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Suplementary Information for

Synthesis and Dynamic Behaviour of Zwiterionic [M(η^6-C_6H_5-BPh_3)(coe)$_2$] (M = Rh, Ir) Cyclooctene Complexes

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NMR spectra for $[(\eta^6\text{-}C_6H_5\text{-}BPh_3)Rh(coe)_2]$ (1)

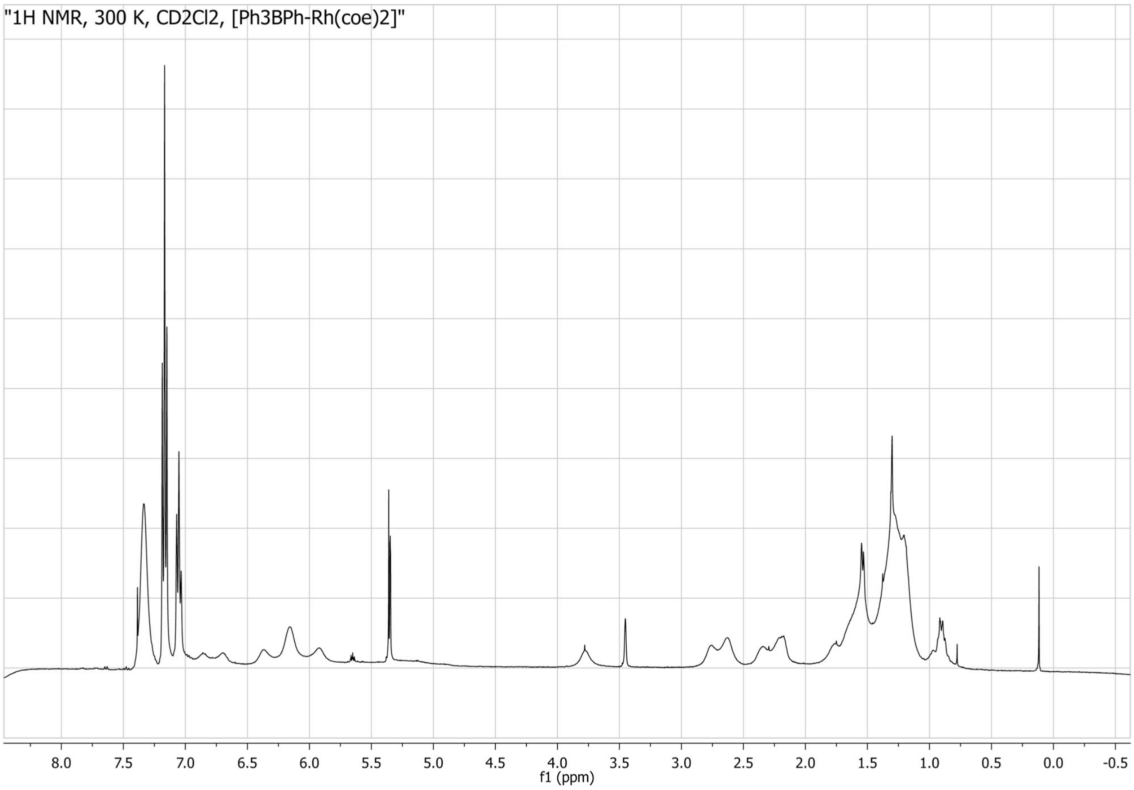


Figure S1. ^{1}H NMR spectrum of **1** in CD_2Cl_2 at 300 K.

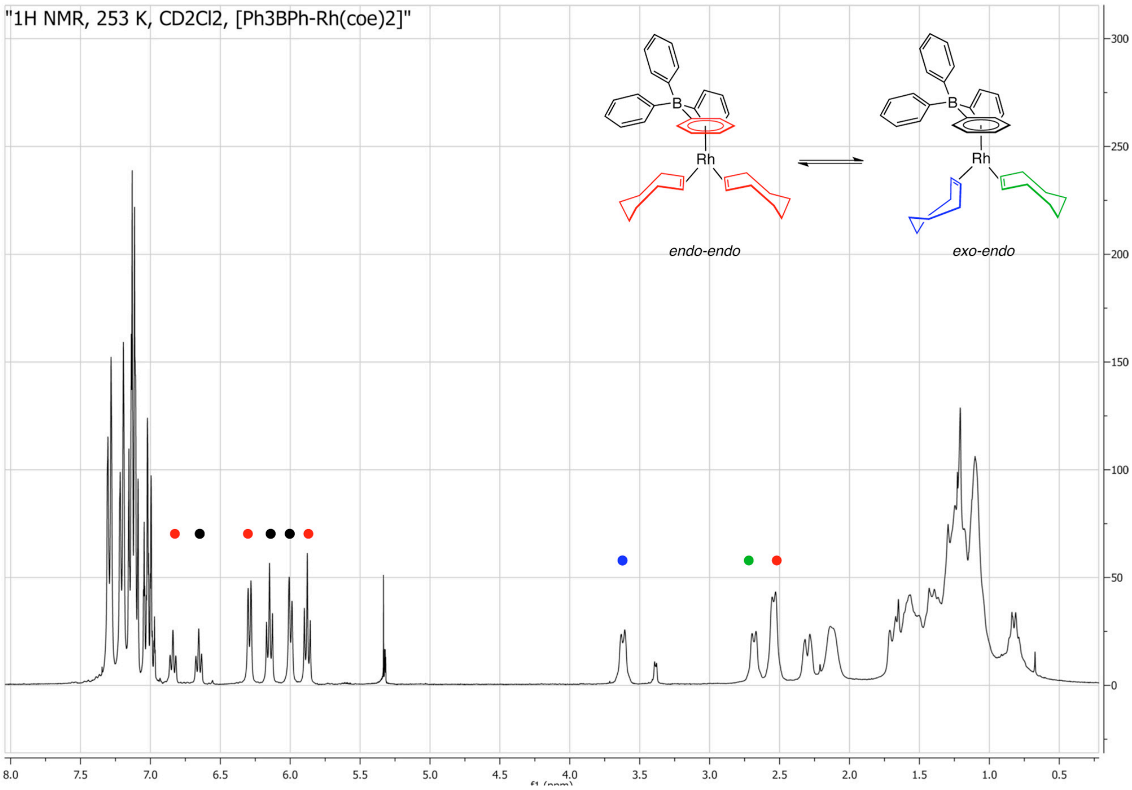


Figure S2. ^{1}H NMR spectrum of **1** in CD_2Cl_2 at 253 K.

