

Probing Secondary Bonding Interactions in Organometallic Complexes by Measurement and Prediction of Metal-Hydrogen NMR Scalar Coupling Constants

Aaron J. Rossini, Department of Chemistry, Iowa State University

Narrative Report

Overview. Organometallic compounds are widely used as catalysts and reagents for the transformation and conversion of petrochemicals to commodity chemicals and valuable fine chemicals. Many organometallic complexes achieve stability by forming secondary bonds between the metal center and hydrogen atoms attached to the coordinating ligands (see examples in **Fig. 1**). These interactions are widely implicated in the mechanisms of metal catalyzed polymerization and C-H bond activation. Depending upon the length of the M-H bonds, the identity of the ligand and the electron count of the metal these secondary intramolecular bonding interactions are typically classified as agostic bonds, anagostic bonds and hydrogen bonds. The presence of secondary intramolecular M-H bonding interactions is normally confirmed by using single-crystal X-ray/neutron diffraction, infrared (IR) spectroscopy and ^1H and ^{13}C NMR spectroscopy. However, these techniques *indirectly* probe the bond between the metal and its ligands; they do not directly confirm the presence of a covalent bond between the hydrogen and metal atoms. We are directly probing secondary metal-hydrogen bonds by measuring one-bond NMR scalar coupling constants between ^1H and metal nuclei $^1J_{\text{HM}}$ with modern solution NMR and solid-state NMR (SSNMR) methods. We have also undertaken new research not originally described in the original proposal. We are using SSNMR spectroscopy to characterize heterogeneous catalysts as described below.

Research Progress. We have *directly* detected hydrogen-metal secondary bonding interactions by measuring $^1J_{\text{HM}}$ and performing J -based 2D correlation NMR experiments. **Figure 1** shows structures and solution $^1\text{H}\{^{89}\text{Y}\}$ NMR spectra of a series of yttrium organometallic compounds from Prof. Aaron Sadow (Iowa State University). All compounds have silyl groups (SiH) that can engage in secondary bonding interactions with yttrium. Consistent with the presence of Y-HSi secondary bonding interactions, $^1\text{H}\{^{89}\text{Y}\}$ HSQC show correlations between hydride ^1H and ^{89}Y . The HSQC spectra were recorded without the central π -pulse on ^1H to show ^{89}Y - ^1H multiplet patterns in the indirect ^{89}Y dimension. The multiplets immediately show how many ^1H spins are J -coupled and secondary bonded to yttrium. For example, a septet is observed in **Figure 1C** because there are 6 equivalent J -coupled ^1H spins. Distortions of the multiplets in **Figure 1** occur due to variations in HSQC transfer efficiencies.

It is well known that the variation of J -couplings mainly occurs due to Fermi contact terms which are proportional to overlap of the orbitals that form the covalent bonds connecting the two atoms. Therefore, the magnitude of $^1J_{\text{HM}}$ should report on the strength of the H-M secondary bonds. For example, **3** shows $^1J_{\text{HY}} = 6$ Hz, while the THF adduct **4** shows $^1J_{\text{HY}} = 3.3$ Hz. The reduction in $^1J_{\text{HY}}$ from **3** to **4** reflects the fact that THF donates additional electrons to the metal, reducing the strength of the Y-HSi secondary bonds. While a $^1J_{\text{HY}}$ of 6 Hz may seem like a small coupling constant, the gyromagnetic ratio of ^{89}Y is about 5 times less than that of ^{13}C , which reduces 1J proportionally; a $^1J(\text{H}-^{89}\text{Y})$ of 6 Hz is therefore comparable to a $^1J_{\text{HC}}$ of 30 Hz which would correspond to ca. 20% of a covalent C-H bond. Therefore, the observed $^1J_{\text{HY}}$ are significant. We currently completing a manuscript that describes measurement and DFT-prediction of $^1J_{\text{HM}}$ in a series of organometallic yttrium compounds.¹ This manuscript will describe correlations between experimental and calculated $^1J_{\text{HM}}$ directly to the strength of bonding interactions and the types of orbitals involved in the bonds. We are now

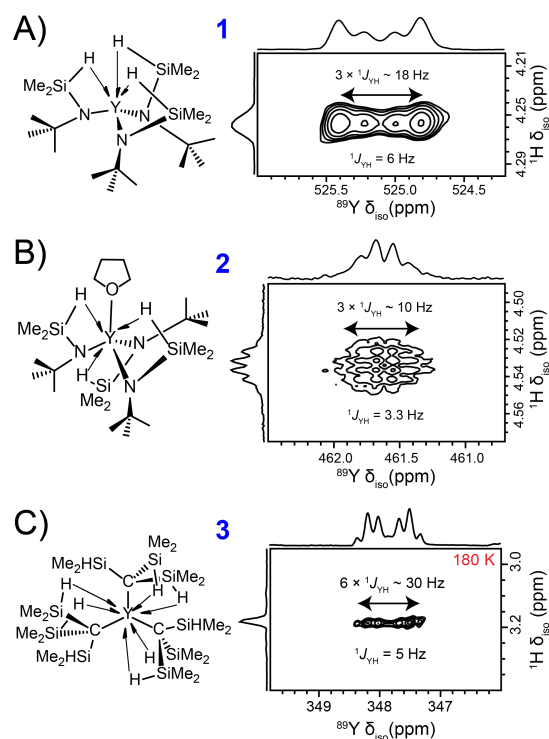


Figure 1. Solution $^1\text{H}\{^{89}\text{Y}\}$ HSQC NMR spectra of yttrium organometallic compounds **1-3** showing Y-HSi secondary bonds.

undertaking new experiments on other transition metals that display agostic/secondary bonding and have spin-1/2 isotopes amenable to NMR such as ^{103}Rh , ^{171}Yb , ^{183}W , ^{195}Pt . Target compounds include tungsten alkylidene metathesis catalysts (^{183}W NMR) and rhodium phosphine hydrogenation catalysts (^{103}Rh NMR).

