Supporting Information

For

**The reaction of Rhenium Nitrosyl with a sterically hindered NHC-carbene**

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**Description of general procedures, tables, general methods and   
copies of 1H,13C, 15N NMR, HR-ESI-MS and FTIR spectra.**

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**EXPERIMENTAL SECTION**

**General Procedures**

1H NMR, 13C{1H} NMR, data were recorded on a Varian Gemini-300, Varian Mercury 200, or Bruker DRX 500 spectrometer using 5 mm diameter NMR tubes. Chemical shifts are expressed in parts per million. 1H and 13C {1H} NMR spectra were referenced to the residual proton or 13C resonances of the deuterated solvent. 15N NMR spectra were referenced to the NH3(l). The software used for the elaboration of the FIDs were: SpinWorks® (ver. 4.2.11, Dr. Kirk Marat, Chemistry NMR Lab, University of Manitoba) and TopSpin® (Bruker). Signal patterns are reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet, q, quartet. IR spectra were obtained by using ATR methods with a Bio-Rad FTS-45 FTIR spectrometer. All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glove-box (M. Braun 150B-G-II) filled with dry nitrogen. Solvents were freshly distilled under N2 by employing standard procedures. The Sodium nitrite 15N had a purity of 98 atom % (95% 15N, (CP)) and was purchased, as the rest of the chemicals, by Sigma Aldrich and used as received. The nitrogen monoxide (NO) gas had a grade of purity of 2.5 (99.5%) purchased by Pan Gas AG (Dagmersellen, Switzerland). The deuterated solvents were dried with sodium/benzophenone and vacuum transferred for storage in Schlenk flasks fitted with Teflon valves. Microanalyses were carried out at the Anorganisch-Chemisches Institut of the University of Zurich, while the ESI-MS spectroscopic data were obtained from an HCT Esquire Bruker Daltonics instrument.   
**WARNING: NO May cause or intensify fire. It is an oxidizer. It may be fatal if inhaled. Symptoms may be delayed. It causes severe skin burns and serious eye damage. Use it only under a fume hood with proper ventilation.**

**Synthesis of the mixture of 2 and 3.**

In a 500 mL round‒bottom flask, to a solution of complex **1** [(PPh3)2ReOCl3] (1000 mg, 1.20 mmol) in toluene (250 mL) was added CH3COOH (150 μL). The suspension was stirred at 80°C while and NO was slowly bubbled in until the yellow suspension became a dark green solution (3 hours). Then the solution was filtrated and the solvent was reduced to 20 mL and the solution was dropped in pentane (250 mL). The green solid precipitated was triturated in Et2O (50 mL) and the filtrated was reduced to 5 mL and then dropped in pentane (70 mL). The solid was washed with further pentane (50 mL) and then dried to afford in 561 mg of a crystalline green powder. IR bands (KBr pellet): ν(NO) = 1882, 1792, 1762 cm-1. The following NMR measurement refers to the diamagnetic complex 3: 31P NMR (300 MHz; THF-d8) 28.76 ppm (sharp), 13C {1H} (75 MHz; THF-d8): δ 132.93, 132.80, 132.33, 132.30, 129.25, 129.09 ppm; 1H NMR (300 MHz, THF-d8): δ 7.71-7.41 ppm (m). HR-ESI-MS (CH3CN+NaOH): value for complex **3**: Anal. Calc.d for C18H16Cl3N2O4ReNa: 652.93151; Found: 652.93094 (S16, SI). Value for complex 2: Anal. Calc.d for: C36H30Cl3NO3P2ReNa: 901.01970; Found: 901.01922 (S17, SI).

**Synthesis of 4.**

In a 50 mL Schlenk vessel, to a solution dark green solution of the mixture of **2** and **3** (100 mg) in toluene (10 mL) was added at once the 1,3-Bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (IMes free carbene) (49 mg, 0.16 mmol) and the solution switched immediately to dark blue-violet. The solution was stirred at room temperature overnight. Then the solvent was evaporated and the violet solid was dissolved in THF (2 mL) and adsorbed on silica. The silica was then dried and the solid obtained was added to the top of a column that was wet packed with Et2O. A rapid elution with Et2O gave the pure product (it is the first that elutes out of the column). The evaporation of the solvent afforded in 113 mg (0.121 mmol) of a blue violet powder. Yield = 76 % (based on the moles of IMes, MW=935.29). IR bands: ν(NO) = 1749 cm-1(sharp). 31P NMR (300 MHz; THF-d8): δ 42.42 ppm (sharp). 13C {1H} (75 MHz; THF-d8): δ 149.27, 139.96, 135.86, 134.70, 134.55, 133.10, 132.99, 132.78, 132.31, 132.28, 130.09, 125.22, 129.06, 128.94, 128.86, 126.69, 21.16, 18.26. 1H (300 MHz, THF-d8): δ 7.65 (m, 6H), 7.55 (m, 3H), 7.45 (dt, 2H), 7.37 (dt, 3H), 7.14 (s, 2H), 7.10 (s, 2H), 6.70 (s, 6H), 2.34 (s, 6H) 2.07 (s, 12H). Elemental analysis: calc.d for C39H39Cl3N4O3PRe (935.29): C, 50.08; H, 4.20; N, 5.99. Found: C, 50.21; H, 4.37; N, 5.77.