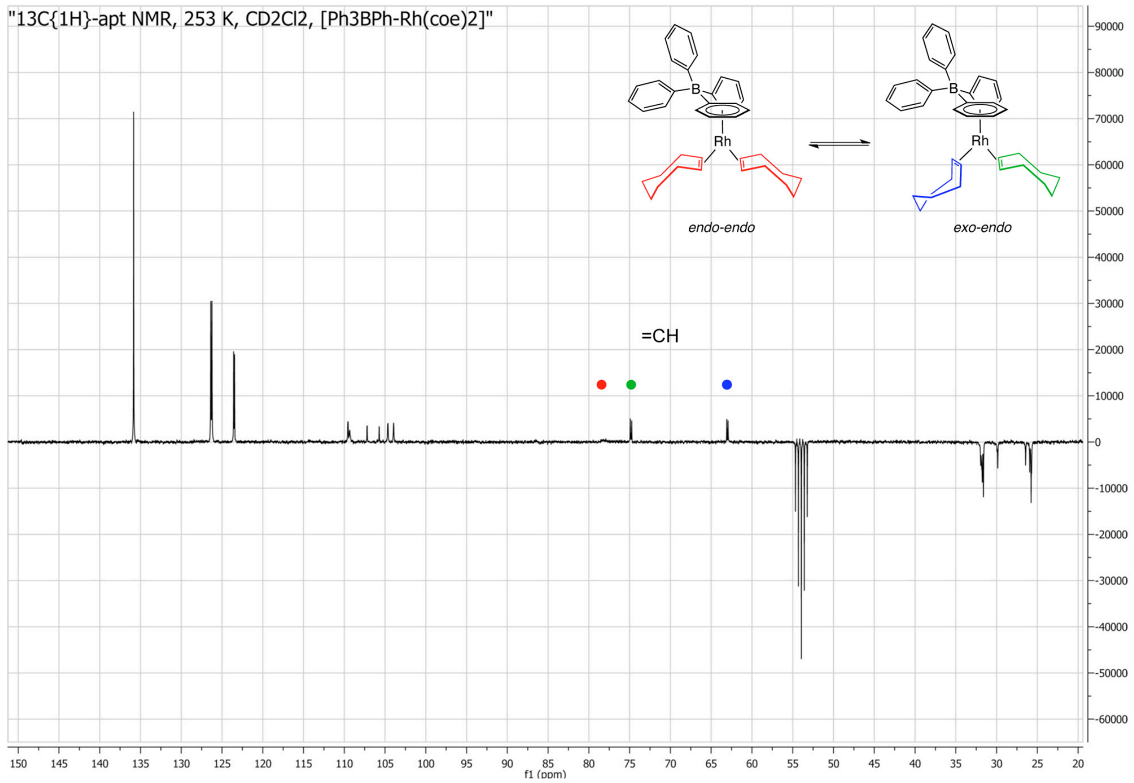


Figure S3. $^{13}C\{^1H\}$APT NMR spectrum of **1** in CD_2Cl_2 at 253 K.

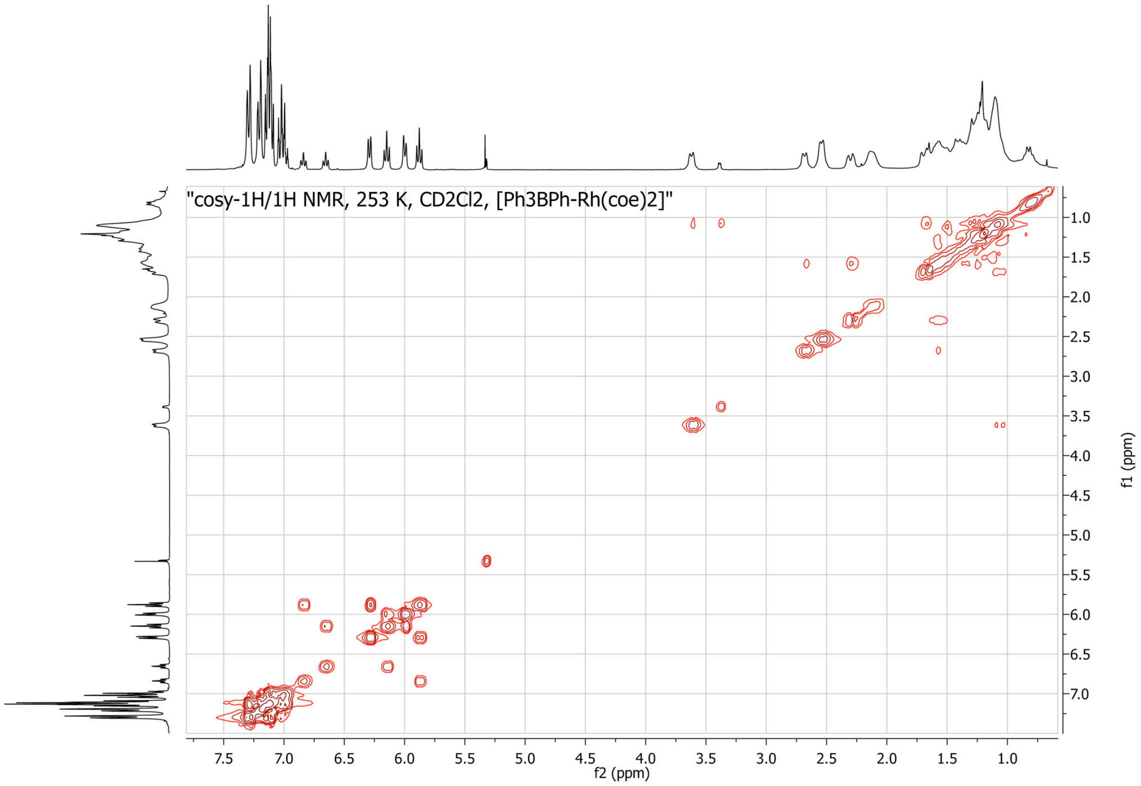


Figure S4. ^1H-^1H COSY NMR spectrum of **1** in CD_2Cl_2 at 253 K.

