

## $\eta^1$ arene coordination in a Rh complex

### Motivation

The formation of dative hydrocarbon-metal bonds is one step in many catalytic reactions. Arene ligands can offer up to  $6\pi$  electrons for bonding, and hapticities from  $\eta^1$ - $\eta^6$  are known. More common are the  $\eta^2$  agostic C-H complexes where arenes interact via the  $\sigma$ -bonding framework. One of the least common forms of M-arene bonding is  $\eta^1$  arene coordination, this can occur as a  $\pi$  or

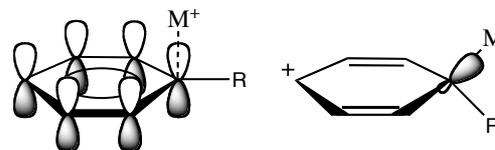


Figure 1  $\eta^1$  arene  $\pi$ -type and  $\sigma$ -type coordination modes

$\sigma$ -type interaction, Figure 1. The authors of this paper propose they have identified the first example of  $\eta^1$  arene coordination to a rhodium center, and that that the interaction in this compound is unusual because it is an *intramolecular*  $\pi$ -type interaction.

### Reference:

J. Krumper, M. Gerisch, A. Magistrato, U. Rothlisberger, R. Bergman and T. Tilley, *J. Amer. Chem. Soc.*, 2004, Vol 126, p12492

### Computational Details

- ◆ Codes are specified ADF and CPMD
- Gas phase calculations (ADF)
- ◆ Basis sets on valence orbitals only
  - Rh ->TZ-STO
  - Cl, C, N, O, H -> DZ-STO
- ◆ Uses frozen core
  - Relativistic effects taken into account
- ◆ DFT => which functional?
  - Becke3 exchange
  - LYP correlation
  - =>B3LYP
- ◆ Second basis set for single point NMR calculations
  - Rh -> full TZ-STO
  - Cl, C, N, O, H -> full DZ-STO
  - NMR includes relativistic corrections

### Molecular Dynamics calculations (CPMD)

Molecular dynamics and solid state calculations use PPs basis sets and DFT functionals like gas phase methods. But the basis sets and therefore PP can be significantly different from those used in gas phase calculations.

- ◆ Martins-Troullier is plane wave based type of PPs. The terms Kleinman and Bylander, and Gauss-Hermite are all information to do with the PP.
- ◆ Use same DFT functionals
- ◆ CPMD uses plane-wave basis sets, cut-off 70Ry tells us how accurate the calculation is. The large the cut-off the more accurate the calculation.
- ◆ Molecular Dynamics need to specify a time step, here it is 0.1fs (1fs =10\*(-15)s!)

**Computational Details.** The static DFT calculations were performed with the program ADF2000.01,<sup>72-74</sup> whereas DFT-based molecular dynamics simulations were performed with the code CPMD.<sup>75</sup> The structure of complex **3a** was optimized for three different spin states using the Amsterdam Density Functional (ADF) program.<sup>72-74</sup> The electronic configurations of the molecular systems were described by a triple-STO basis set on the transition metal center for the ns, np, nd, (n+1)s, and (n+1)p valence shells, whereas a double-STO basis set was used for Cl (2s, 2p), C (2s, 2p), N (2s, 2p), O(2s, 2p), and H(1s). The inner shells of the atoms were treated with the frozen core approximation. Energy differences were calculated including Becke's exchange<sup>88</sup> and Perdew's correlations gradient corrections.<sup>89</sup> First-order scalar relativistic corrections<sup>90,91</sup> were added to the total energy for the rhodium atom.

Calculations of the NMR chemical shifts of the most relevant atoms were also performed with ADF2000.01<sup>92-94</sup> performing single-point calculations on the gas-phase optimized geometry and on some frames of the molecular-dynamics simulations generated with CPMD.<sup>75</sup> Chemical shifts were calculated with a triple STO basis set on Rh, while for all the other elements these were calculated with a double STO basis set considering all the core and the valence electrons. In both cases ZORA<sup>95,97</sup> relativistic corrections were added. The singlet structure of **3a** was also optimized, using the program CPMD. In the CPMD calculations, an analytical local pseudopotential was used for hydrogen, and nonlocal, normconserving pseudopotentials of the Martins-Troullier type<sup>98</sup> were employed for all the other elements.