**Labelling procedure to obtain the mixture of the labelled complexes 7 and 8.**

Under nitrogen, in a double necked 50 mL round bottom flask, to a solution of the complex 1 [(PPh3)2ReOCl3] (250 mg, 0.30 mmol) in toluene (20 mL) was added glacial acetic acid (20 μL). In another 50 mL double necked round bottomed flask connected to the above mentioned one through a short rubber hose, the 15NO gas was generated dropping H2SO4 conc. (9.8 mL) on a mixture of solid FeSO4\*7H2O (3810 mg, 7.5 mmol) and Na15NO2 (450 mg, 6 mmol). The evolved gas was transferred inside the reaction vessel containing complex 1, were vacuum was created. The solution was stirred in closed vessel at 80°C and during this time the starting yellow suspension became a dark green solution (3 hours). Then, the solvent was removed and the sticky solid triturated in THF (10 mL), filtrated (to have rid of the starting material) and the filtrate dropped into pentane (70 mL). The light green-yellow solid precipitate was then collected by filtration. The solid was washed with Et2O (70 mL) and then with pentane (30 mL) and then dried to afford in 156 mg of a crystalline green powder. IR bands (KBr pellet): ν(15NO)= 1842 cm-1 (broad); ν(15NO) = 1744 cm-1 (broad). 31P NMR (500 MHz; THF-d8): δ 27.01 ppm (sharp). 1H NMR (500 MHz; THF-d8): δ 7.70 (dd, 2H, J =7.5Hz), 7.56 (t, 1H, J = 7.5 Hz), 7.47 (td, 2H, J = 7.5 Hz). 13C {1H} (125 MHz, THF-d8) δ 132.90, 132.76, 132.31, 132.27, 129.22, 129.07.

