

### Reactivity of the Chiral Metallic Brønsted Acid $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4i\text{Pr})\text{Ru}(k^3\text{P},\text{O},\text{O}'\text{-POH})][\text{SbF}_6]_2$ (POH = $(S_{C1},R_{C2})\text{-Ph}_2\text{PC(Ph)HC(OH)HCH}_2\text{OMe}$ ) toward Aldimines

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## General

All preparations have been carried out under argon. All solvents were treated in a PS-400-6 Innovative Technologies Solvent Purification System (SPS) and degassed prior to use. Infrared spectra were recorded on Perkin-Elmer Spectrum-100 (ATR mode) FT-IR spectrometer. Carbon, hydrogen and nitrogen analyses were performed using a Perkin-Elmer 240 B microanalyzer.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker AV-300 (300.13 MHz), a Bruker AV-400 (400.16 MHz) or a Bruker AV-500 (500.13 MHz) spectrometers. In both  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR measurements the chemical shifts are expressed in ppm downfield from  $\text{SiMe}_4$ . The  $^{31}\text{P}$  NMR chemical shifts are relative to 85 %  $\text{H}_3\text{PO}_4$ .  $J$  values are given in Hz. COSY, NOESY, HSQC, HMQC, and HMBC  $^1\text{H}$ -X (X =  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ,  $^{15}\text{N}$ ) correlation spectra were obtained using standard procedures. Analytical high performance liquid chromatography (HPLC) was performed on an Alliance Waters 2695 (Waters 2996 PDA detector) instrument using a chiral column Daicel Chiralpak OD-H ( $0.46 \times 25$  cm) and Chiralpak IC ( $0.46 \times 25$  cm) and IC guard ( $0.46$  cm  $\times$   $5$  cm). Mass spectra were obtained with a Micro ToF-Q Bruker Daltonics spectrometer. CD spectra were determined in dichloromethane (ca.  $4 \times 10^{-4}$  mol  $\text{L}^{-1}$  solutions) in a 1 cm path length cell by using a JASCO J-810 spectropolarimeter.

## Crystal structure determination for complexes 3 and 4

X-ray diffraction data were collected at 100(2)K on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å) by using narrow rotation ( $0.3^\circ$ ). Intensities were integrated and corrected for absorption effects with SAINT<sup>+</sup><sup>1</sup> and SADABS<sup>2</sup> programs, included in APEX2 package. The

structures were solved by direct methods with SHELXS-97<sup>3</sup> and refined by full-matrix least squares on  $F^2$  with SHELXL-97.<sup>4</sup> Particular details concerning disorder and hydrogen atoms refinement are listed below.

*Crystal data for complex 3:* C<sub>38</sub>H<sub>41</sub>F<sub>6</sub>NO<sub>2</sub>PRuSb·CH<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O,  $M = 1014.45$ ; orange prism; 0.217x0.180x0.158 mm<sup>3</sup>; monoclinic;  $P2_1/c$ ;  $a = 10.2729(5)$ ,  $b = 16.6169(8)$ ,  $c = 25.1147(12)$  Å,  $\beta = 99.749(5)^\circ$ ;  $Z = 4$ ;  $V = 4225.3(4)$  Å<sup>3</sup>;  $\rho_{\text{calc}} = 1.595$  g cm<sup>-3</sup>;  $\mu = 1.224$  mm<sup>-1</sup>, min. and max. transmission factors: 0.778 and 0.846;  $2\theta_{\text{max}} = 55.78^\circ$ ; 72100 reflections collected, 9971 unique [ $R_{\text{int}} = 0.0261$ ]; number of data/restraints/parameters: 9971/2/475; final GoF: 1.036,  $R_1 = 0.0417$  [9301 reflections,  $I > 2\sigma(I)$ ],  $wR2 = 0.1033$  for all data; largest difference peak: 1.860 e Å<sup>-3</sup>. Two phenyl groups of the Ru complex have been found to be disordered. Carbon atoms have been included in the model in two sets of positions with complementary occupancy factors, and isotropically refined. Dichloromethane molecule has also been found to be disordered in two parts. Carbon atom of the majority part and one chlorine atom of the minor component share their positions. Most of the hydrogen atoms have been included in the model in calculated positions and refined with a riding model. Those of water molecule have been observed in Fourier difference maps and refined with geometrical restraints. Their isotropic atomic displacement parameters have been related to that of the oxygen atom.

