

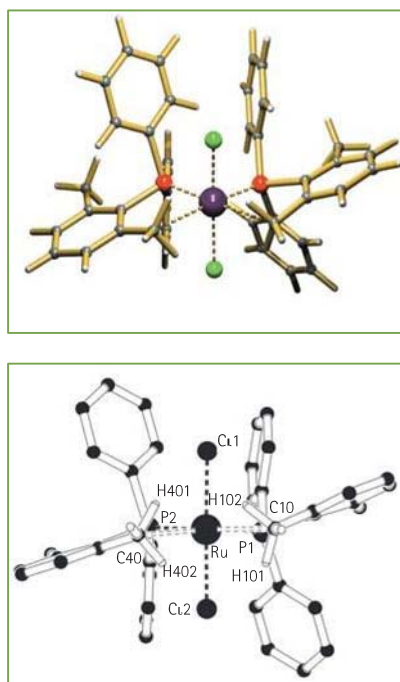
**materials**

# Non classical metal...H<sub>3</sub>C-C agostic interactions in a 14-electron ruthenium(II) system

A neutron diffraction study has established the precise nature of the  $\delta$  agostic interactions in the complex  $\text{RuCl}_2[\text{PPh}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3)]_2$  (1). By contrast to classical agostic bonding, it is shown that two *ortho*-methyl groups of the xylyl substituents interact with the unsaturated metal center through two C-H bonds each. The result is also substantiated by NMR data in solution. Re-examination of all X-ray structures with  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\epsilon$   $\text{M}\cdots\text{H}_3\text{C-C}$  moieties as well as DFT calculations on models of 1 shows that the agostic interactions span the range between the classical ( $\text{M}\cdots\eta^2\text{HC}$ ) and the non-classical ( $\text{M}\cdots\eta^2\text{H}_2\text{C}$ ) types, depending on the number of atoms between the metal and the methyl group.

**The coordination** of inert C-H bonds to a transition metal is of fundamental interest for stoichiometric and catalytic reactions, with particular regard to the problem of alkane functionalisation via C-H bond activation [1]. Unfortunately, information on the nature of the primary adduct is still very scarce, since saturated hydrocarbons are notoriously unreactive and are very poor ligands [1d]. From DFT calculations a somewhat asymmetric  $\text{M}\cdots\eta^3\text{-H}_2\text{C}$  bonding mode has emerged for adducts between an unsaturated metal center and a methane molecule [2]. This result is in apparent disagreement with the extensive experimental and theoretical information available for agostic complexes that is usually interpreted in terms of dihapto  $\text{M}\cdots\eta^2\text{-HC}$  bonding between the unsaturated metal ion and a dangling C-H bond of the same molecular fragment [3].

A neutron diffraction study on the ILL single-crystal diffractometer D19 at 100 K of the 14-electron complex  $\text{RuCl}_2[\text{PPh}_2(2,6-$



**Figure 1:** (a) Birds-eye view of the complex 1 in the solid state. Colour code: violet=Ru, red=P, green=Cl, grey=C, white=H (b) View down the pseudo C<sub>2</sub> axis (hydrogen atoms are omitted except those of agostic CH<sub>3</sub> groups).

W. Baratta, P. Rigo (University of Udine)

C. Mealli, A. Ienco (ICCOM-CNR, Florence)

E. Herdtweck (TU Munich)

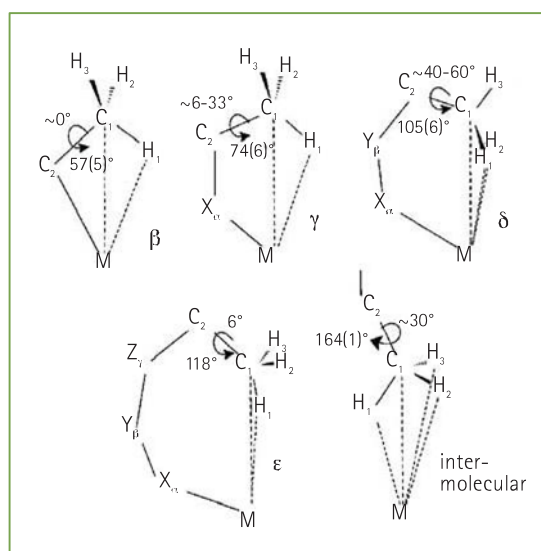
S.A. Mason (ILL)

$\text{Me}_2\text{C}_6\text{H}_3$ )]<sub>2</sub> (1), precisely defines the geometric features of the  $\delta$  agostic interaction between the unsaturated metal center and two *ortho*-methyl groups of the xylyl substituents [4] (see different views in figure 1).

Two CH<sub>3</sub> carbon atoms lie in the RuP<sub>2</sub> equatorial plane with relatively short non bonding Ru...C distances (2.637(7) and 2.668(6) Å). The correct and accurate location of the *ortho*-methyl hydrogen atoms clearly indicates a double agostic arrangement for each methyl group. In fact, two hydrogen atoms lie closer to the metal and are off the mean plane Ru,P1,P2,C10,C40 (figure 1b), whereas the third hydrogen atom is approximately in the mean plane but away from the metal. For each methyl group the two shorter Ru...H distances are clearly asymmetric (Ru...H101 = 2.507(11), Ru...H102 = 2.113(10) Å and Ru...H401 = 2.137(12), Ru...H402 = 2.399(14) Å). Moreover, ideal  $\text{M}\cdots\eta^3\text{-H}_2\text{C}$  coordination is not achieved because the metal atom does not lie exactly in the CH<sub>2</sub> plane. In spite of the non negligible standard deviations, the geometry of the CH<sub>3</sub> groups is much more reliably determined by neutrons than by X-rays and confirms the perturbing effects of the agostic interaction. The two C-H bonds closest to the metal are slightly longer than the others and particularly significant is the opening of the H-C-H angles subtended by the metal atom. Thus the values of 112.0(8)° and 110.4(10)° for H101-C10-H102 and H401-C40-H402 are definitely larger than all the other H-C-H angles at the interacting methyl groups (in

the range 103.8(10) – 104.8(10)° indicating that the interaction with the metal affects significantly the geometry of the methyl group.