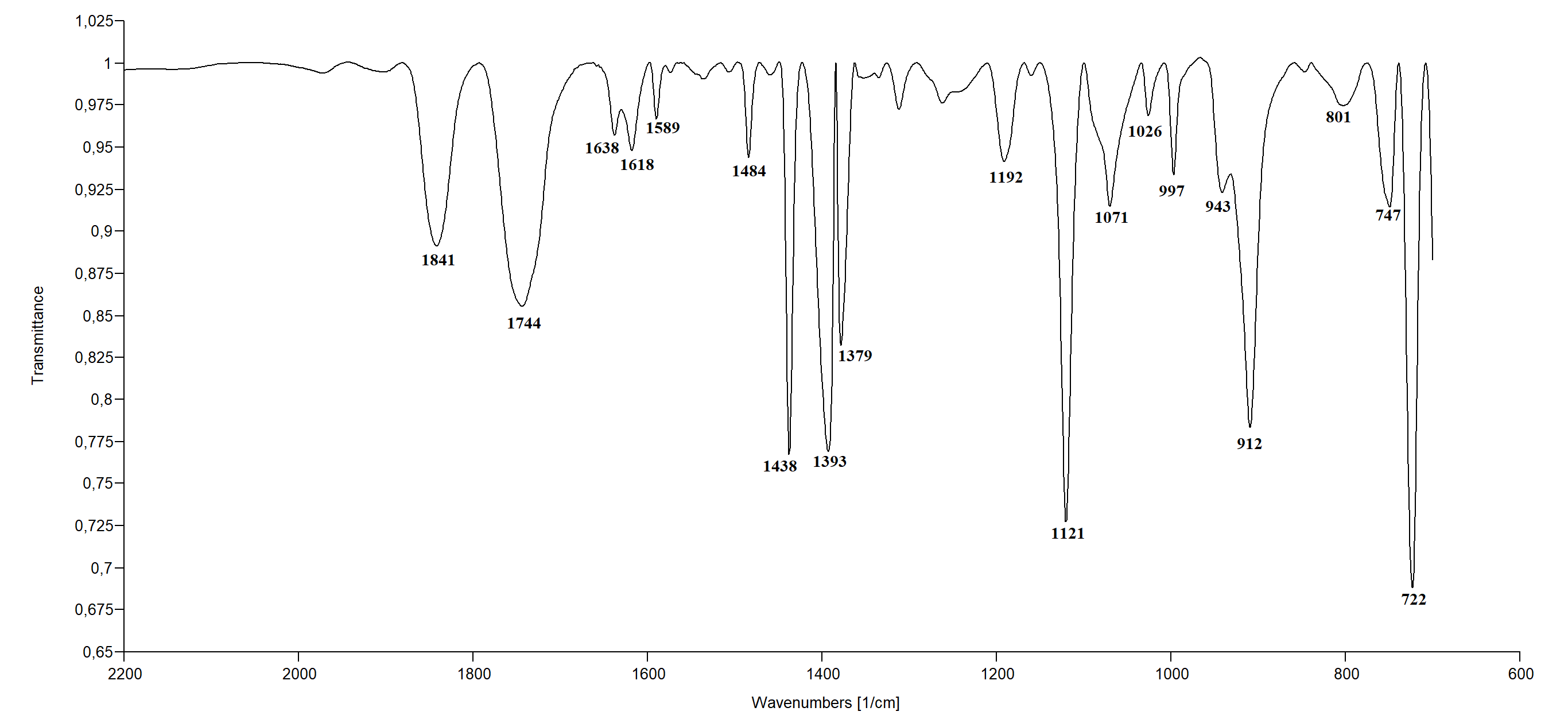


Figure S5. FTIR spectrum of the labelled complexes **7** and **8** as solid KBr pellet.

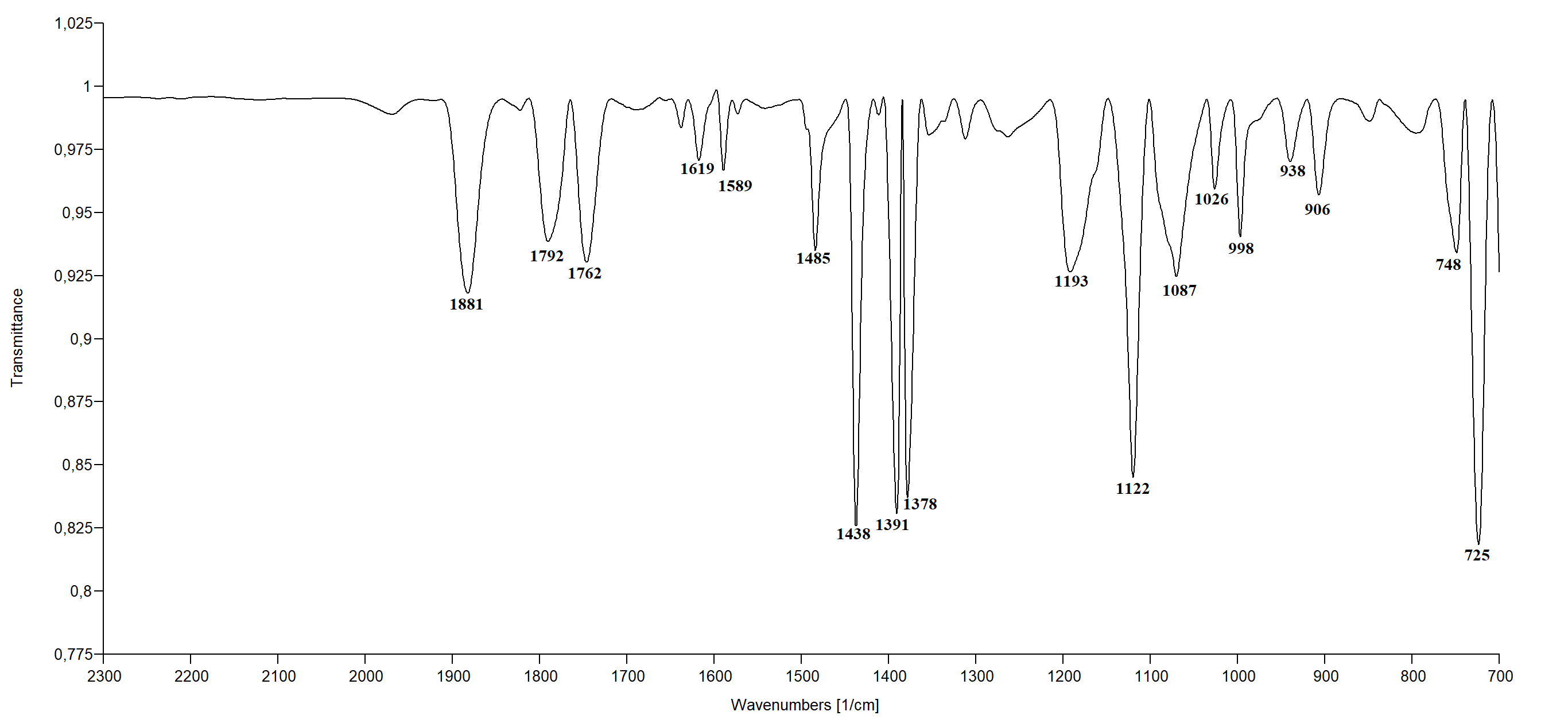
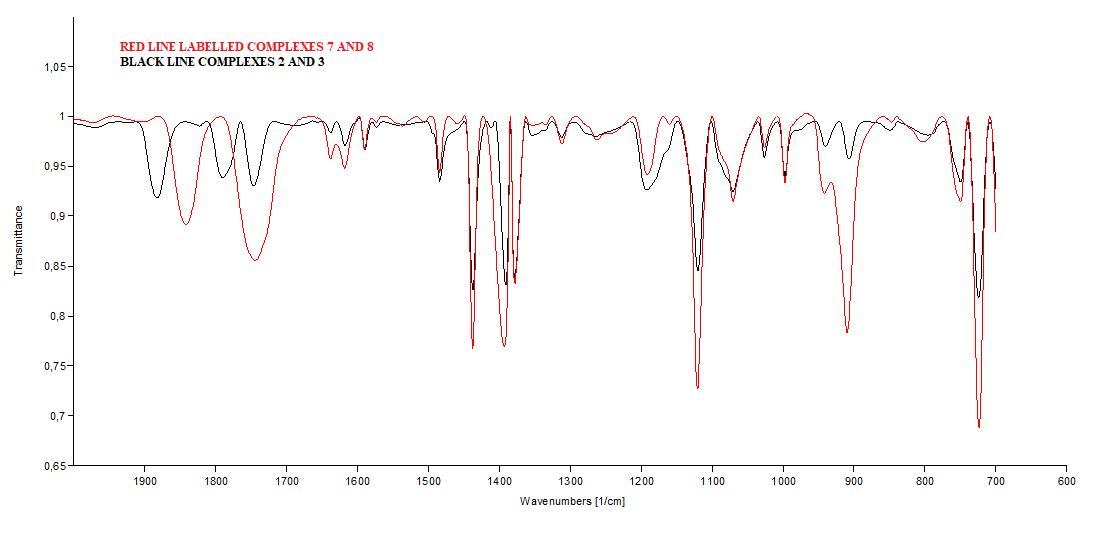