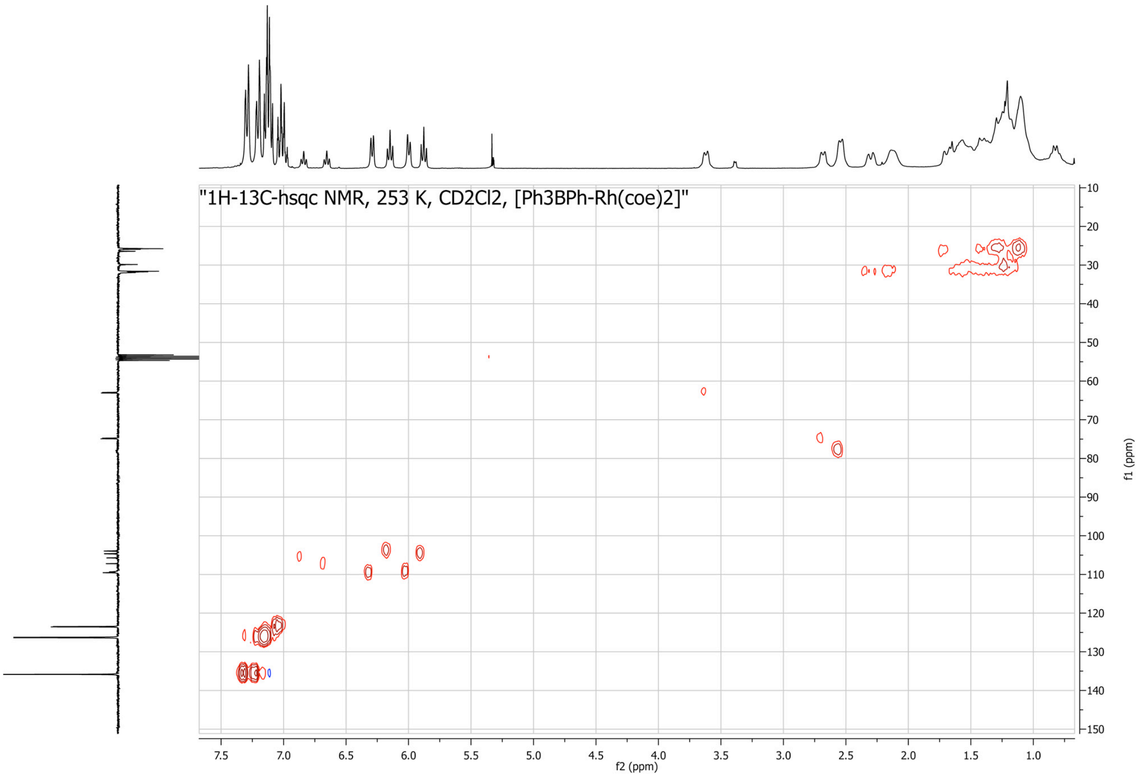


Figure S5. ^{1}H-^{13}C HSQC NMR spectrum of **1** in CD_2Cl_2 at 253 K.

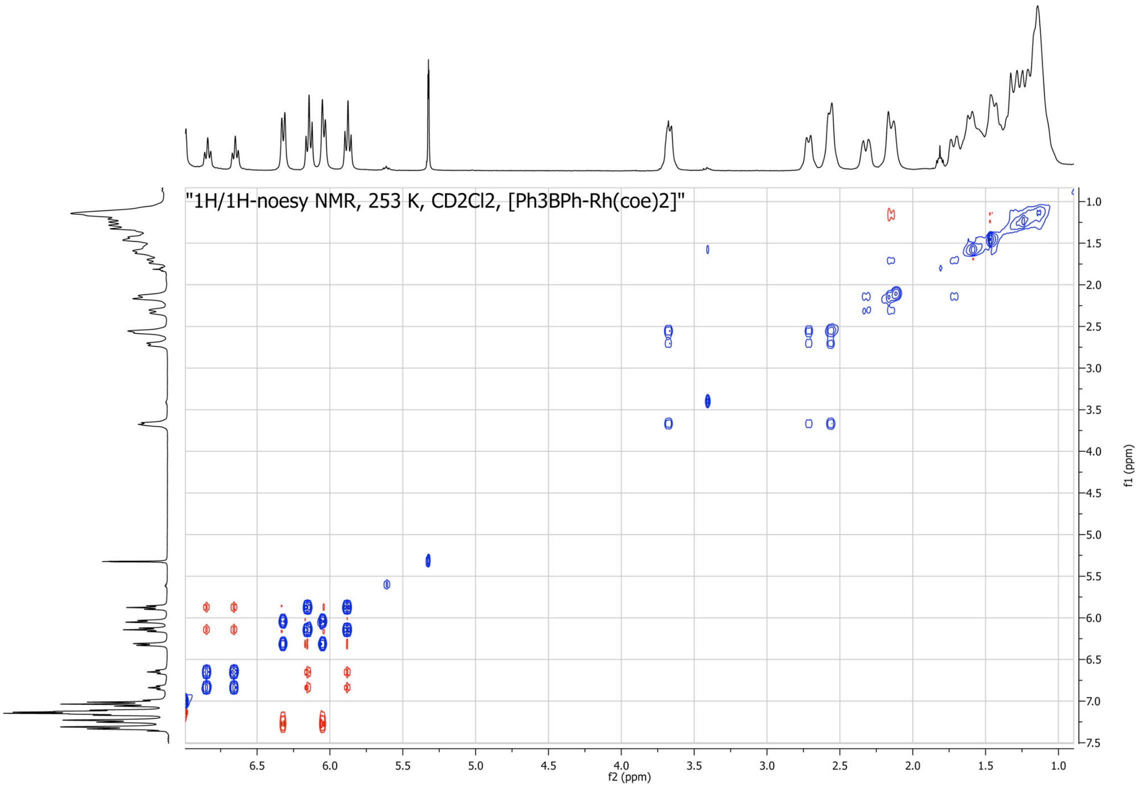


Figure S6. ^{1}H-^{1}H NOESY NMR spectrum of **1** in CD_2Cl_2 at 253 K.

NMR spectra for [(η^6-C$_6$H$_5$-BPh$_3$)Ir(coe)$_2$] (2).

