

## Supporting Information

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### **Surprising Differences of Alkane C-H Activation Catalyzed by Ruthenium Nanoparticles: Complex Surface-Substrate Recognition?**

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# Surprising Differences of Alkane C-H Activation catalyzed by Ruthenium Nanoparticles: Complex Surface-Substrate Recognition?

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## Supporting Information

### Reagents and General Procedures

All reactions were carried out using Schlenk or Fischer-Porter bottle techniques to protect the precursor and MNPs from air and moisture. THF was distilled over CaH<sub>2</sub> and pentane over sodium. The solvents were degassed by means of three freeze-pump cycles. 1,4-bis(diphenylphosphino)butane was purchased from Sigma-Aldrich - and (cyclooctadiene)(cyclooctatriene)ruthenium(0) (Ru(COD)(COT)) for the synthesis of Ru/dppb from NanoMePS.

Deuterium gas (99.82%) was purchased from Eurisotop, and all substrates were supplied by Sigma-Aldrich in quality of analytical standards. The MNP syntheses followed the well-known organometallic approach established by some of us recently.<sup>[1-3]</sup> The protocol is based on the decomposition of the Ru(COD)(COT) in a dilute solution of THF and the presence of a sub-stoichiometric amount of dppb under an atmosphere of 3 bar H<sub>2</sub> at room temperature. Similarly, Siralox® supported RuNPs were synthesized by dissolving 30 mg of Ru(COD)(COT) in a suspension of 200 mg of Siralox® in THF. The mixture was agitated during 1 h for homogenization and let agitated overnight under an atmosphere of 3 bar of H<sub>2</sub> gas at room temperature. The supported RuNPs were washed three times with THF.

All substrates were used as received from the supplier. Typically, in a 95 mL Fischer-Porter bottle, 10 mg of Ru/dppb were mixed with 1 mL THF. The mixture was put in an ultrasonic bath to disperse the particles. At room temperature, THF was evaporated under vacuum and then 1 mL of the substrate was added. The resulting mixture of the nanoparticles and the substrate was cooled with liquid nitrogen (77 K). As soon as the mixture became solid, a vacuum was applied to remove the argon atmosphere. After the mixture had reached room temperature, the bottle was pressurized with 6 bar D<sub>2</sub> gas and was heated to 60°C for 24 h under stirring,.

If more than one batch cycle was conducted, the mixture was frozen as described before, the gas phase was removed in vacuum and a fresh D<sub>2</sub> atmosphere of 6 bar was applied.

The mass spectra for the deuteration experiments were recorded with a Finnigan MAT 95 mass spectrometer with double focusing sector field and inverted Nier-Johnson geometry. The peak intensities of the isotopologues of a given product, C<sub>n</sub>L<sub>m</sub>, where L = H, D, were expressed as fractions of the total intensity sum and are assembled in Table S1.

The data presented in Table 1 and Figure 1 was obtained from a sample prepared in a glove box. To exclude that the observed differences between cyclohexane and cyclopentane were caused by spurious rest

oxygen in the atmosphere of the glove box, we performed control experiments, where the sample was prepared under fully inert conditions.

In these control experiments, 10 mg of Ru/dppb were mixed with 1 mL THF in a 90 mL Fischer-Porter bottle. The substrates (cyclopentane or cyclohexane) were degassed with nitrogen. At room temperature, THF was evaporated under vacuum and then 1 mL of the substrate was added. The resulting mixture of the nanoparticles and the substrate was cooled with liquid nitrogen (77 K). As soon as the mixture became solid, the argon atmosphere was removed via a vacuum pump. Then the mixture was slowly heated to room temperature. Then the bottle was pressurized with 4 bar D<sub>2</sub> gas and was heated to 60°C or 100°C for 24 h under stirring.

Finally, the deuteration of the substrates cyclopentane and cyclohexane was also performed with ruthenium nanoparticles supported on Siralox®, employing the previous described experimental conditions (4 bar D<sub>2</sub>, 60°C, 24 h stirring).

## Results of the mass spectra analysis

The deuterium fraction of a given product listed in Table 1 was calculated according to the equation

$$x_D = \sum_{i=0}^N x_i y_i$$

where  $i$  is the number of deuterium atoms in the isotopologue  $i$ ,  $x_i$  the fraction of the isotopologue  $i$ ,  $y_i$  the fraction of deuterons in the isotopologue  $i$ .