Figure S6. FTIR spectrum of the complexes **2** and **3** as solid KBr pellet.

Figure S7. Overlapped FTIR spectra of the complexes **2** and **3** and of the labelled complexes **7** and **8** as solid KBr pellets.



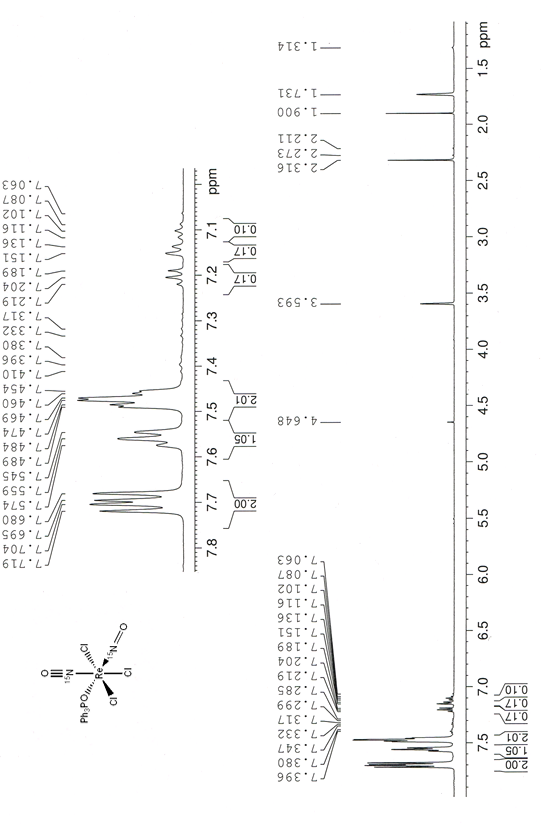
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Figure S8. 500 MHz, 1H NMR complexes **7** and **8** in THF d8.

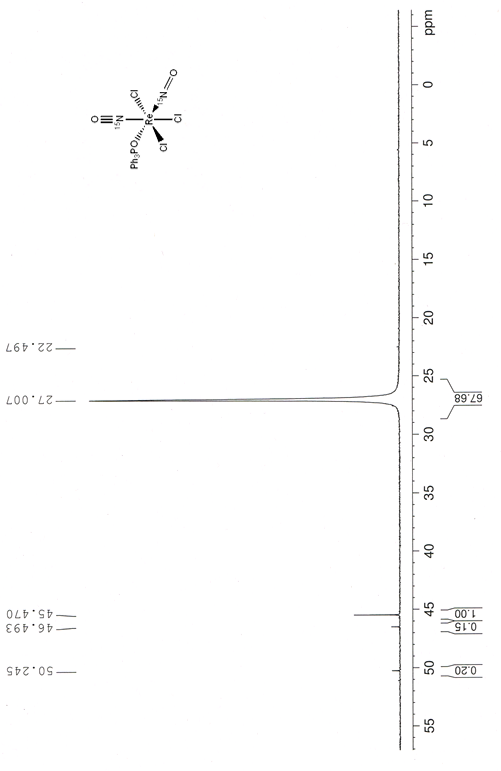
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Figure S9. 500 MHz, 31P NMR complexes **7** and **8** in THF d8.