In order to compare the experimental results with those in the literature, we made a survey of all X-ray structures (no neutron data have been previously



**Figure 2:** Variation of the methyl torsion about the C1-C2 bond in agostic complexes ( $\beta$  through  $\epsilon$ ) and in one documented intermolecular case.

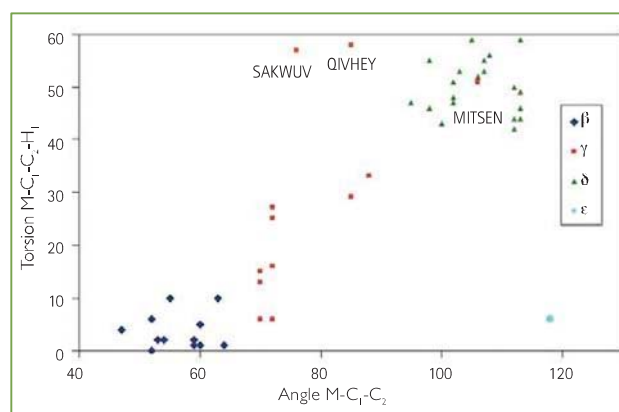
reported), deposited in the CSD, which feature  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\epsilon$   $M\cdots H_3C-C$  agostic interactions, as well as a unique case of intermolecular interaction (figure 2).

In the  $\beta$  agostic complexes, the  $sp^3$  character of the alkylic carbon atom is fully consistent with the metal lying in the  $C_2C_1H_1$  plane and this arrangement represents the most classical form of  $M\cdots\eta^2-HC$  interaction. When the angle  $M\cdots C_1-C_2$  is larger than  $55^\circ$  ( $\gamma$  through  $\epsilon$  cases), rotation of the methyl group about the  $C_1-C_2$  bond is forced so that the hydrogen atom closest to the metal slips off the  $M, C_1, C_2$  plane. Such a rotation is progressively larger ( $< 30^\circ$  for the  $\gamma$  complexes,  $>$

$30^\circ$  for the  $\delta$  ones) but, even at the  $60^\circ$  limit, the connectivity between the metal and the agostic methyl group does not allow the metal to attain ideal  $M\cdots\eta^3-H_2C$  coordination.

As shown in figure 3, a linear correlation is found between the angle at the methyl carbon atom and the  $CH_3$  torsion itself related to the different types of metal $\cdots$ methyl connectivity, and the agostic interactions span the range between the classical ( $M\cdots\eta^2-HC$ ) and the non-classical ( $M\cdots\eta^3-H_2C$ ) types. A solution study of **1** shows intramolecular rearrangement of each xyllyl substituent that equilibrates the environments of its two *ortho*  $CH_3$  groups. Activation parameters, evaluated from the analysis of  $^1H$  NMR line shape as a function of temperature, are  $\Delta H^\ddagger = 9.6 \pm 0.2$  kcal mol $^{-1}$  with  $\Delta S^\ddagger = -15.4 \pm 0.7$  eu (CDCl $_3$ ) and are consistent with a relatively strong agostic interaction.

Theoretical calculations reproduce well the non classical  $Ru\cdots\eta^3-H_2C$  agostic mode



**Figure 3:** Scatter plot showing the essentially linear relationship between the opening of the  $M\cdots C_1-C_2$  angle and the torsion of the  $CH_3$  group about the  $C_1-C_2$  bond.

for the model complex  $RuCl_2[PH_2(2,6-Me_2C_6H_3)]_2$  (**1a**). and significantly, the classical

$Ru\cdots\eta^2-HC$  agostic geometry features an optimized transition state (for the rotation of the  $CH_3$  group about the external C-C bond) and implies an energy barrier of 3.4 kcal mol $^{-1}$ . Finally, the MO analysis addresses the intrinsic stability of the isolated 14-electron complex  $RuCl_2(PH_3)_2$ . Calculations of the adduct between the latter and two  $CH_4$  molecules highlight the appreciable involvement of one carbon p orbital in each interaction which is of the ideal non-classical  $M\cdots\eta^3-H_2C$  agostic type.

In summary, these studies have led to the following important conclusions. A non-classical agostic interaction, where a whole  $CH_2$  group acts as a donor in place of the single C-H bond ( $M\cdots\eta^3-H_2C$  vs.  $M\cdots\eta^2-HC$  coordination), has been definitely established, through a neutron diffraction study of **1**. For agostic complexes, which have links between the  $CH_3$  group and the metal center, the interaction type depends on the length of the joining chain. For short chains, only the  $M\cdots\eta^2-HC$  coordination mode is allowed but the  $M\cdots\eta^3-H_2C$  type becomes

favoured for long chains or intermolecular adducts. The present results will be helpful for designing new coordinatively unsaturated complexes as well as for elucidating the key steps in the metal-promoted C-H bond activation of saturated hydrocarbons.

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