*Crystal data for complex 4:* C<sub>32</sub>H<sub>36</sub>F<sub>12</sub>O<sub>2</sub>PRuSb<sub>2</sub>·C<sub>6</sub>H<sub>8</sub>N,  $M = 1150.28$ ; yellow needle; 0.300x0.059x0.035 mm<sup>3</sup>; monoclinic;  $C2$ ;  $a = 29.518(3)$ ,  $b = 10.8722(11)$ ,  $c = 12.9904(14)$  Å,  $\beta = 94.993(2)^\circ$ ;  $Z = 4$ ;  $V = 4153.1(7)$  Å<sup>3</sup>;  $\rho_{\text{calc}} = 1.840$  g cm<sup>-3</sup>;  $\mu = 1.778$  mm<sup>-1</sup>, min. and max. transmission factors: 0.682 and 0.841;  $2\theta_{\text{max}} = 57.12^\circ$ ; 19172 reflections collected, 9403 unique [ $R_{\text{int}} = 0.0482$ ]; number of data/restraints/parameters: 9403/2/518; final GoF: 1.034,  $R_1 = 0.0556$  [7270 reflections,  $I > 2\sigma(I)$ ],  $wR2 = 0.1140$  for all data; Flack parameter: -0.03(3); largest difference peak: 1.614 e Å<sup>-3</sup>. Hydrogen

atoms have been included in the model in calculated positions and refined with a riding model, except hydrogen atom bounded to N(1) atom. This later has been observed at difference Fourier maps and refined with a restraint in N-H bond length. One of the  $\text{SbF}_6$  counterions has been found to be disordered. Fluorine atoms have been isotropically refined, in two set of positions with complementary occupancy factors.

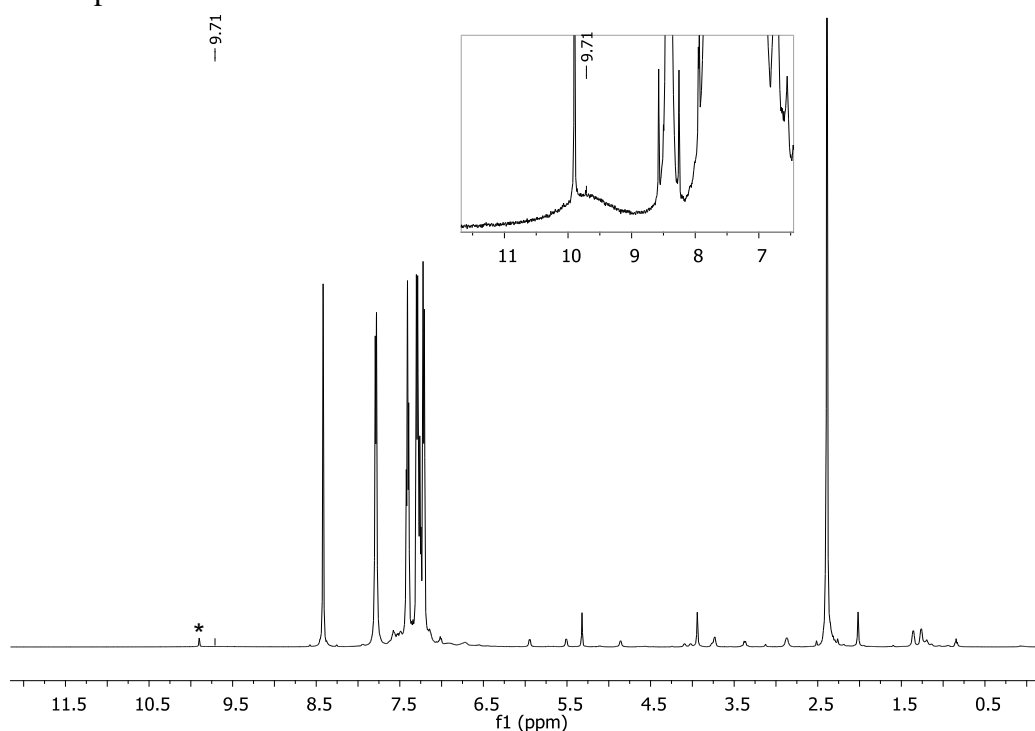
## References

- [1] SAINT+, 6.01, Bruker AXS, Inc., Madison, USA, 2000.
- [2] Sheldrick, G. M. SADABS program University of Göttingen, Göttingen, Germany, **1999**.
- [3] Sheldrick, G. M. *Acta Crystallogr., Sect. A*, **1990**, *46*, 467-473.
- [4] Sheldrick, G. M. *Acta Crystallogr., Sect. A*, **2008**, *64*, 112-122.

