**Optimization or Breakthrough? The First Highly *cis*- and Enantioselective
Asymmetric Cyclopropanation of 1-Octene by “Electronic and Counterion”
Tuning of [RuCl(PNNP)]⁺ Catalysts**

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Supporting Information

Variable-Temperature ^{19}F NMR Spectroscopy

The room-temperature ^{19}F NMR spectrum of **3b** BF_4 shows a multiplet at $\delta -63.4$ (12F) for the CF_3 groups and an extremely broad signal at $\delta -153.1$ (4F) for the BF_4 anion ($w_{1/2} = 400$ Hz vs. 60 Hz for **2a**, $^{10}\text{BF}_4$ and $^{11}\text{BF}_4$ signals not resolved),^{1§} which decoalesces upon lowering the temperature. At -40 °C, the main $[\text{BF}_4]^-$ signal sharpens up ($\delta -150.4$, $w_{1/2} = 130$ Hz), and new low-intensity signals are observed at $\delta -146$ and -148 . Although no resolved spectrum is obtained even at the lowest temperature reached (formally -110 °C), some important observations were made. At this temperature, the new signals between $\delta -144$ and -148 are still broad, but their intensity has increased, accounting for as much as 20% of total $[\text{BF}_4]^-$, whose main signal appears at $\delta -150.1$ ($w_{1/2} = 180$ Hz).

Similar observations were made with the reaction of **2a** with AgBF_4 (1 equiv) in CD_2Cl_2 , which gives five-coordinate $[\text{RuCl}(\mathbf{1a})]\text{BF}_4$ (**3a** BF_4) as the main product (77% based on starting **2a**), as indicated by a broadened AX system at $\delta 59.1$ and 49.1 in the room-temperature ^{31}P NMR spectrum. Also the ^{31}P NMR data at -20 °C closely match those of $[\text{RuCl}(\mathbf{1a})]\text{PF}_6$ (**3a** PF_6) and of $[\text{RuCl}(\mathbf{1a})]\text{SbF}_6$ (**3a** SbF_6) (Table 1). However, along with **3a** BF_4 , an additional product is formed that features a broad signal at $\delta 42$ (23%), which resolves at -60 °C into two doublets at $\delta 54.3$ and 35.7 ($J_{\text{P,P}'} = 29.0$ Hz). Again, the spectral changes are fully reversible with temperature. At 20 °C, the $[\text{BF}_4]^-$ anion gives a broad and featureless ^{19}F NMR signal in which the $^{10}\text{BF}_4^-$ and $^{11}\text{BF}_4^-$ signals are not resolved. The line width of the $[\text{BF}_4]^-$ signal increases from 60 Hz at 20 °C ($\delta -151.6$) to 98 Hz at -60 °C ($\delta -150.8$), but no decoalescence occurs upon lowering the temperature.

In sum, the low-temperature ^{19}F NMR data of $[\text{RuCl}(\text{PNNP})]\text{BF}_4$ suggest that the $[\text{BF}_4]^-$ anion undergoes desymmetrization at low temperature, and the ^{31}P NMR spectroscopic

behavior shows that major reversible changes occur in the coordination sphere of $[\text{RuCl}(\text{PNNP})]^+$ at low temperature. Thus, the observed phenomena could well be related to an anion / cation association process at low temperature. The fact that cation **3b** is a stronger Lewis acid than **3a** is consistent with the observation that the ^{31}P NMR signals of **3b** lose in intensity at low temperature, which points to increasing association.

Unfortunately, the ^{19}F NMR spectra of the $[\text{SbF}_6]^-$ and $[\text{PF}_6]^-$ salts were not informative. No ^{19}F NMR signal can be attributed to the $[\text{SbF}_6]^-$ anion of **3bSbF₆**, whereas the ^{19}F NMR spectrum of **3aSbF₆** features a broad ($w_{1/2} = 7.5$ kHz), featureless signal at $\delta -124$. It should be appreciated that the ^{19}F NMR signal of $[\text{SbF}_6]^-$ is rarely observed owing to the short relaxation times of the ^{19}F nuclei caused by coupling to quadrupolar ^{121}Sb and ^{123}Sb .²⁸ Also, of the hexafluorophosphate salts of $[\text{RuCl}(\text{PNNP})]^+$, only $[\text{RuCl}(\mathbf{1a})]\text{PF}_6$ (**3aPF₆**) is available, and the ^{19}F NMR signal of its $[\text{PF}_6]^-$ anion broadens upon lowering the temperature (see below), but shows no sign of decoalescence down to -80 °C.

As these attempts were not conclusive, Pulse Gradient Spin Echo (PGSE) NMR measurements were attempted to assess the diffusion coefficients of anion and cation, which are diagnostic of ion pairing.³⁸ As the ^{19}F NMR signals of $[\text{SbF}_6]^-$ and $[\text{BF}_4]^-$ are too broad at any temperature, it was not possible to obtain useful diffusion data for $[\text{RuCl}(\text{PNNP})]\text{Y}$ ($\text{Y} = \text{SbF}_6$ or BF_4). The hexafluorophosphate salt $[\text{RuCl}(\mathbf{1a})]\text{PF}_6$ turned out to be unsuitable, too. Indeed, the ^{31}P NMR spectrum of five-coordinate $[\text{RuCl}(\mathbf{1a})]^+$ cation is slightly broadened at room temperature and sharpens up at -40 °C, whereas the ^{19}F NMR signal of the $[\text{PF}_6]^-$ anion is a fairly sharp doublet (δ 73.0, $J_{\text{P,F}} = 712$ Hz, $w_{1/2} = 7$ Hz) at room temperature but broadens at low temperature ($w_{1/2} = 40$ Hz at -80 °C). Though interesting, as it suggests that some interaction might occur at low temperature, this circumstance precluded diffusion measurements on the complex cation and on the anion at the same temperature.

References

- (1) For comparison, the signal of free $[\text{BF}_4]^-$ is observed in the ^{19}F NMR spectrum of KBF_4 (376 MHz, CD_2Cl_2 solution, 20 °C, in the presence of 18-crown-6) as a well resolved and sharp 1:1:1:1 quartet at $\delta -152.81(^{11}\text{BF}_4, J_{\text{F,B}} = 1.1 \text{ Hz})$ with the isotopically shifted $^{10}\text{BF}_4$ signal at -152.76 .
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- (3) (a) Pregosin, P. S.; Martinez-Viviente, E.; Kumar, P. G. A. *Dalton. Trans.* **2003**, 4007.
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