

# Relativistic and Dynamic effects in Computational $^1\text{H}$ -NMR Spectroscopy of Iridium Polyhydride complexes

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In the field of transition-metal complexes, the accurate calculation of NMR parameters is a challenging task and requires elaborate computational models. Several factors, such as relativity and dynamics, can significantly alter the NMR chemical shift values. For instance, there is evidence demonstrating that conformational dynamics is essential for a proper determination of the NMR chemical shifts in various transition-metal complexes.<sup>1</sup>

Transition-metal hydride complexes often play an important role as transfer hydrogenation catalysts. Recently, various iridium deactivation products formed in the catalytic dehydrogenation of glycerol have been analyzed by experimental and computational approaches.<sup>2</sup> A point of special interest, the hydride positions, could not be established in the X-ray studies, however, because of their proximity to the heavy metal atoms.<sup>3</sup>

In this regard, we have established a computational protocol for the rational calculation of  $^1\text{H}$ -NMR chemical shifts for the iridium polyhydride  $[\text{Ir}_6(\text{IME})_8(\text{CO})_2\text{H}_{14}]^{2+}$  complex (see Figure 1) to validate the assignments previously made. In particular, the hydride resonances were investigated by static and dynamic  $^1\text{H}$ -NMR chemical shift calculations, using a full four-component relativistic method and in conjunction with *ab-initio* molecular dynamics simulations to describe the relativistic effects and conformational dynamics, respectively.

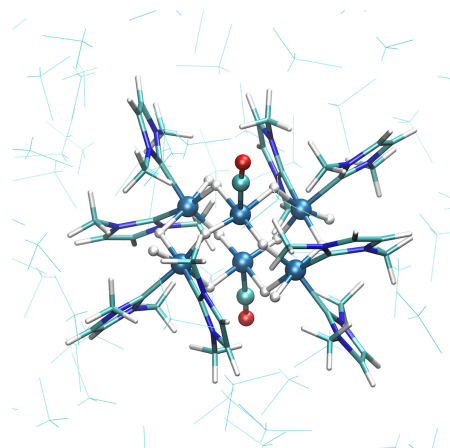


Figure 1:  $[\text{Ir}_6(\text{IME})_8(\text{CO})_2\text{H}_{14}]^{2+}$  complex

## References

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