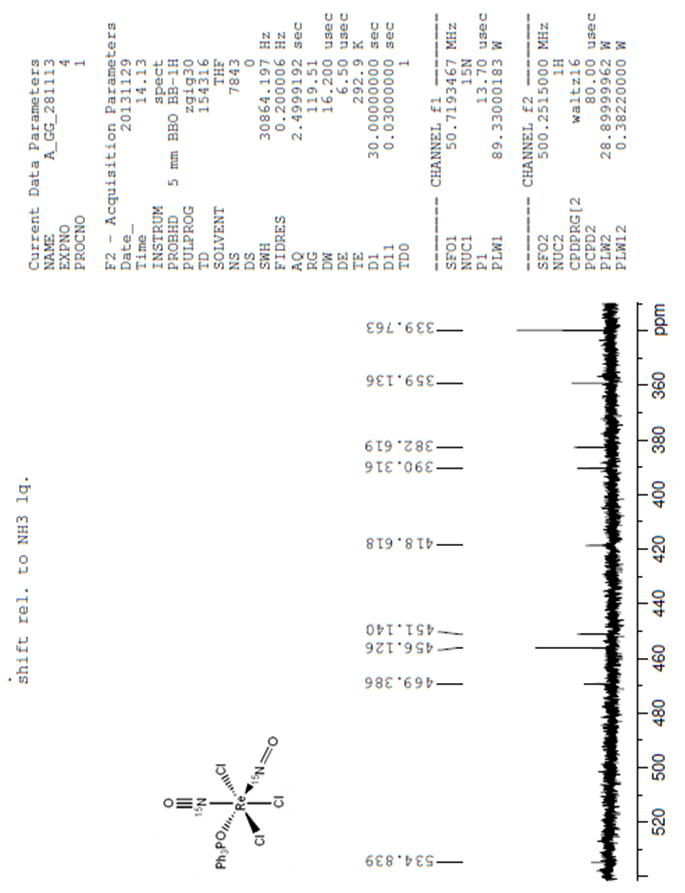


Figure S10. 500 MHz, 15N NMR complexes **7** and **8** in THF d8.

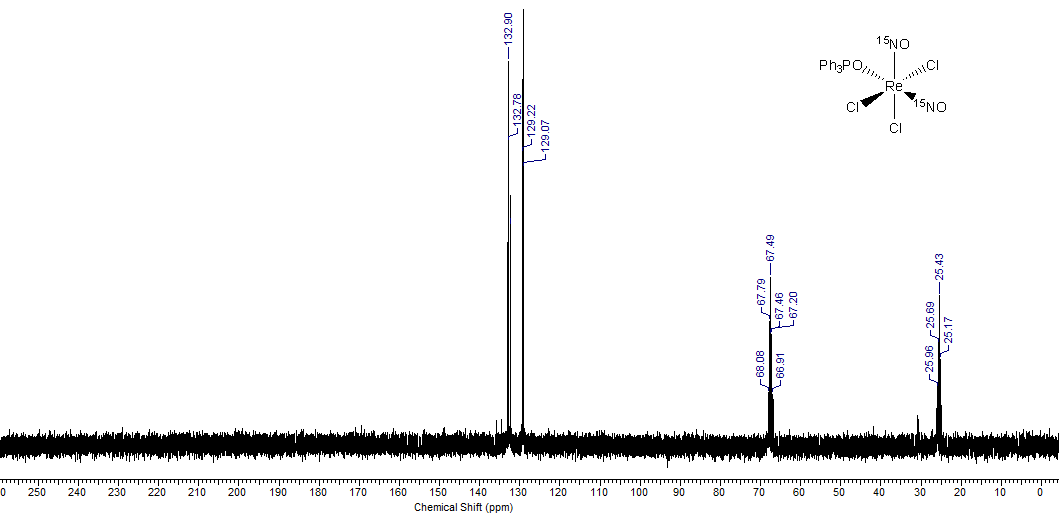


Figure S11. 125 MHz, 13C NMR complexes **7** and **8** in THF d8.