The average number of deuterium atoms of a given product was calculated according to

$$n_D = \sum_{i=0}^N x_i n_i,$$

where  $n_i$  is the number of deuterium atoms in the isotopologue  $i$ . The values in Table 1 were based on those assembled in Table S1.

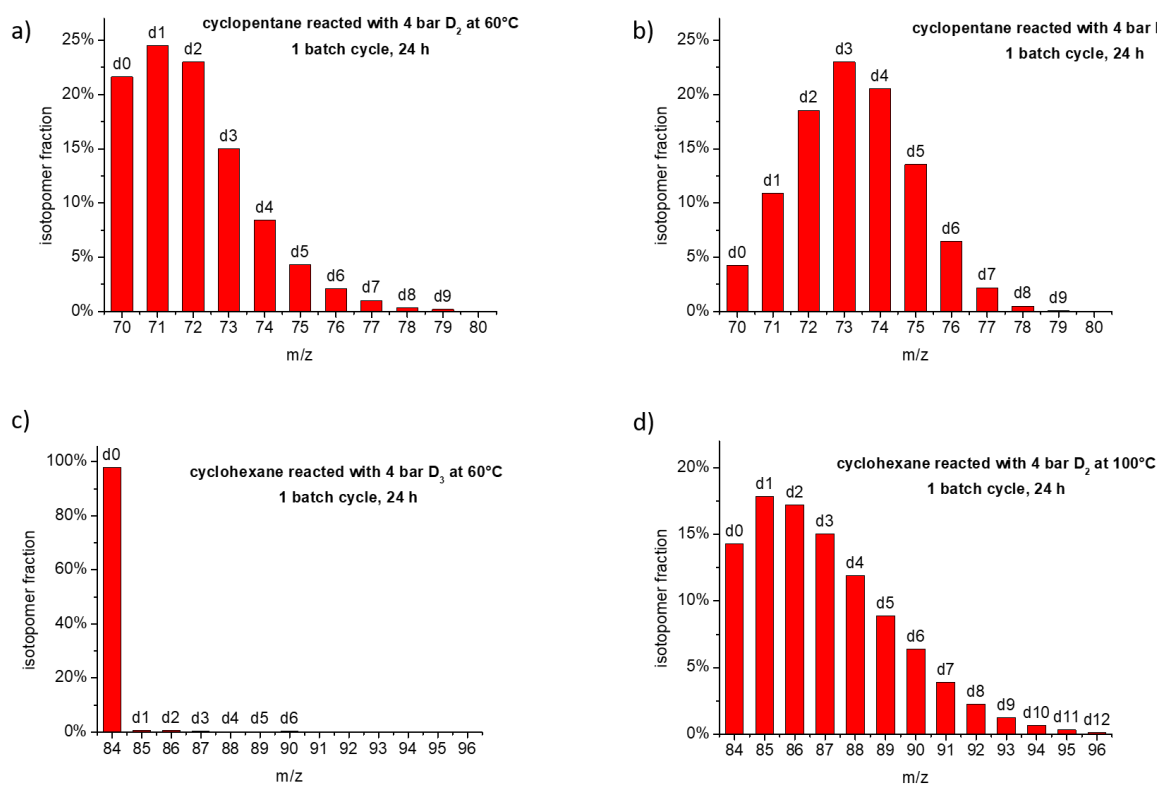
**Table S1.** Alkane isotope fractions of different isotopologues determined by mass spectroscopy

$n_i$	cyclopentane 1 batch cycle	cyclopentane 3 batch cycles	cyclopentane 5 batch cycles	cyclohexane 3 batch cycles	isopentane 3 batch cycles	<i>n</i> -pentane 3 batch cycles	<i>n</i> -octane 3 batch cycles
$i$	$x_i$	$x_i$	$x_i$	$x_i$	$x_i$	$x_i$	$x_n$
0	64,18%	37,36%	4,12%	93,05%	94,76%	92,96%	89,20%
1	19,08%	18,61%	8,31%	6,43%	4,99%	5,69%	8,83%
2	10,62%	19,53%	13,22%	0,37%	0,14%	0,69%	1,40%
3	3,74%	10,10%	16,61%	0,07%	0,03%	0,22%	0,32%
4	1,59%	6,63%	17,74%	0,03%	0,03%	0,16%	0,14%
5	0,57%	3,64%	15,51%	0,02%	0,05%	0,13%	0,06%
6	0,15%	1,95%	11,47%	0,02%	0,00%	0,09%	0,02%
7	0,05%	1,06%	7,15%	0,01%	0,00%	0,04%	0,01%