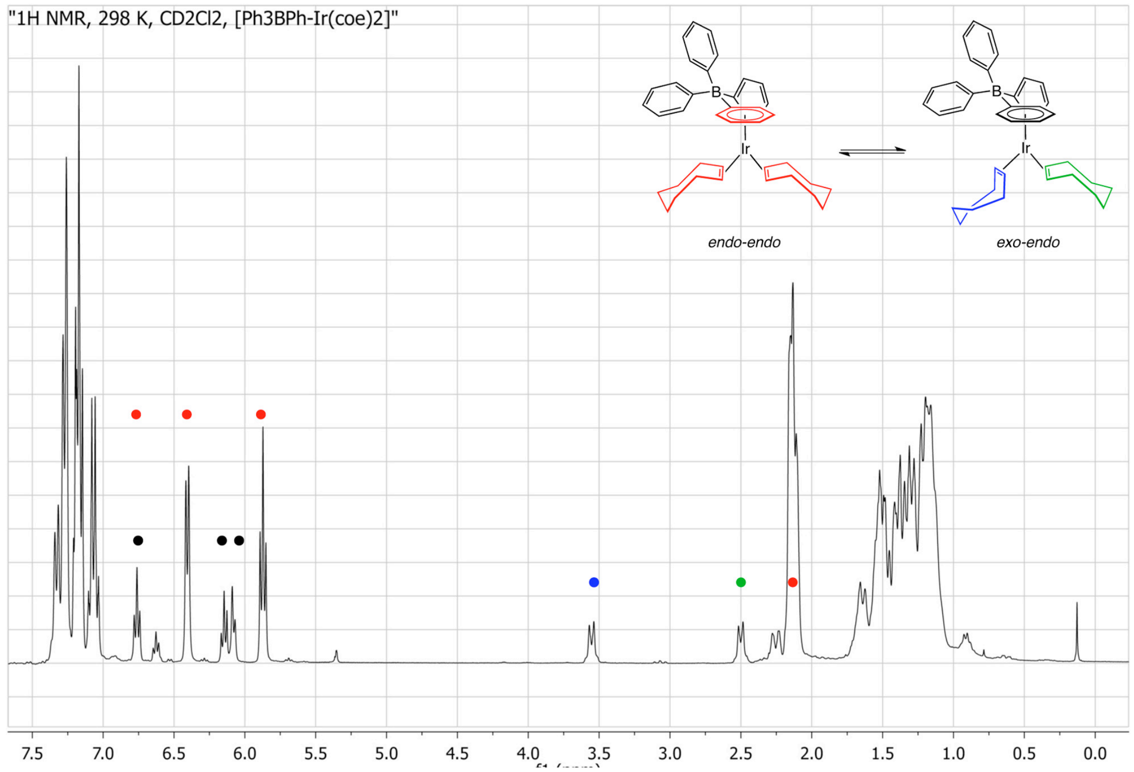


Figure S7. ^{1}H NMR spectrum of **2** in CD$_2$Cl$_2$ at 298 K.

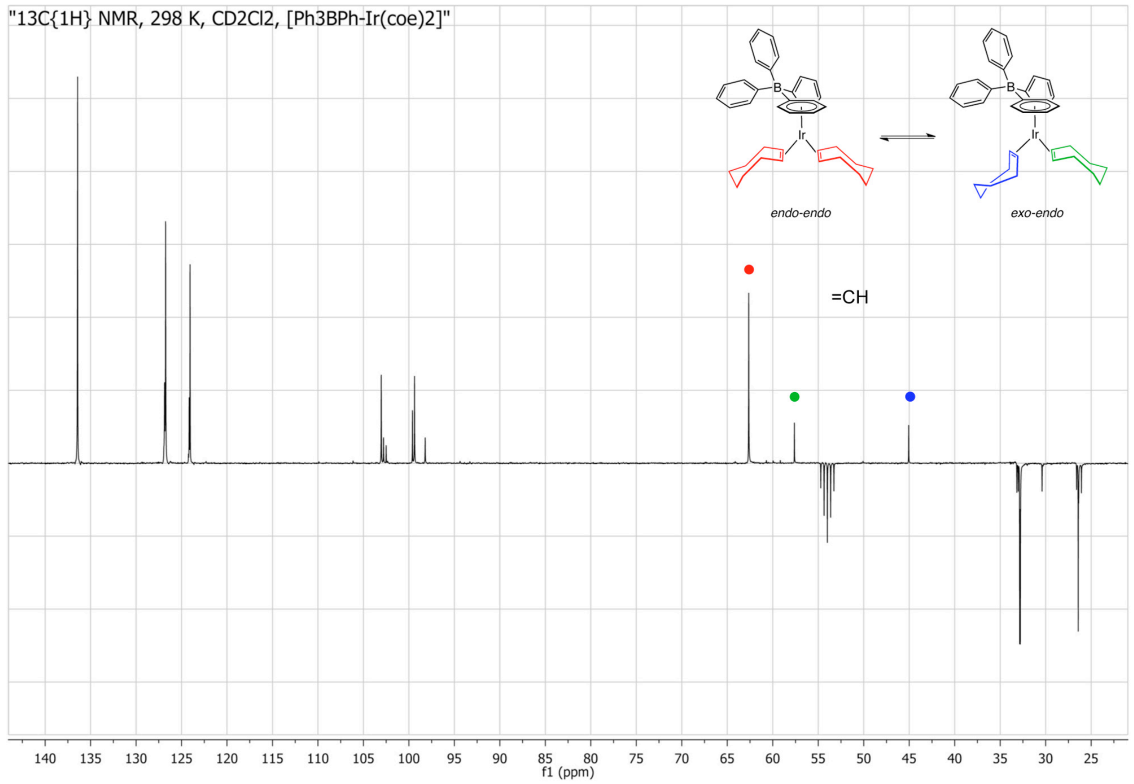


Figure S8. ^{13}C{^{1}H}APT NMR spectrum of **2** in CD$_2$Cl$_2$ at 298 K.