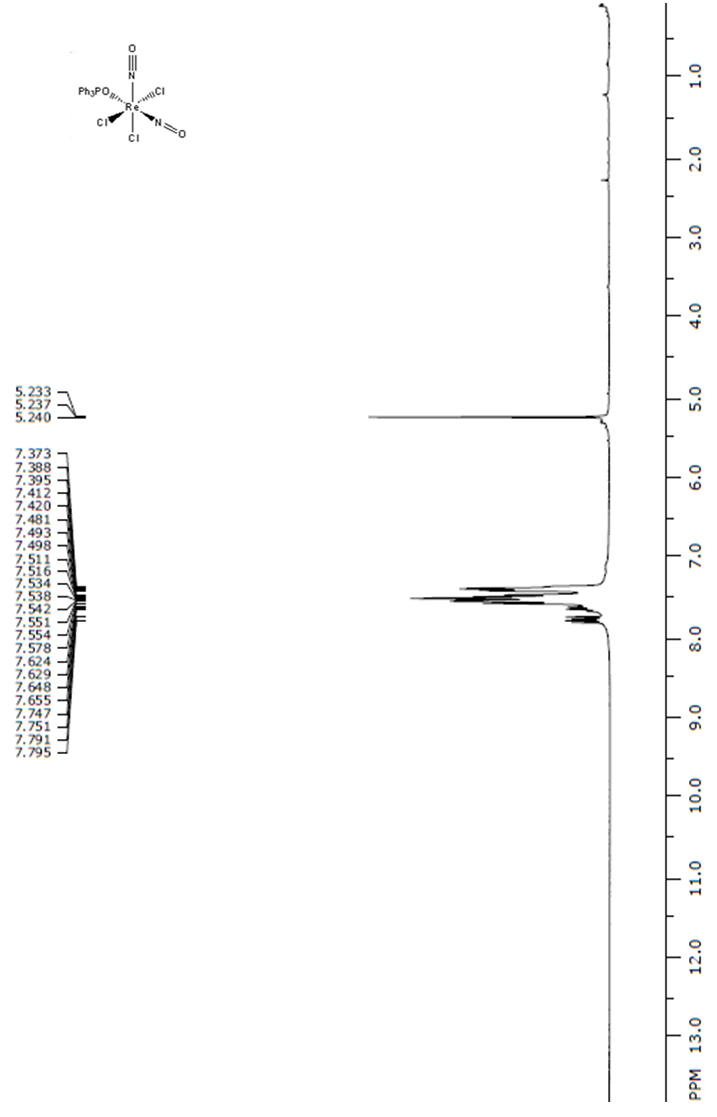


Figure S12. 300 MHz, 1H NMR complexes **2** and **3** in CD2Cl2.

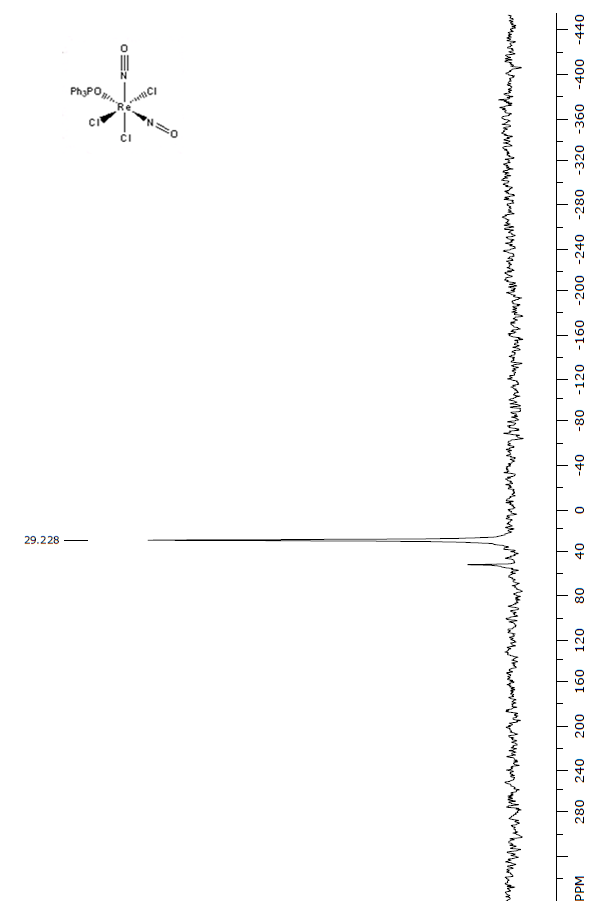


Figure S13. 300 MHz, 31P NMR complexes **2** and **3** in CD2Cl2.