Angular momentum components up to  $l_{\max}$  S have been included for carbon, nitrogen and oxygen and  $l_{\max}$  P for chlorine atoms. For rhodium, a semicore pseudopotential ( $l_{\max}$  D) for which the  $4s^2 4p^6 4d^7$  and  $5s^2$  valence electrons are treated explicitly was constructed. All pseudopotentials, with the exception of that of rhodium, were transformed to a fully nonlocal form using the scheme developed by Kleinman and Bylander.<sup>99</sup> For rhodium, the nonlocal part of the pseudopotential was integrated numerically using a Gauss-Hermite quadrature. The same exchange-correlation functional was used as in the ADF calculations.

## NMR Characterisation

The compound of interest is shown in Figure 2,  $R_1=H$  or Me and  $R_2=Et$ ,  $iPr$  or Me. The experimental NMR spectra of these compounds showed several interesting features related to  $H_a$  and  $H_b$ . The  $H_b$  spectrum exhibits a doublet of doublets, coupling to the rhodium nucleus and (unexpectedly) coupling to  $H_a$ .  $H_a$ - $H_b$  coupling was confirmed by homonuclear decoupling and  $^1H$ - $^1H$  TOCSY experiments. Coupling of this kind could be due to a C-H-Rh-H agostic interaction. The  $H_a$  peaks however are not coupled to the rhodium nucleus and appear shifted downfield. Most of this paper is about determining the arene-Rh interaction and thus determining the origin of the  $H_a$ - $H_b$  coupling

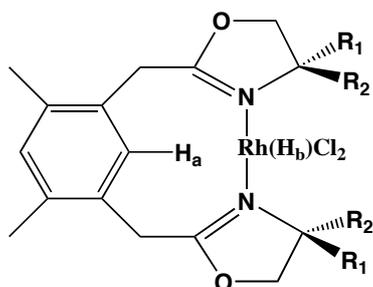
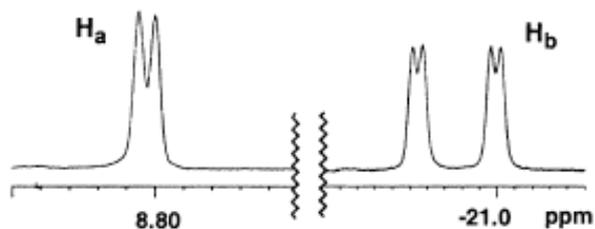


Figure 2 Rhodium(III) hydride complex



H	shift (ppm)	splitting	$J_{H-H}$ (Hz)
$H_b$	-20.76	dd	2.5
$H_a$	8.88	doublet	2.5

Figure 3 NMR spectrum and tabulated data

## Bonding Characterisation

X-ray structures indicate a square-based pyramidal geometry with a trans chloride ligands, Rh-H and C- $H_b$  distances indicate there is no agostic interaction. The paper further details data to support the absence of an agostic interaction, we won't discuss it any further. This leaves four other bonding mechanisms that may give rise to  $H_a$ - $H_b$  coupling, and these are depicted below:

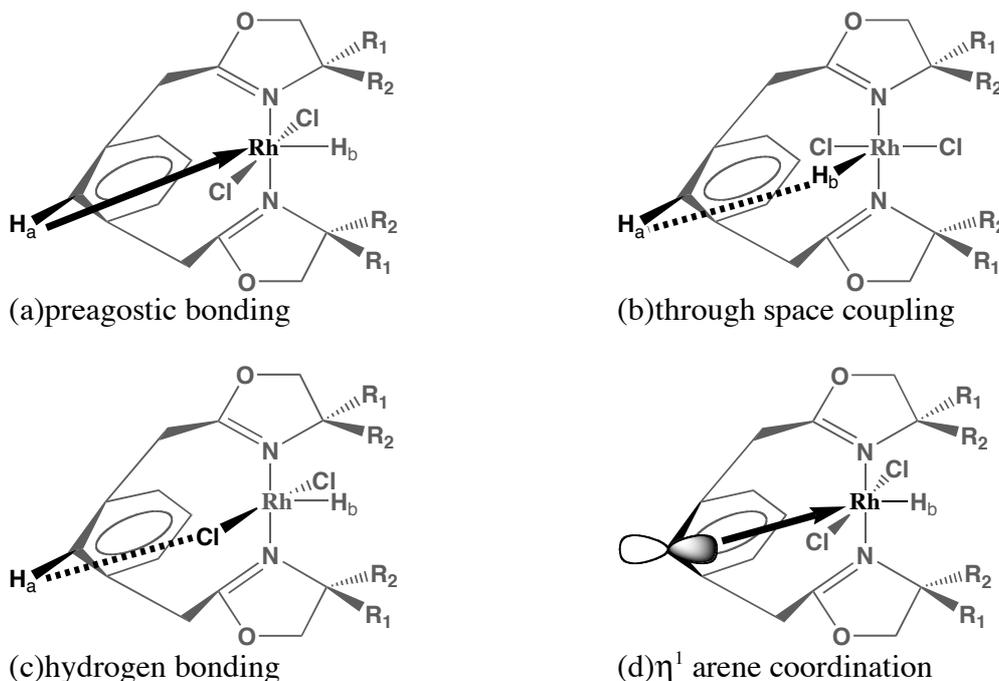
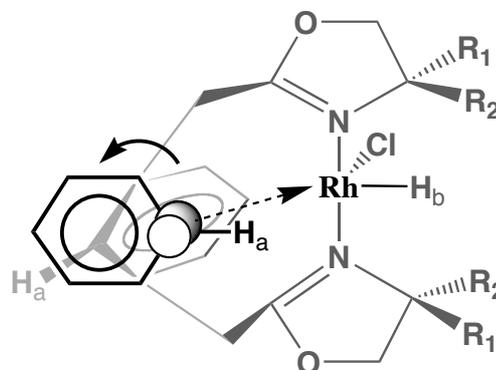


Figure 4 Possible bonding modes

The downfield shift of  $H_a$ , the  $H_a-H_b$  coupling and the X-ray Rh-H and C- $H_a$  are all consistent with the rare, preagostic bonding mode. Ample precedent exists for H bonding with halides ligated to transition metals, but  $H_a$  was found to be unreactive towards acids or bases, undermining the case for a Cl- $H_a$  interaction. While the X-ray structures are not consistent with the pseudo-trans arrangement of  $H_a$  and  $H_b$  required for the through space  $H_a-H_b$  interaction, cis-trans isomerisation is possible in solution. However this was discounted using various spectroscopic means.

Theoretical calculations (on the  $R_1=H$ ,  $R_2=Et$  complex) were now introduced in an effort to distinguish between the preagostic and  $\eta^1$  arene bonding modes. The computed structure and NMR chemical shift of  $H_a$  (8.5 ppm) matched the experimental data well (8.9ppm). The  $H_a-H_b$  coupling calculated for the optimised structure (1.8 Hz) is in reasonable agreement with the experimental value (2.5 Hz). Molecular dynamics simulations found rotation of the ligand aryl ring which lead to large oscillations in the Rh- $H_a$  bond distance ranging from 2.97-2.03Å. However, this interaction is consistent with both bonding modes.



	opt	1	2	3	4
$H_a$ shift (ppm)	8.5	8.4	7.7	11.2	11.1
$J(H_a-H_b)$ (Hz)	1.8	1.7	6.6	10.4	12.0
$r(Rh-H_a)$ (Å)	2.72	2.47	2.32	2.29	2.03

**Figure 5** Rotated arene and related tabulated data

The  $^1H$  NMR chemical shift of  $H_a$  was found to move downfield as the Rh- $H_a$  bond distance shortened. A calculation of the  $H_a-H_b$  and Rh- $H_a$  coupling constants for the rotational motion gave very small constants for Rh- $H_a$  coupling (<1 Hz) and  $H_a-H_b$  coupling highly dependent on the  $H_a-H_b$  distance. Thus, a theoretical investigation into the NMR parameters related to this compound did not shed any additional light on the bonding mode.

However, an investigation of the orbitals for this complex did provide more information, no orbital interactions could be identified that supported a pre-agostic interaction. Orbitals were located that showed a direct overlap of  $C_a-H_a$  pAO with Rh p and dAOs, these MOs showed no contribution from the  $H_a$  AOs, indicating a weak  $\eta^1$  arene bonding mode.