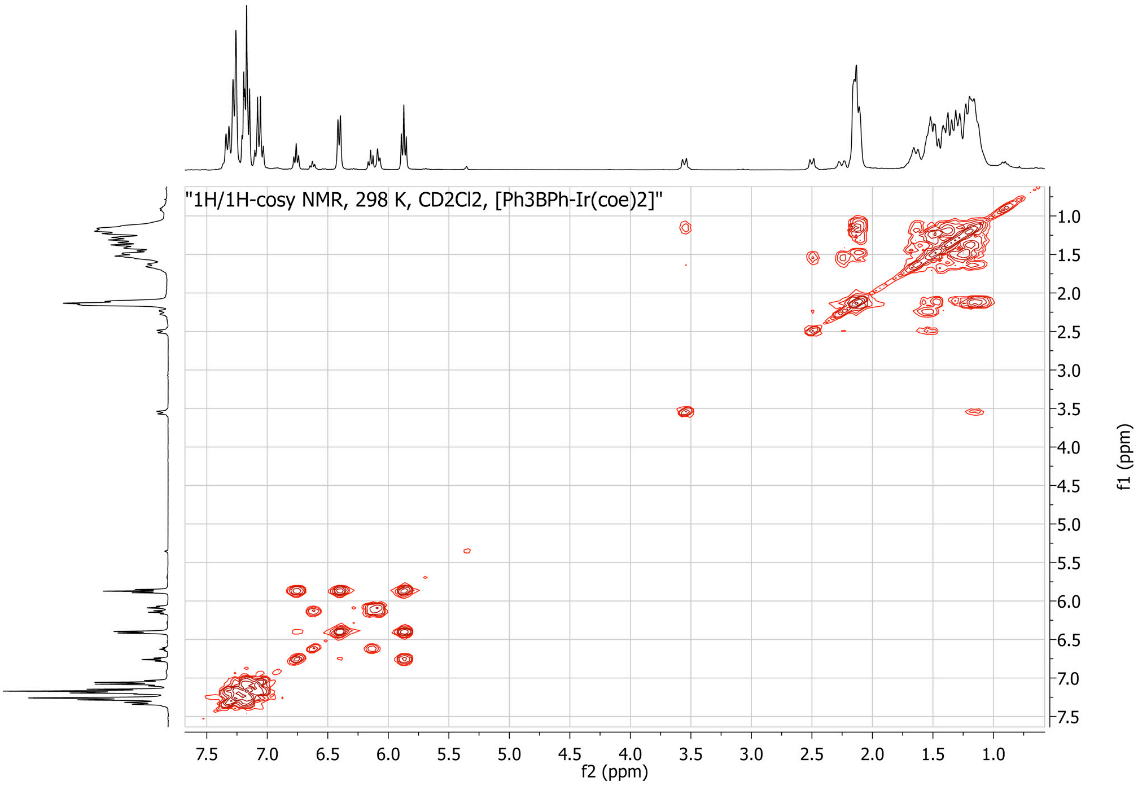


Figure S9. ^{1}H-^{1}H COSY NMR spectrum of **2** in CD_2Cl_2 at 298 K.

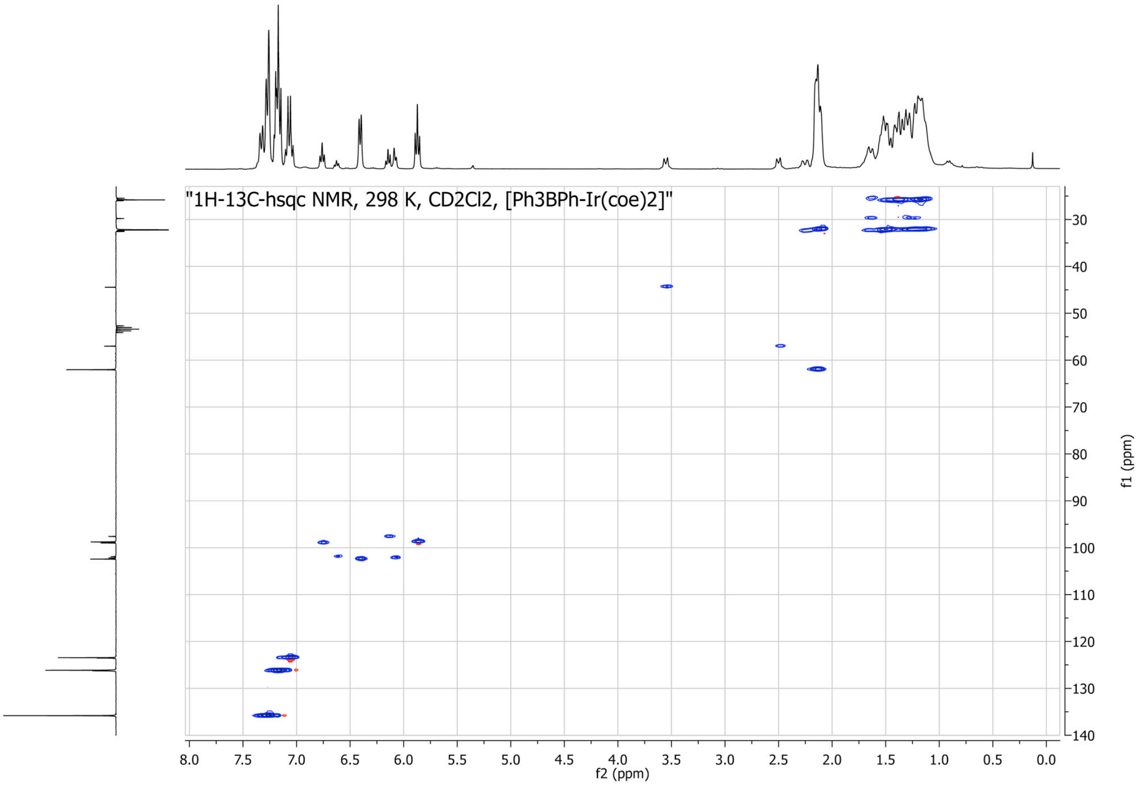


Figure S10. ^{1}H-^{13}C HSQC NMR spectrum of **2** in CD_2Cl_2 at 298 K.