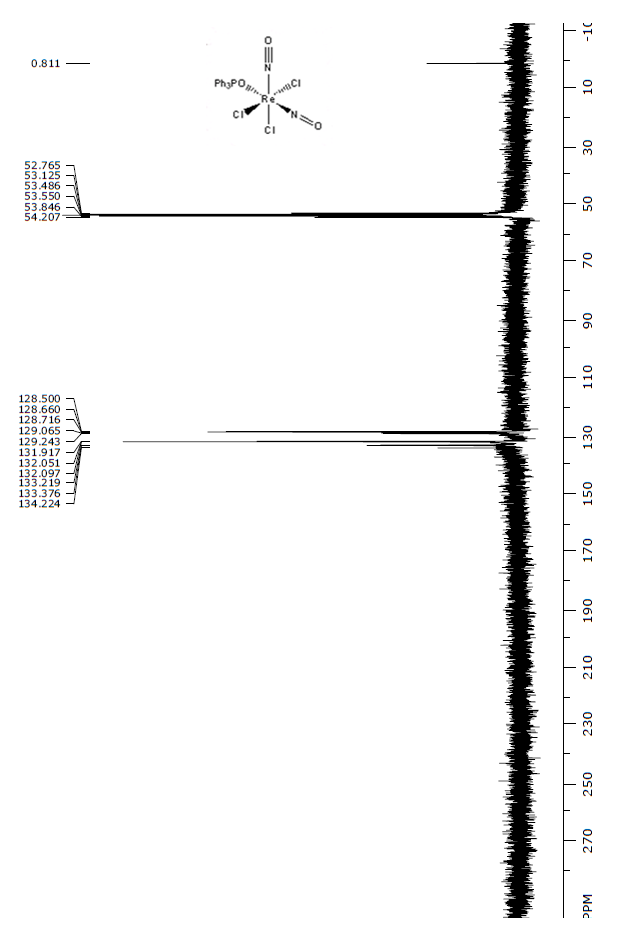


Figure S14. 75 MHz, 13C NMR complexes **2** and **3** in CD2Cl2.

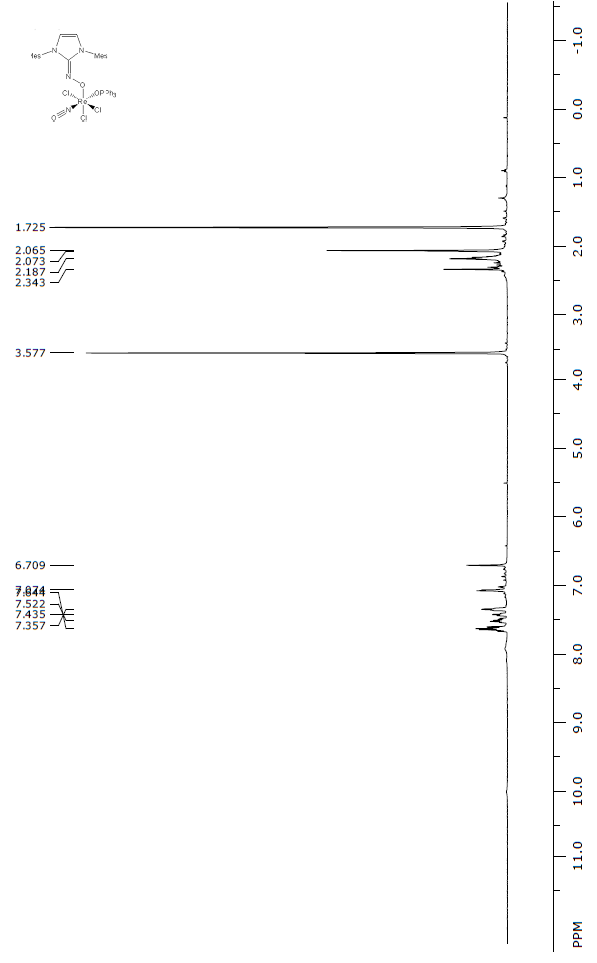


Figure S15. 300 MHz, 1H NMR complex **4** in THF d8.