## NMR study of the interaction of **1** with 20 equivalents of **I**

At 183K, in an NMR tube, to a solution of **1** (15.0 mg, 0.014 mmol) in 0.6 mL of CD<sub>2</sub>Cl<sub>2</sub>, imine **I** (55.4 mg, 0.284 mmol) and 15.0 mg of MS 4 Å were added. Then, <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were measured at different temperatures (from 193K to 293K).

<sup>1</sup>H NMR spectrum at 193K



\*The asterisk denote the aldehydic proton of 4-methylbenzaldehyde.

## General catalytic procedure for the ADA and AFC reaction with HBF<sub>4</sub>·Et<sub>2</sub>O as a catalyst

**General catalytic procedure for the Aza-Diels-Alder reaction with HBF<sub>4</sub>·Et<sub>2</sub>O as a catalyst.** Under argon, in a Schlenk flask equipped with a magnetic stirrer, the acid HBF<sub>4</sub>·Et<sub>2</sub>O (4.1 μL, 0.03 mmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (3 mL), at RT, and the imine **I** (117.2 mg, 0.60 mmol) was added. After stirring for 10 minutes, freshly distilled cyclopentadiene (0.3 mL, 3.60 mmol) in 1 mL of dry CH<sub>2</sub>Cl<sub>2</sub> was added. The

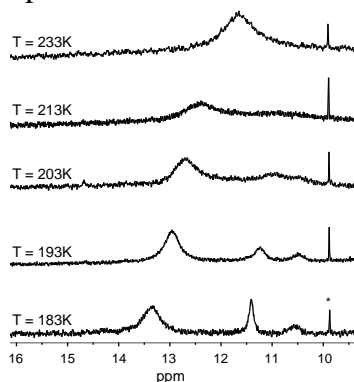
reaction was monitored by TLC chromatography. After 48 hours, the solution was concentrated under vacuum to dryness and the residue was extracted with  $3 \times 10$  mL of diethyl ether. The resulting suspension was filtered over Celite and evaporated to dryness. The crude was purified by column chromatography with silica as a stationary phase and an *n*-hexane/ether (8/2) mixture as eluent. A conversion of > 99 % and an *endo/exo* ratio of 90/10 were determined by  $^1\text{H}$  NMR. E. e.: 0 %, determined by HPLC with a Daicel Chiralpak OD–H column (90/10, *n*-hexane/*i*PrOH; 1.00 mL/min;  $t_R$  17.4 and 21.2 min (*endo*-adducts);  $t_R$  13.6 and 19.2 min (*exo*-adducts)).

**General catalytic procedure for the Aza-Friedel-Crafts reaction with  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  as a catalyst.** Under argon, in a Schlenk flask equipped with a magnetic stirrer, the acid  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (4.1  $\mu\text{L}$ , 0.03 mmol) was dissolved in dry  $\text{CH}_2\text{Cl}_2$  (2 mL), at RT, and the imine **I** (175.7 mg, 0.90 mmol) was added. After stirring for 10 minutes, 1,2-dimethylindole (88.0 mg, 0.60 mmol) was added. The reaction was monitored by TLC chromatography. After 60 hours, the solution was concentrated under vacuum to dryness and the residue was extracted with  $3 \times 10$  mL of diethyl ether. The resulting suspension was filtered over Celite and evaporated to dryness. The crude was purified by column chromatography with silica as a stationary phase and an *n*-hexane/ethyl acetate (from 9/1 to 5/5) mixture as eluent. A conversion of 40 % was determined by  $^1\text{H}$  NMR. The product contained 20 % of FC adduct and 80 % of the corresponding bisindole. The FC adduct was racemic: e. e. = 0 %, determined by HPLC with a Daicel Chiralpak OD–H column (80/20, *n*-hexane/*i*PrOH; 1.00 mL/min;  $t_R$  15.4 and 16.8 min).

