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

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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 $(Cy_3P)_2Cl_2Ru\equiv C\text{-}PtCl_2L$, [L][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 {Ru≡C} unit in [L][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][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][RuCPt] complexes.

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