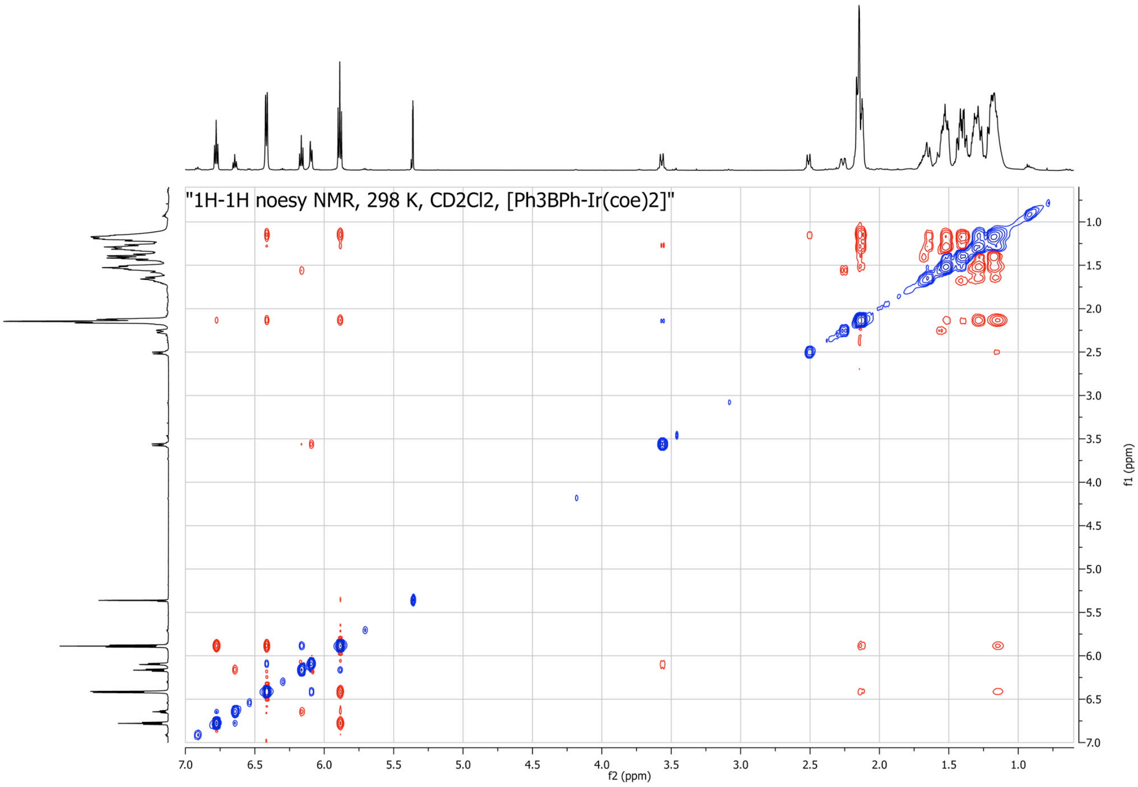


Figure S11. ^{1}H-^{1}H NOESY NMR spectrum of **2** in CD_2Cl_2 at 298 K.

Theoretical Calculations.

The z-matrix setup used as starting point in the study of the rotation of the coe ligand in [(η^6-C_6H_5-BPh_3)Rh(coe)$_2$] (**1**) was generated using MOLDEN[1]. It is included in file RhCOE.zmat as supplementary material. The initial optimization was performed in Gaussian 09 using the keywords:

```
#p fopt=(z-matrix,calcall) b3pw91/genecp
```

The dihedral dih72 was varied from 0 to +180 and -180 degrees in 15° steps in order to obtain the data for Figure 4 (only electronic energy was calculated and no frequency analysis were performed).

The accompanying file MCOE.xyz contains the optimized structures of the minima found for [(η^6-C_6H_5-BPh_3)Rh(coe)$_2$] (**1**) and [(η^6-C_6H_5-BPh_3)Ir(coe)$_2$] (**2**) named as RhEndo-Endo, RhExo-Endo, RhExo-Exo, IrEndo-Endo, IrExo-Endo, IrExo-Exo and the two intermediates structures shown in Figure 4 which correspond to the +90° and -105° values of the dihedral dih72 are Rh_90posit and Rh_105neg, respectively

(1) Schaftenaar, G.; Noordik, J. H. *J. Comput.-Aided Mol. Design* **2000**, *14*, 123–134.

Experimental procedure for the determination of the kinetic parameters by 2D-EXSY spectroscopy.

Rate constants (k_1 and k_{-1}/s^{-1}) for the rotamer equilibrium, *endo-endo* ⇆ *exo-endo,* in zwiterionic [M(η^6-C_6H_5-BPh_3)(coe)$_2$] (M = Rh, Ir) complexes were obtained from the 2D EXSY NMR spectra by using a gradient-selected NOESY program from Bruker (noesygpph). All spectra were recorded at 500.13 MHz with mixing times (t_m) optimised for 273 K (**1**, M = Rh) or 300 K (**2**, M = Ir). The spectra were recorded with a sweep of 33 ppm, 2048 data points in the *F*2 direction, 512 increments in the *F*1, eight transients per increment, acquisition time (t_{ac}) of 75 ms, and relaxation delay (d_1) optimised by using the equation:

$$3\,T_1 = t_{ac} + t_m + d_1$$

The spectra were apodised with a qsine function and zero filled. They were phased to give negative signals along the diagonal. The baseline in *F*1 and *F*2 was corrected and then, all spectra were phased using the phase-sensitive method from Bruker. The basis of the calculation of the kinetic data (k_1 and k_{-1}/s^{-1}) from the EXSY experiments was the integration of the cross-peak amplitudes of the 2D EXSY spectra performed by using MestReC software.[1] The *para* phenyl proton resonances of the B(η^6-C_6H_5) fragment for the two rotamers involved in the exchange process are well separated from the rest in the NMR spectrum, which allows the application of the MestReC approach. Two different 2D EXSY NMR spectra were acquired and processed under identical conditions (temperature, number of scans, etc.) for each sample. The first spectrum was an EXSY experiment acquired at the optimised mixing time (t_m) and the second was an EXSY experiment acquired at 0 or very short mixing times (reference experiment). The amplitudes (intensities) of the signals in exchange, A_{ij}, were quantified for both spectra, both diagonal and cross-peaks in the first spectrum and only the diagonal peaks, A(0), in the reference spectrum.

The longitudinal relaxation times, T_1, were measured by using the inversion-recovery method with the appropriate pulse sequence. For a system with two exchange sites, i and j, of equal relaxation time, T_1, the optimum value of the mixing time (t_m) to maximise the cross-peaks intensities could be calculated using the following equation, in which k_ij and k_ji are the exchange rate constants between them.[2, 3]

$$t_\mathrm{m} = \left(1/k_\mathrm{ij}+k_\mathrm{ji}\right)\left[\ln\left(1+\left(k_\mathrm{ij}+k_\mathrm{ji}\right)T_1\right)\right]$$

An adequate approximation for the optimum mixing time (t_m) derived from a statistical analysis is the following equation.[4]

$$t_\mathrm{m} \approx 1/\left[T_1^{-1}+k_\mathrm{ij}+k_\mathrm{ji}\right]$$

The activation energies, $\Delta G_1^{\#}$ and $\Delta G_{-1}^{\#}$ ($\mathrm{kJ\cdot mol^{-1}}$) were calculated from the chemical exchange-rate constants obtained from ESXYCalc, k_1 and k_{-1}, using the Eyring equation.

$$\Delta G^{\#} = -RT\ln\left(hk/k_BT\right)$$

(1) Cross peaks were integrated and processed with the EXSYCalc software distributed by Mestrelab Research (http://mestrelab.com/).

