



Unraveling the Mysteries of the Platinum Group Elements with ^{103}Rh Solid-State NMR Spectroscopy

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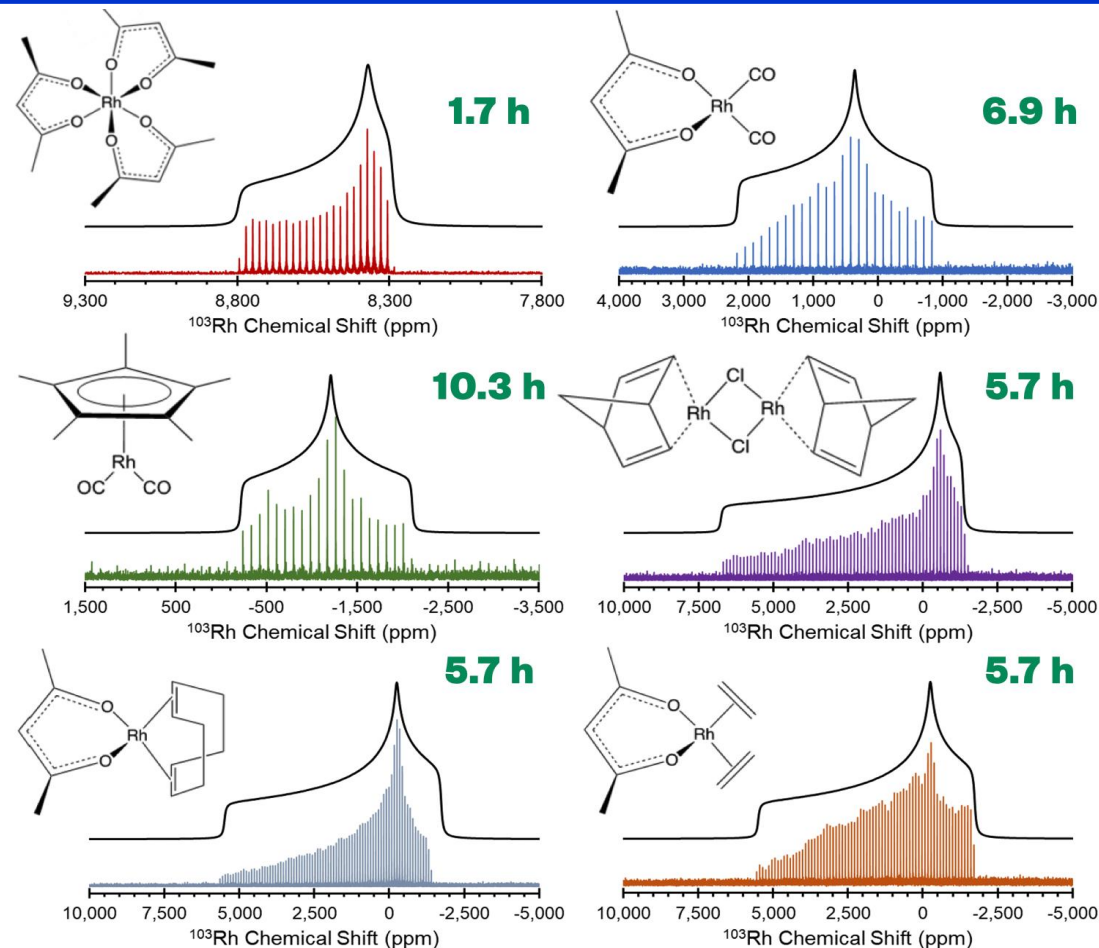


Rhodium, a member of the platinum group elements (PGEs), is one of the most costly and scarce elements; however, it is of great importance in numerous applications such as catalytic converters, fiberoptic cables, electronics, and medical devices. As such, there is ongoing research into finding replacement metals for Rh and other PGEs. It is hypothesized that the unique properties of inorganic and organometallic coordination compounds featuring PGEs arise from unique *dative bonding* (i.e., covalent bonding by donation of electrons from coordinating ligands).

^{103}Rh solid-state NMR (ssNMR) and density functional theory (DFT) calculations provide pathways to understanding the nature of dative bonding; however, both are wrought with challenges. ^{103}Rh , a spin-1/2 nucleus, is among the most unreceptive nuclides in the Periodic Table, largely due to its low gyromagnetic ratio and broad powder patterns. Furthermore, DFT calculations of ^{103}Rh chemical shifts require careful consideration of relativistic effects and exchange-correlation functionals.

In this work, MagLab users present the first ^{103}Rh ssNMR study of a series of inorganic and organometallic compounds. ^{103}Rh ssNMR spectra are obtained using ultra-wide line pulse sequences (i.e., ^1H - ^{103}Rh broadband adiabatic inversion cross-polarization, BRAIN-CP) and high-field NMR platforms at the MagLab, which feature the 36T Series Connected Hybrid and 21.1T ultra-wide bore magnets, operating at $\nu_0(^1\text{H}) = 1.5\text{GHz}$ and 900MHz, respectively ($\nu_0(^{103}\text{Rh}) = 47.5$ and 28.7MHz).

The ^{103}Rh ssNMR spectra provide unique spectral fingerprints for each complex, from which chemical shift tensors can be extracted, and compared to those obtained from DFT calculations. Then, with the aid of natural bond orbital (NBO) and natural localized molecular orbital (NLMO) analyses, users can gain insight into the nature of Rh-ligand bonding. Our new experimental and theoretical methods open the doors for the study of other PGEs and will aid in the rational design of new materials.



^1H - $^{103}\text{Rh}\{^1\text{H}\}$ BRAIN-CP/WURST-CPMG NMR spectra of inorganic and organometallic coordination complexes at 21.1T ($\nu_0(^1\text{H}) = 900\text{MHz}$; $\nu_0(^{103}\text{Rh}) = 28.7\text{MHz}$). Total experimental times (in hours) are listed in green.

Facilities and instrumentation used: Solid-State NMR facility – 21.1T/900MHz/105mm solid-state NMR instrument; 36T/40mm Series Connected Hybrid Magnet (35.2T/1.5GHz)

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