



## Relativistic effects in NMR properties of L[RuCpt] complexes: ZORA versus four-component calculations

Glent-Madsen, Iben; Bendix, Jesper; Sauer, Stephan P. A.

*Publication date:*  
2019

*Document version*  
Other version

*Citation for published version (APA):*  
Glent-Madsen, I., Bendix, J., & Sauer, S. P. A. (2019). *Relativistic effects in NMR properties of L[RuCpt] complexes: ZORA versus four-component calculations*. Poster session presented at Grand Challenges for Theoretical Chemistry, Helsingør, Denmark.

# Relativistic effects in NMR properties of $^L[\text{RuCpt}]$ complexes: ZORA versus four-component calculations

Iben Glent-Madsen, Jesper Bendix and Stephan P. A. Sauer  
Department of Chemistry, University of Copenhagen, Denmark

Ruthenium-carbide complexes are of great interest due to the possible bond formation and breakage to the carbide, e.g. as a catalyst in the Fischer-Tropsch synthesis [1,2] or the natural nitrogen fixation at nitrogenase cofactors [3,4]. Hetero-metallic carbide-bridged complexes  $(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}-\text{PtCl}_2\text{L}$ ,  $^L[\text{RuCpt}]$ , with various ligands L have been synthesized and characterized using NMR spectroscopy by Reinholdt and Bendix [5]. The ligands L differ in their electron donating ability and thereby their *trans*-influence propensity in relation to the  $\{\text{Ru}\equiv\text{C}\}$  unit in  $^L[\text{RuCpt}]$ .

The experimental NMR studies are supplemented with theoretical studies using two relativistic methods: a four-component fully relativistic approach using the ReSpect program [6] and the Zeroth-order regular approximation (ZORA) [7] two-component method as implemented in the ADF program [8]. NMR chemical shifts of ruthenium, platinum and the carbide in various  $^L[\text{RuCpt}]$  complexes were calculated at the DFT level using the PBE0 exchange-correlation functional. Basis set dependency, relativistic effects and contributions when calculating NMR properties, and a comparison of calculated results with experimental chemical shifts will be presented with focus on the results from two  $^L[\text{RuCpt}]$  complexes.

[1] H. Schulz, *Applied Catalysis A: General*, 186(1):3–12 (1999).

[2] C. K. Rofer-DePoorter, *Chemical Reviews*, 81(5):447–474 (1981).

[3] J. A. Wiig, Y. Hu, C. C. Lee, M. W. Ribbe, *Science*, 337(6102):1672–1675 (2012).

[4] H. Yilin, M. W. Ribbe, *Angewandte Chemie International Edition*, 55(29):8216–8226 (2016).

[5] A. Reinholdt, J. Bendix, *Inorganic chemistry*, 56(20):12492–12497 (2017).

[6] ReSpect, version 5.0.1 (2018); Relativistic Spectroscopy DFT program of authors Repisky M.; Komorovsky S.; Malkin V. G.; Malkina O. L.; Kaupp M.; Ruud K., with contributions from Bast R.; Ekstrom U.; Knecht S.; Malkin Ondik I.; Malkin E. (see [www.respectprogram.org](http://www.respectprogram.org)).

[7] E. van Lenthe, J. G. Snijders, E. J. Baerends, *The Journal of Chemical Physics*, 105(15):6505–6516 (1996).

[8] G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders and T. Ziegler, *Journal of Computational Chemistry*, 22, 931 (2001). ADF2017, <https://www.scm.com>.