

## On the fluxional behavior of $[\text{CpMn}(\text{CO})_2(\sigma\text{-alkane})]$ complexes

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### INTRODUCTION

The coordination chemistry of alkanes has been widely discussed since the 1970s.<sup>1</sup> Though counterintuitive, alkane complexes have been proposed as unstable intermediates in a number of organometallic transformations.<sup>1</sup> Spectroscopic evidence and crystallographic data have shown that alkane complexes exhibit C-H  $\sigma$  bonds coordinated to metal centers.<sup>1,2</sup> In effect, fundamental questions concerning the structures and properties of  $\sigma$ -alkane complexes, including their fluxional behavior toward rapid exchange of geminal or vicinal protons, are still challenging.<sup>2,3</sup> In this work, we have performed a DFT study of the fluxional behavior of  $[\text{CpMn}(\text{CO})_2(\sigma\text{-CH}_4)]$  (**1**) and  $[\text{CpMn}(\text{CO})_2(\sigma\text{-C}_2\text{H}_6)]$  (**2**).

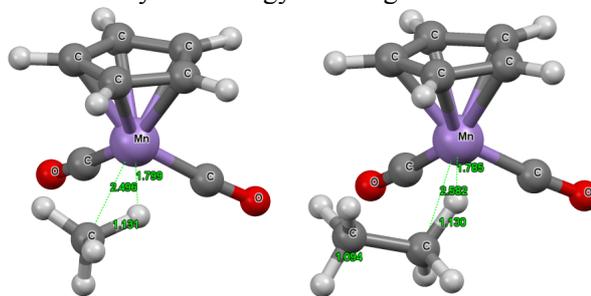
### COMPUTATIONAL DETAILS

All calculations have been carried out in the gas phase at the DFT B3PW91-D3/LACV3P\*\*++ level using Jaguar 7.9.<sup>4</sup> This functional has been chosen because it provides reliable geometries and binding energies for  $\sigma$ -alkane complexes.<sup>5</sup>

### RESULTS AND DISCUSSION

IR and NMR spectroscopic pieces of evidence support the formation of  $\sigma$ -alkane complexes from UV photolysis of  $[\text{CpMn}(\text{CO})_3]$  in liquid alkane.<sup>2,3</sup> However, a detailed investigation of the structures of  $[\text{CpMn}(\text{CO})_2(\sigma\text{-alkane})]$  complexes is lacking.<sup>6</sup> Methane coordinates to Mn according to the  $\eta^2\text{-C,H}$  mode (**Figure 1a**). Ethane exhibits two modes upon coordination to Mn, namely  $\eta^2\text{-C,H}$  and  $\eta^1\text{-H}$  (**Figure 1b**).  $\eta^1\text{-H-2}$  is 0.9 kcal/mol less stable than  $\eta^2\text{-C,H-2}$ . Coordinated C-H bonds are ca. 0.04 Å longer than the uncoordinated ones. According to **Table 1**, all structures exhibit close values for the  $\nu(\text{CH})$  and  $\nu(\text{CO})$  vibration modes.  $\eta^2\text{-C,H-1}$  and  $\eta^2\text{-C,H-2}$  have similar calculated alkane binding enthalpies ( $\Delta H_{\text{bind}}$ ): 10.5 and 12.6 kcal/mol, respectively. Calculated  $\Delta H^\ddagger$  values for

the exchange of geminal protons are 0.57 ( $\eta^2\text{-C,H-1}$ ) and 0.95 ( $\eta^2\text{-C,H-2}$ ) kcal/mol. They show that the fluxional behavior of both **1** and **2** results from the very low energy exchange barriers.



**Figure 1.** Structures obtained for  $\eta^2\text{-C,H-1}$  and  $\eta^1\text{-H-2}$ .

**Table 1.** Vibrational frequencies ( $\text{cm}^{-1}$ ) calculated for  $[\text{CpMn}(\text{CO})_n]$  ( $n = 2$  or  $3$ ), **1** and **2**.<sup>a</sup>

Complexes	$\nu(\text{CH})_{\text{coordinated}}$	$\nu(\text{CO})$
$[\text{CpMn}(\text{CO})_2]$	-	2075, 2017 (1961, 1893)
$[\text{CpMn}(\text{CO})_3]$	-	2117, 2050 (2035, 1955)
$\eta^2\text{-C,H-1}$	2644	2066, 2012 (1972, 1908)
$\eta^2\text{-C,H-2}$	2599	2064, 2010 (1968, 1901)
$\eta^1\text{-H-2}$	2686	2064, 2011

<sup>a</sup> Experimental frequencies at 298 K are given in brackets.<sup>3</sup>

### CONCLUSIONS

This work contributes to the current knowledge of the structure and thermodynamics of  $[\text{CpMn}(\text{CO})_2(\sigma\text{-alkane})]$  complexes.

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