

## <sup>35</sup>Cl solid-state NMR of transition-metal organometallic complexes

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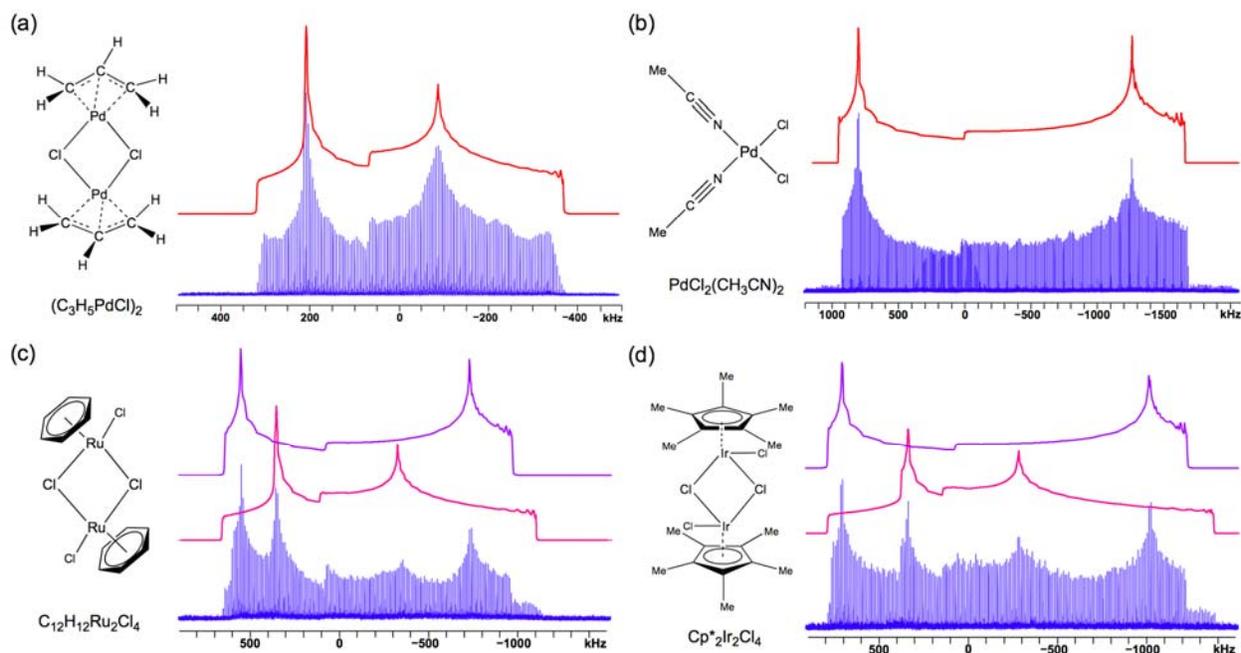
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Transition-metal organometallic complexes are routinely used as homogeneous and heterogeneous catalysts in a wide range of organic reactions and polymerization processes. Within many such complexes the metal centre is often the active catalytic site. It can therefore be highly informative to try and probe this site directly to gain information regarding the catalytic activity of the complex. However, it can be experimentally challenging to probe certain metal centres using techniques such as solid-state NMR, e.g., Hf, Ta, Ru, Os, Ir etc. In such cases, it can be more informative to investigate the ligands surrounding the metal, as is often done using <sup>1</sup>H and <sup>13</sup>C solution-state NMR. Chlorine is a commonly occurring ligand in many transition-metal complexes and could potentially act as a useful and informative NMR probe.

Despite the relatively favourable nuclear properties of <sup>35</sup>Cl ( $I = 3/2$ ) there are currently very few publications in the literature and, until recently, the application of <sup>35</sup>Cl solid-state NMR was predominantly restricted to systems with Cl in spherically symmetric ground state electronic environments. However, recent work by Rossini *et al.* [1], and Chapman *et al.* [2], demonstrated it is possible to probe chlorine environments exhibiting considerably lower spherical symmetry.

Using the WURST-QCPMG pulse sequence<sup>3</sup> at 21.1 T we have successfully acquired ultra-wideline <sup>35</sup>Cl powder patterns for a series of Cl-containing transition-metal organometallic complexes exhibiting a range of quadrupolar coupling constants ( $C_Q = 15 - 40$  MHz) in relatively short timeframes. Of the twelve complexes investigated, five contain purely bridging Cl sites, four contain solely terminal Cl positions and the remaining three possess both bridging and terminal Cl environments. Our findings suggest that using <sup>35</sup>Cl solid-state NMR it is possible to accurately distinguish between bridging and terminal Cl environments with relative ease. Chlorines in a bridging environment typically possess smaller quadrupolar coupling constants ( $C_Q = 15 - 30$  MHz) and relatively high asymmetry



**Figure 1:**  $^{35}\text{Cl}$  solid-state NMR spectra and analytical simulations of spectra for (a)  $(\text{C}_3\text{H}_5\text{PdCl})_2$  with  $C_Q = 17.85$  MHz,  $\eta_Q = 0.48$ , (b)  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$  with  $C_Q = 39.80$  MHz,  $\eta_Q = 0.14$ , (c)  $\text{C}_{12}\text{H}_{12}\text{Ru}_2\text{Cl}_4$  with  $C_Q = 28.4$  and  $31.0$  MHz,  $\eta_Q = 0.50$  and  $0.10$ , (d)  $\text{Cp}^*_2\text{Ir}_2\text{Cl}_4$  with  $C_Q = 30.3$  and  $35.1$  MHz,  $\eta_Q = 0.62$  and  $0.07$ .

parameters e.g.,  $\eta_Q = 0.2 - 0.5$ , Figure 1(a). Terminal chlorine environments typically possess much larger quadrupolar coupling constants ( $C_Q = 30 - 40$  MHz) and lower asymmetry parameters, e.g.,  $\eta_Q = 0.06 - 0.2$ , Figure 1(b). These findings were particularly evident when complexes containing both bridging and terminal Cl environments were investigated, as shown in Figures 1(c) and 1(d).

Ultra-wideline  $^{35}\text{Cl}$  NMR experiments therefore show great potential as structural probes for a wide range of transition-metal organometallic complexes. We hope to extend our current NMR knowledge to larger, more complex Cl-containing systems.

### References

- [1] A.J. Rossini, R.W. Mills, G.A. Briscoe, E.L. Norton, S.J. Geier, I. Hung, S. Zheng, J. Autschbach and R.W. Schurko, *J. Am. Chem. Soc.* **131** (2009) 3317.
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- [3] L.A. O'Dell and R.W. Schurko, *Chem. Phys. Lett.* **464** (2008) 97.