetonitrile (5 mL) was added dropwise to an orange suspension of **3** (80.3 mg, 0.23 mmol) in acetonitrile (10 mL) at room temperature. During the addition of the ligand the reaction mixture turned purple, and the solution was stirred overnight. The solvent was removed under reduced pressure. The residue was dissolved in 5 mL THF and the product precipitated with *n*-hexane (30 mL). Filtration, washing with *n*-hexane ( $2 \times 10$  mL) and drying *in vacuo* afforded the product as a purple solid (128.2 mg, 83%). Anal. Calcd for  $\text{C}_{29}\text{H}_{49}\text{BF}_4\text{N}_6\text{Ru}$ : C, 52.02; H, 7.38; N, 12.55. Found: C, 51.98; H, 7.59; N, 12.40.  $^1\text{H}$  NMR (400 MHz, acetone-*d*<sub>6</sub>,  $25\text{ }^\circ\text{C}$ ):  $\delta = 5.40$  (sept,  $^3J_{\text{H,H}} = 7.1$  Hz, 4 H, NCH), 3.52 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 2.72 (s, 4 H, C<sub>2</sub>H<sub>4</sub>), 2.41 (s, 12 H, CCH<sub>3</sub>), 1.68 (d, 12 H, CHCH<sub>3</sub>,  $^3J_{\text{H,H}} = 7.1$  Hz), 1.56 (d, 12 H, CHCH<sub>3</sub>,  $^3J_{\text{H,H}} = 7.1$  Hz), ppm.  $^{13}\text{C}$  NMR (100 MHz, acetone-*d*<sub>6</sub>,  $25\text{ }^\circ\text{C}$ ):  $\delta = 156.9$  (NCN), 121.1 (NCCH<sub>3</sub>), 58.3 (C<sub>5</sub>H<sub>5</sub>), 57.8 (C<sub>2</sub>H<sub>4</sub>), 49.6 (NCH), 22.1 (CHCH<sub>3</sub>), 21.7 (CHCH<sub>3</sub>), 10.2 (CCH<sub>3</sub>) ppm.

### General procedure for transfer hydrogenation

Potassium hydroxide (11.2 mg, 0.2 mmol) was added to the catalyst solution (0.02 mmol, 1 mol%) in 2-propanol (10 mL) at room temperature. The solution was heated to  $81\text{ }^\circ\text{C}$ , and the ketone (2 mmol, 0.2 M) was added. Approximately 0.1 mL samples were regularly taken and filtered through the short silica gel column by using diethyl ether as a solvent. The reaction progress was monitored by gas chromatography (GC).



Table 4 Crystallographic data<sup>a</sup>

	4a·THF (polym. A)	4a·THF (polym. B)	4b	5b
Empirical formula	C <sub>27</sub> H <sub>47</sub> BF <sub>4</sub> N <sub>6</sub> ORu	C <sub>27</sub> H <sub>47</sub> BF <sub>4</sub> N <sub>6</sub> ORu	C <sub>31</sub> H <sub>55</sub> BF <sub>4</sub> N <sub>6</sub> Ru	C <sub>29</sub> H <sub>49</sub> BF <sub>4</sub> N <sub>6</sub> Ru
Formula weight	659.59	659.59	699.69	669.62
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2/ <i>c</i>
<i>a</i> [Å]	8.0534(2)	7.4989(5)	15.7948(2)	18.4902(4)
<i>b</i> [Å]	13.6581(4)	11.8261(4)	14.0426(4)	11.6717(2)
<i>c</i> [Å]	14.1481(4)	17.6250(8)	31.4970(9)	15.5756(2)
$\alpha$ [°]	100.097(2)	100.627(3)	90	90
$\beta$ [°]	97.841(2)	95.959(4)	99.176(2)	110.188(2)
$\gamma$ [°]	96.840(2)	97.082(4)	90	90
<i>V</i> [Å <sup>3</sup> ]	1501.38(7)	1511.62(13)	6896.6(3)	3154.89(10)
<i>Z</i>	2	2	8	4
<i>T</i> [K]	100(2)	100(2)	100(2)	100(2)
$\lambda$ [Å]	0.71073	0.71073	0.71073	0.71073
$\rho_{\text{calc}}$ [g cm <sup>-3</sup> ]	1.459	1.449	1.348	1.410
$\mu$ [mm <sup>-1</sup> ]	0.58	0.58	0.51	0.55
Reflections collected	42 715	60 750	128 239	94 761
Independent reflections	7446 [ <i>R</i> <sub>int</sub> = 0.052]	9616 [ <i>R</i> <sub>int</sub> = 0.041]	17 068 [ <i>R</i> <sub>int</sub> = 0.036]	6935 [ <i>R</i> <sub>int</sub> = 0.053]
Goodness of fit on <i>F</i> <sup>2</sup>	0.89	0.94	1.11	0.89
<i>R</i> ( <i>F</i> <sub>o</sub> ) [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0313	0.0258	0.0418	0.0260
w <i>R</i> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) (all refl.)	0.0621	0.0554	0.0971	0.0546
$\Delta\rho$ [e Å <sup>-3</sup> ]	0.63/−0.57	0.74/−0.63	1.10/−0.99	0.46/−0.52

<sup>a</sup> CCDC 1054781–1054784 contain the supplementary crystallographic data for this paper.

### Single-crystal X-ray structure determinations

Numerical data are summarized in Table 4. Crystals were mounted in inert oil on glass fibres. Intensity data were recorded at low temperature on an Oxford Diffraction Xcalibur E diffractometer using monochromated Mo K $\alpha$  radiation. Absorption corrections were performed on the basis of multi-scans. Structures were refined anisotropically on *F*<sup>2</sup> using the program SHELXL-97.<sup>37</sup> Methyls were refined as idealized rigid groups allowed to rotate but not tip; other hydrogens were included using a riding model starting from calculated positions. *Exceptions and special features:* For both polymorphs of **4a**, the hydrogens at C17, C19 and C21 were refined freely (but with DFIX distance restraints). The THF of **4a** (polymorph A) and the methylene bridge (C41–C42) of **4b** are disordered over two positions. The refinements were stabilized using similarity restraints, but the dimensions of disordered groups should be interpreted with caution. For **5b**, the tetrafluoroborate anions lie with their B atoms on crystallographic twofold axes.

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