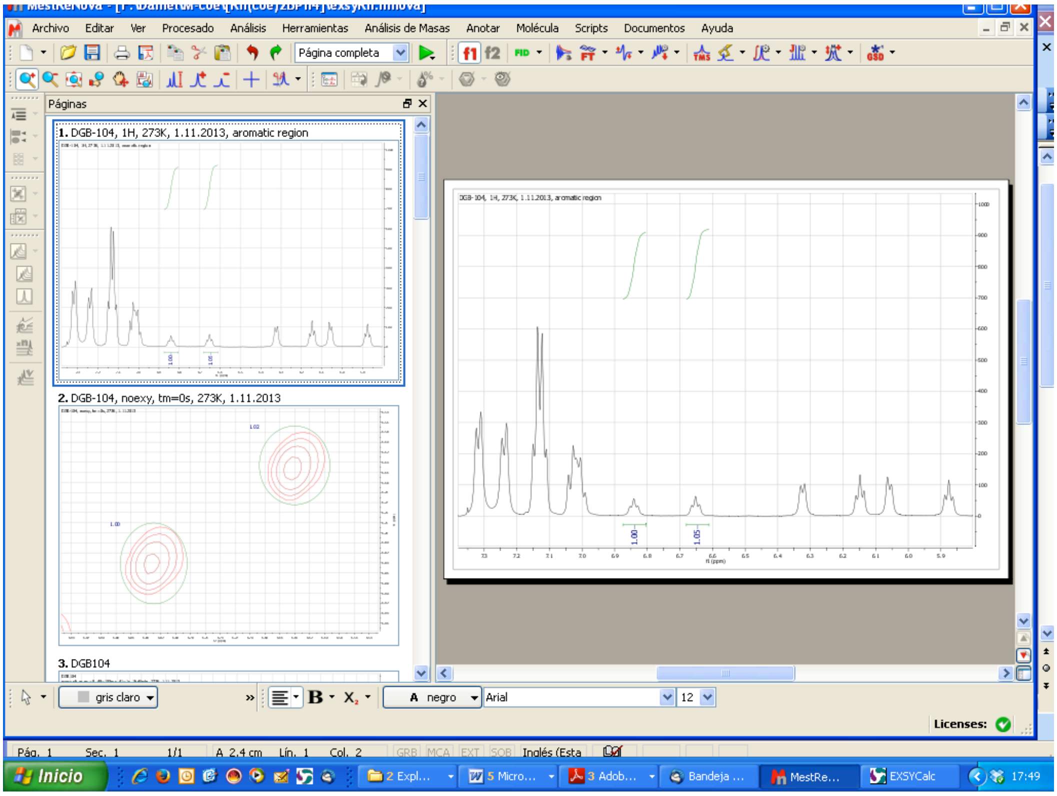
(2) (a) Perrin, C. L.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935–967. (b) Abel, E. W.; Coston, T. P. J.; Orrell, K. G.; Šik, V.; Stephenson, D. *J. Magn. Reson.* **1986**, *70*, 34–53; (c) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, Oxford University Press, Oxford, 1983.

(3) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546–4553.

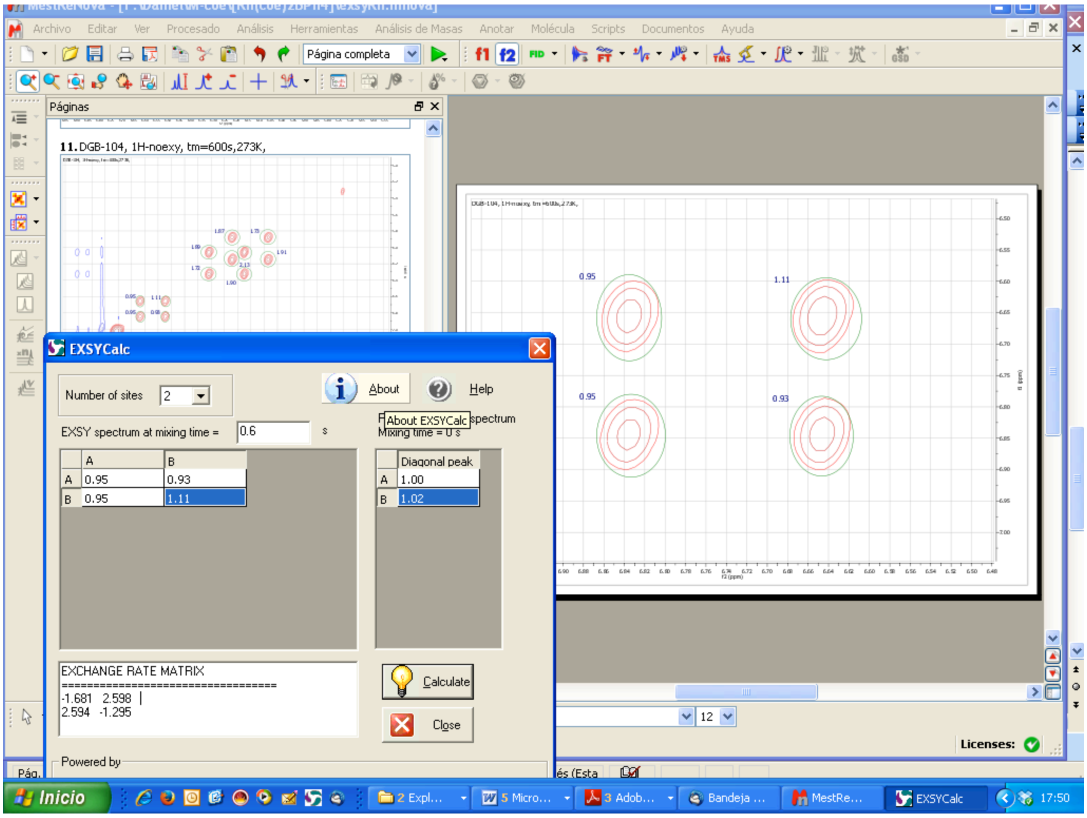
(4) Perrin, C. *J. Magn. Resn.* **1989**, *82*, 619–621.