## NMR study of the interaction of **1** with an equivalent of **I**

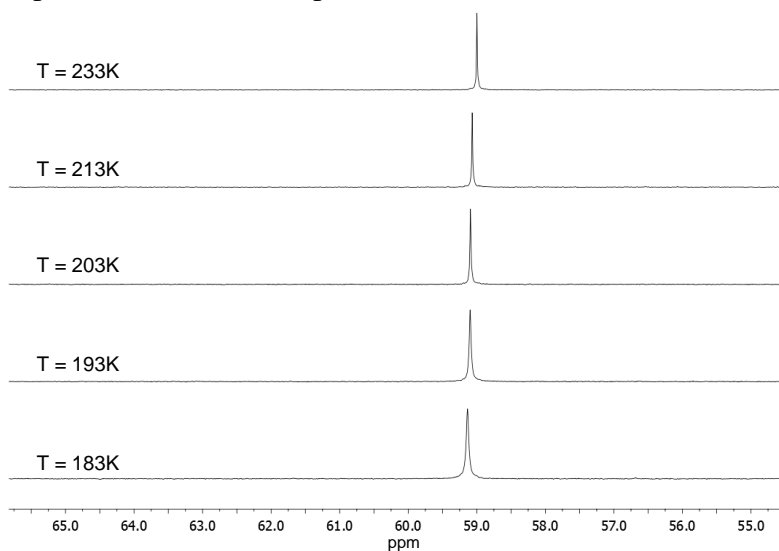
At 183K, in an NMR tube, to a solution of **1** (15.0 mg, 0.014 mmol) in 0.6 mL of  $\text{CD}_2\text{Cl}_2$ , imine **I** (2.8 mg, 0.014 mmol) and 15.0 mg of MS 4 Å were added. Then,  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were measured at different temperatures (from 183K to 233K).

$^1\text{H}$  NMR spectra at different temperatures



\*The asterisk denotes the aldehydic proton of 4-methylbenzaldehyde.