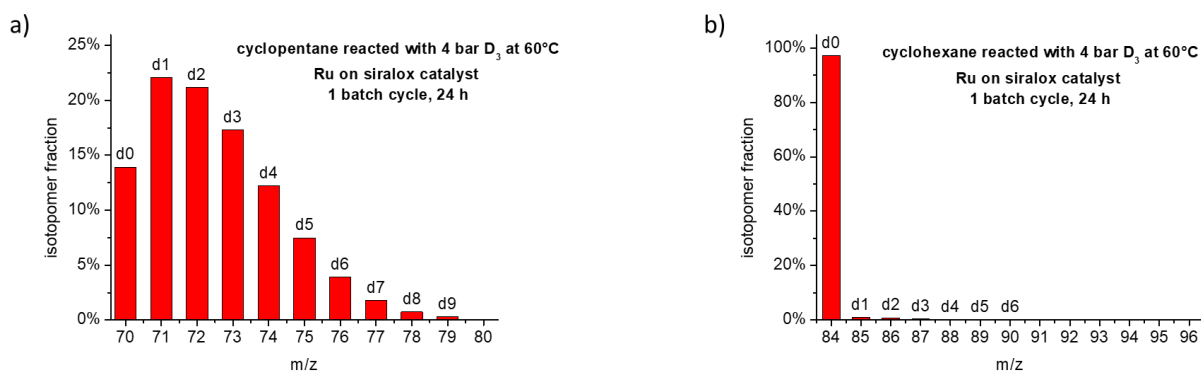
8	0,01%	0,60%	3,71%	0,00%	0,00%	0,00%	0,00%
9	0,00%	0,33%	1,62%	0,00%	0,00%	0,00%	0,00%
10	0,00%	0,19%	0,54%	0,00%	0,00%	0,00%	0,00%

$i$ : number of deuterons in isotopologue  $i$ .  $x_i$ : fraction of isotopologue  $i$ .

Note that the results of this calculation are affected by a minor error caused by the  $^{13}\text{C}$  isotope. In the case of cyclopentane with its five C atoms that means that 5.5% of the intensity of peak  $m/z$  belongs to the peak with  $(m/z)-1$  if molecules with one  $^{13}\text{C}$  are considered. Nevertheless, that error affects the result by less than 0.4% and thus a correction can be neglected. Contributions of  $^{14}\text{C}$  or two or more  $^{13}\text{C}$  per molecule are less likely and therefore also not taken into account.



**Figure S1.** Isotopomer fraction patterns obtained under inert reaction conditions for deuteration experiments on the substrates cyclopentane (a,b) and cyclohexane (c,d). Reactions were performed at 60°C (a,c) as well as at 100°C (b,d) employing Ru/dppb nanoparticles as catalyst.