$[\mathrm{Rh}(\eta^6\text{-}\mathrm{C_6H_5\text{-}BPh_3})(\mathrm{coe})_2]$ (1)

Exsy, $t_\mathrm{m} = 0$



Exsy, $t_\mathrm{m} = 600$



Number of sites: 2

EXSY spectrum at mixing time = 0.6 s

	A	B
A	0.95	0.93
B	0.95	1.11

Mixing time = 0 s

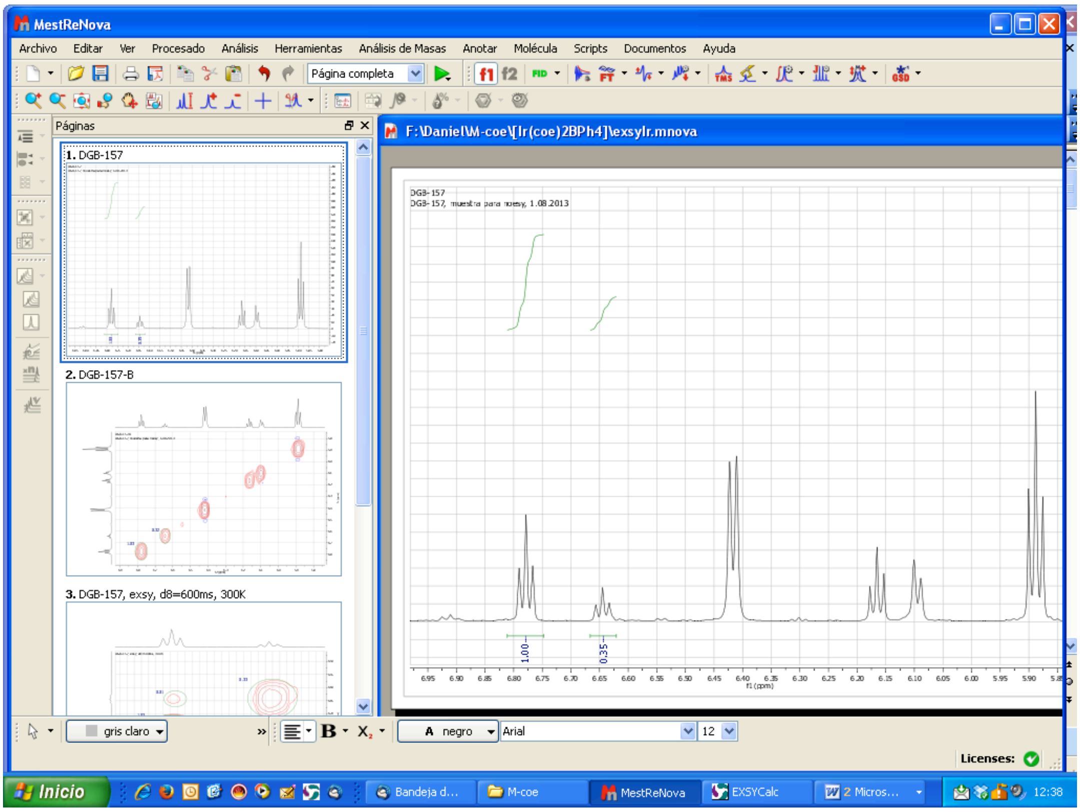
	Diagonal peak
A	1.00
B	1.02

```
EXCHANGE RATE MATRIX
================================
-1.681   2.598  |
2.594   -1.295
```

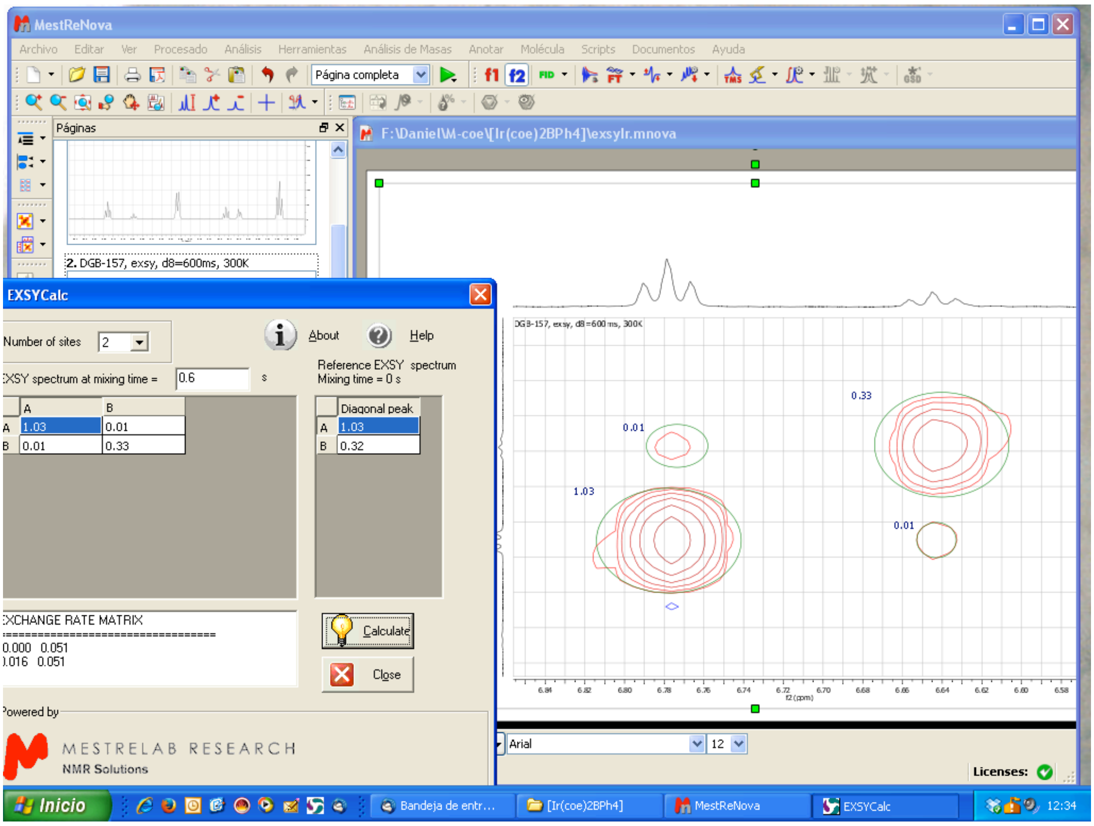
$k_1 = 2.594$; $k_{-1} = 2.598$, **K = 2.594/2.598 = 0.998**

- **[Ir(η^6-C$_6$H$_5$-BPh$_3$)(coe)$_2$] (2)**.

Exsy, $t_m = 0$



Exsy, $t_m = 700$



Number of sites 2

XSY spectrum at mixing time = 0.6 s

	A	B
A	1.03	0.01
B	0.01	0.33

Reference EXSY spectrum
Mixing time = 0 s

	Diagonal peak
A	1.03
B	0.32

```
XCHANGE RATE MATRIX
================================
0.000  0.051
.016  0.051
```

$k_1 = 0.016$; $k_{-1} = 0.051$, **K = 0.016/0.051 = 0.314**