$^{31}\text{P}\{^1\text{H}\}$  NMR spectra at different temperatures

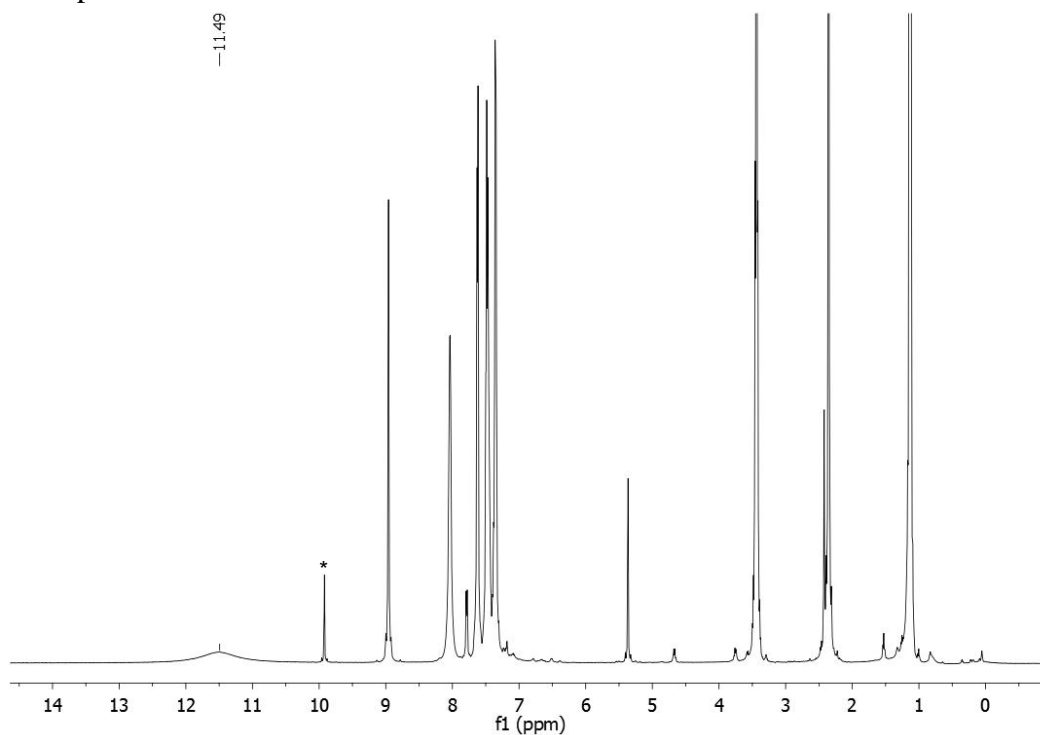


## NMR study of the formation of $\text{HI}^+$ and $\text{I}\cdots\text{HI}^+$

### Formation of $\text{HI}^+$

At RT, in an NMR tube, to 11.1 mg of the imine **I** (0.057 mmol) in 0.6 mL of  $\text{CD}_2\text{Cl}_2$ ,  $\text{HBF}_4\cdot\text{Et}_2\text{O}$  (7.8  $\mu\text{L}$ , 0.057 mmol) was added.  $^1\text{H}$  NMR spectra were measured at different temperatures (from 183K to 253K).

$^1\text{H}$  NMR spectrum at 183K



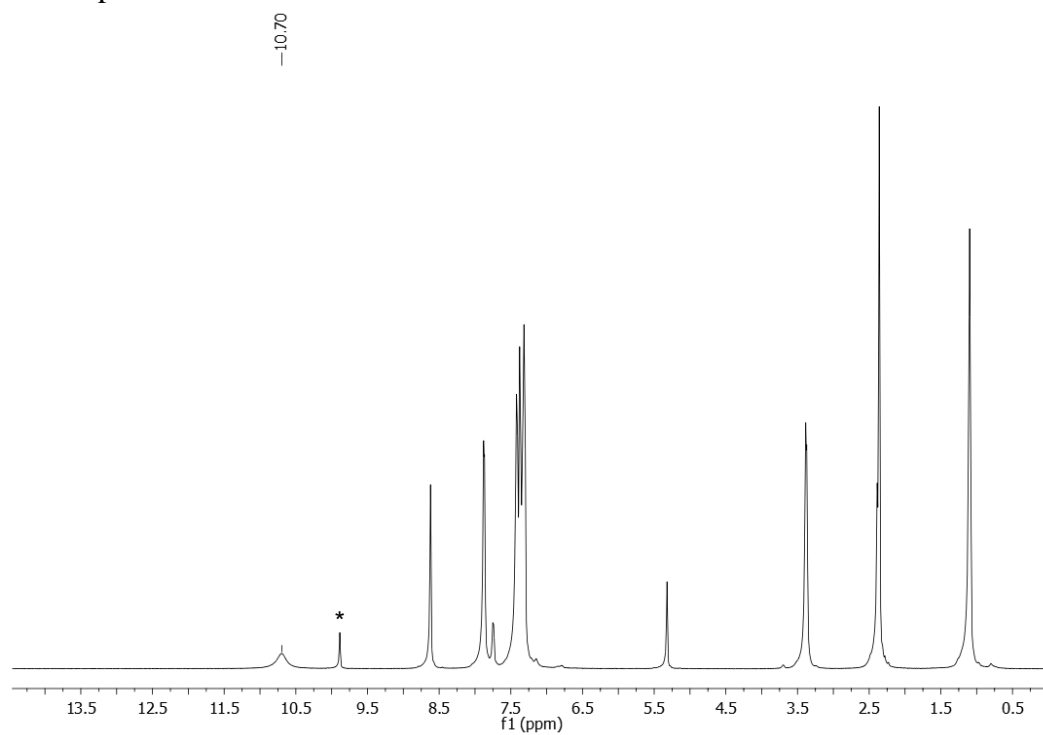
\*The asterisk denotes the aldehydic proton of 4-methylbenzaldehyde.



### Formation of $\text{I} \cdots \text{HI}^+$

At RT, in an NMR tube, to 10.4 mg of the imine **I** (0.053 mmol) in 0.6 mL of  $\text{CD}_2\text{Cl}_2$ ,  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (3.6  $\mu\text{L}$ , 0.026 mmol) was added.  $^1\text{H}$  NMR spectra were measured at different temperatures (from 183K to 273K).

$^1\text{H}$  NMR spectrum at 183K



\*The asterisk denotes the aldehydic proton of 4-methylbenzaldehyde.