

# Ligand NMR Shielding in Transition-Metal Complexes: NMR Contributions from Spin-Orbit Coupling

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Relativistic effects significantly affect various spectroscopic properties of compounds containing heavy elements. Particularly in Nuclear Magnetic Resonance (NMR) spectroscopy, the heavy atoms strongly influence the NMR shielding constants of neighboring light atoms. In this account we analyze paramagnetic contributions to NMR shielding constants and their modulation by relativistic spin-orbit effects in a series of transition-metal complexes of Pt(II), Au(I), Au(III), and Hg(II). We show how the paramagnetic NMR shielding and spin-orbit effects relate to the character of metal-ligand (M–L) bond. A correlation between the (back)-donation character of the M–L bond in  $d^{10}$  Au(I) complexes and the propagation of the spin-orbit (SO) effects from M to L through the M–L bond influencing the ligand NMR shielding via Fermi-contact mechanism is found and rationalized by using third-order perturbation theory. The SO effects on the ligand NMR shielding are demonstrated to be driven by both the electronic structure of M and the nature of the *trans* ligand, sharing the  $\sigma$ -bonding metal orbital with the NMR spectator atom L. The deshielding paramagnetic contribution is linked to the  $\sigma$ -type M–L bonding orbitals, which are notably affected by the *trans* ligand. The *SO deshielding* role of  $\sigma$ -type orbitals is enhanced in  $d^{10}$  Hg(II) complexes with Hg  $6p$  atomic orbital involved in the M–L bonding (HOMO). In contrast, in  $d^8$  Pt(II) complexes, occupied  $\pi$ -type orbitals play a dominant role in the SO-altered magnetic couplings due to the accessibility of vacant antibonding  $\sigma$ -type MOs in a formally open 5d-shell ( $d^8$ ). This results in a significant *SO shielding* at the light atom. The energy- and composition-modulation of  $\sigma$ - vs  $\pi$ -type orbitals by spin-orbit coupling is rationalized and supported by visualizing the SO-induced changes in the electron density around the metal and light atoms (spin-orbit electron deformation density, SO-EDD).

## References:

1. Novotný et al., *J. Chem. Theory Comput.*, **2017**, 13 (8), 3586-3601