We are also complementing our solution NMR experiments on organometallic compounds with SSNMR experiments. There are four scenarios where SSNMR is needed: (i) many organometallic compounds are fluxional (dynamic) at elevated temperatures in both solution and the solid-state. In the solid-state it is possible to reduce temperature and eliminate fluxionality. (ii) Quadrupolar nuclei are generally not amenable to solution NMR because they possess short transverse and longitudinal relaxation times; In the solid-state the transverse relaxation times are longer, enabling coherent manipulation of quadrupolar spins. (iii) The crystal structures of organometallic compounds may be disordered. (iv) Heterogeneous catalysts are often formed by immobilizing organometallic compounds on solid supports.

For example, the research group of Prof. Matthew Conley (University of California Riverside) is developing solid acid catalysts by reacting the surface hydroxyl groups of silica with tris(fluoroisopropoxide)aluminum [$\text{Al}(\text{O}i\text{PrF})_3$]. This reaction yields a surface-supported aluminum compound linked to the silica by a bridging hydroxyl group (compound **4**, **Fig. 2A**). Our group has performed $^1\text{H}\{^{27}\text{Al}\}$ RESPDOR experiments to measure a ^1H - ^{27}Al distance of 2.5 Å for the bridging hydroxyl group (**Fig. 2B**), in excellent agreement with the Al-H distance predicted by the DFT-optimized structural model.² We are currently working on characterizing other surface compounds made by reacting **4** with amines, palladium organometallics and allyltriisopropylsilane.

Additionally, we have initiated a collaboration with the research group of Prof. Ivo Hermans (University of Wisconsin – Madison) to characterize heterogeneous catalysts for the oxidative dehydrogenation of propane.³ We have used 1D and 2D ^{11}B and ^1H - ^{11}B SSNMR experiments to study catalyst made by grafting boron isopropoxide onto silica. Our SSNMR experiments show that both oxide and hydroxide coordinated boron sites result and that grafting results in the formation of chains of boron oxide species on the surface.

Impact of ACS PRF Award on Senior Personnel and Students. This DNI award has allowed us to obtain preliminary data used for three manuscripts; one is currently in preparation¹ and the other two have been submitted for publication.^{2,3} Preliminary data and publications supported by this DNI have been used to apply for further funding from the National Science Foundation to further develop solution and SSNMR methods to characterize organometallic catalysts. The PI was also able to obtain a jointly funded grant from the NSF with Prof. Hermans to continue working on the characterization of boron-based catalysts for the oxidative dehydrogenation of propane. The DNI award has also provided salary support for a graduate student researcher. The student researcher has learned how to apply a variety of different NMR techniques for the molecular level characterization of homogeneous and heterogeneous catalysts. The student has also authored several scientific publications.

References: (1) Venkatesh A., Boteju K., Sadow A.D., Rossini A.J., Directly Probing Secondary Bonding Interactions in Organometallic Complexes By Measurement of Proton-Metal One-Bond NMR Scalar Coupling Constants, *Manuscript in Preparation*. (2) Culver D.B., Venkatesh A., Huynh W., Rossini A.J., Conley M.P., Generation of the Strongest Heterogeneous Brønsted Acid for the Support of a Heterogeneous Silylium on Silica, *Submitted for Publication*. (3) Love A.M., Cendejas M.C., Thomas B., McDermott W.P., Uchupalanun P., Kruszynski C., Burt S.P., Agbi T., Rossini A.J., Hermans I. Synthesis and Characterization of Silica Supported Boron Oxide Catalysts for the Oxidative Dehydrogenation of Propane, *Submitted for Publication*.

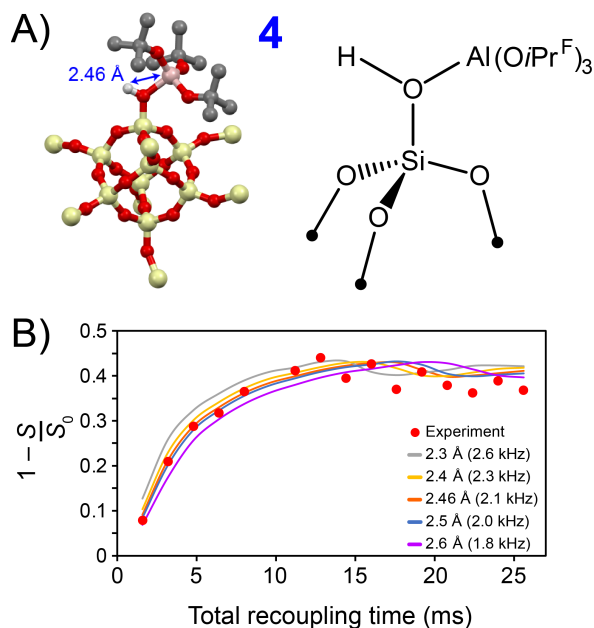


Figure 2. (A) DFT model and molecular structure of **4**. (B) $^1\text{H}\{^{27}\text{Al}\}$ RESPDOR dipolar dephasing curves. Experimental points are shown as red circles and simulated curves for different dipolar couplings (distances) are shown as solid lines.