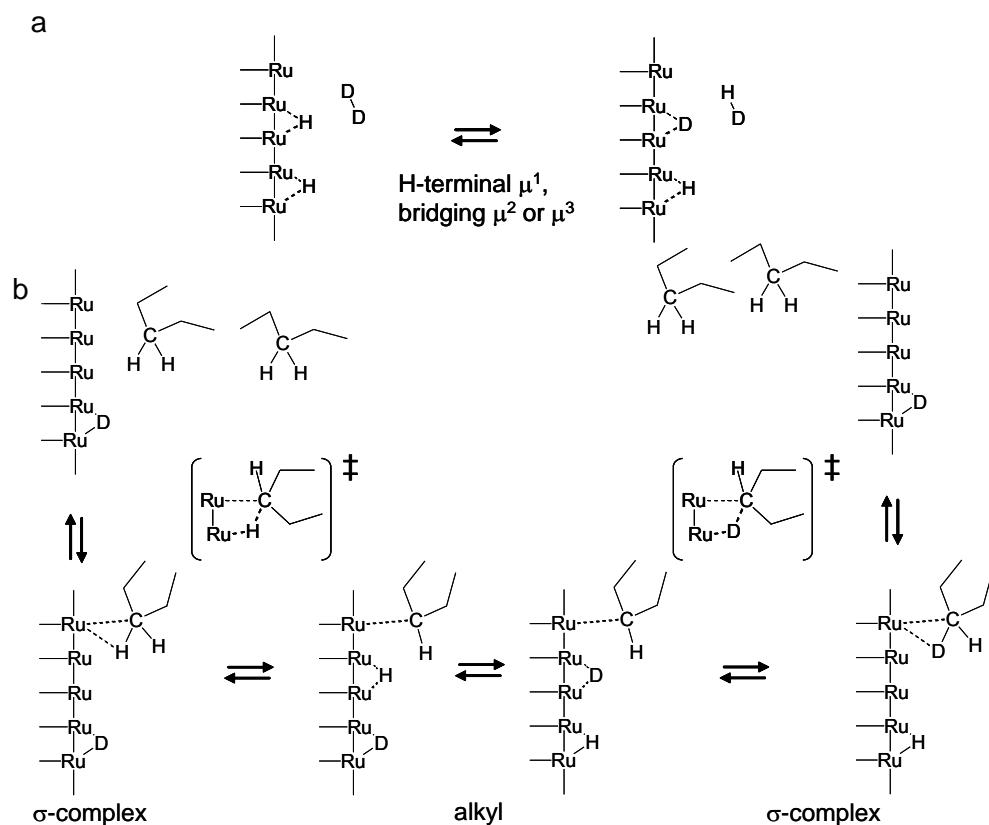


**Figure S2.** Isotopomer fraction patterns obtained under inert reaction conditions for deuteration experiments on the substrates cyclopentane (a) and cyclohexane (b). Reactions were performed at 60°C employing ruthenium nanoparticles supported on Siralox® as catalyst.

### Computational details

The computational mechanistic study was calculated within the framework of the DFT considering periodic boundary conditions and the spin polarized constraint. The exchange-correlation potential was approximated by the generalized gradient approach proposed by Perdew, Burke, and Ernzerhof (PBE).<sup>[4]</sup> Calculation of the energetic parameters as well as the geometry optimizations were carried out using the projector augmented waves (PAW) full-potential reconstruction<sup>[5]</sup> implemented in the Vienna *ab initio* simulation package, VASP.<sup>[6]</sup> Regarding Ru, and in order to minimize errors arising from the frozen core approximation, we used the PAW data sets treating the 4p, 4d and 5s Ru states (14 valence electrons). A kinetic energy cut-off of 500 eV was sufficient to achieve a total energy convergence within several millielectronvolts for ligands adsorption. The supercell used was  $23 \times 24 \times 25 \text{ \AA}$  large, ensuring at least 16 Å of vacuum between two successive images of ligand-covered Ru<sub>13</sub> clusters.  $\Gamma$ -centered calculations were performed with a Gaussian smearing ( $\sigma$ ) of 0.02 eV, the energies being therefore extrapolated to  $\sigma = 0.00 \text{ eV}$ .

The atom positions were optimized until the criterion of the residual forces on any direction being less than  $0.02 \text{ eV \AA}^{-1}$  was met. Two methods were considered for transition states (TS) search: (i) a rough exploration of the reaction pathway between two species with the climbing image nudge elastic band (CINEB) method<sup>[7]</sup> with a spring force between images of 5 eV and a force tolerance of  $0.08 \text{ eV \AA}^{-1}$ ; (ii) one possible TS were identified, a TS search was undertaken with the improved dimer algorithm<sup>[8]</sup> (The original dimer method is described in Ref.<sup>[9]</sup>). The harmonic vibrational modes were systematically calculated in order to confirm the minimum or saddle point nature of calculated extrema by using the dynamical matrix code implemented in VASP as well as the VASPTST tools developed in Henkelman's group.



**Scheme S1:** Reaction steps of alkane H/D exchange catalyzed by Ru nanoparticles. (a) Oxidative addition (dissociative adsorption) of D<sub>2</sub> gas to the Ru surface and release of HD.<sup>[10]</sup> (b) Alkane coordination and formation of a  $\sigma$ -complex with Ru followed by oxidative cleavage as rate determining step creating a surface alkyl. Fast surface hydrogen exchange and reverse reaction  $\mu$  leads to alkane deuteration.<sup>[11]</sup>

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