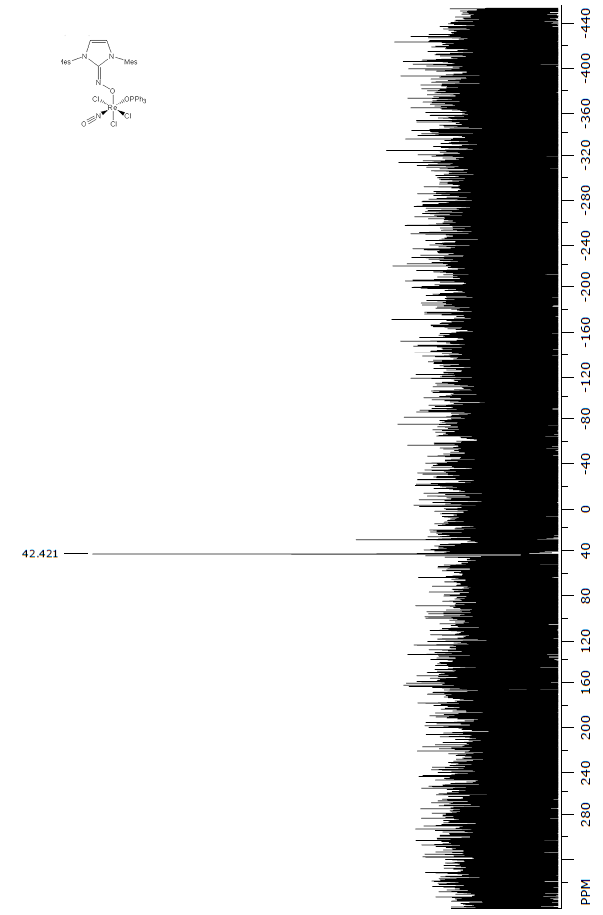
in

Figure S16. 300 MHz, 31P NMR complex **4** in THF d8.

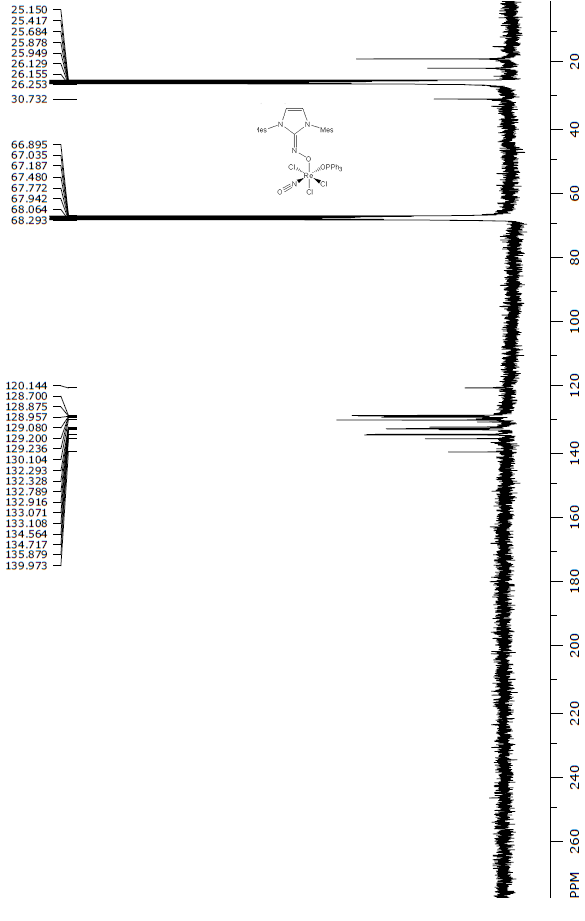


Figure S17. 75 MHz, 13C NMR complex **4** in THF d8.

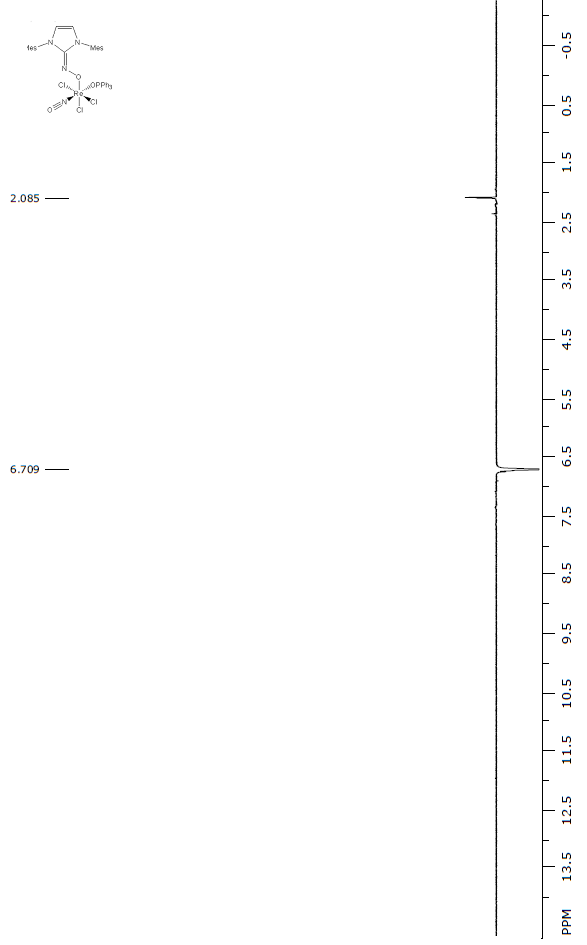


Figure S18. 500 MHz, NOE complex **4** in THF d8.

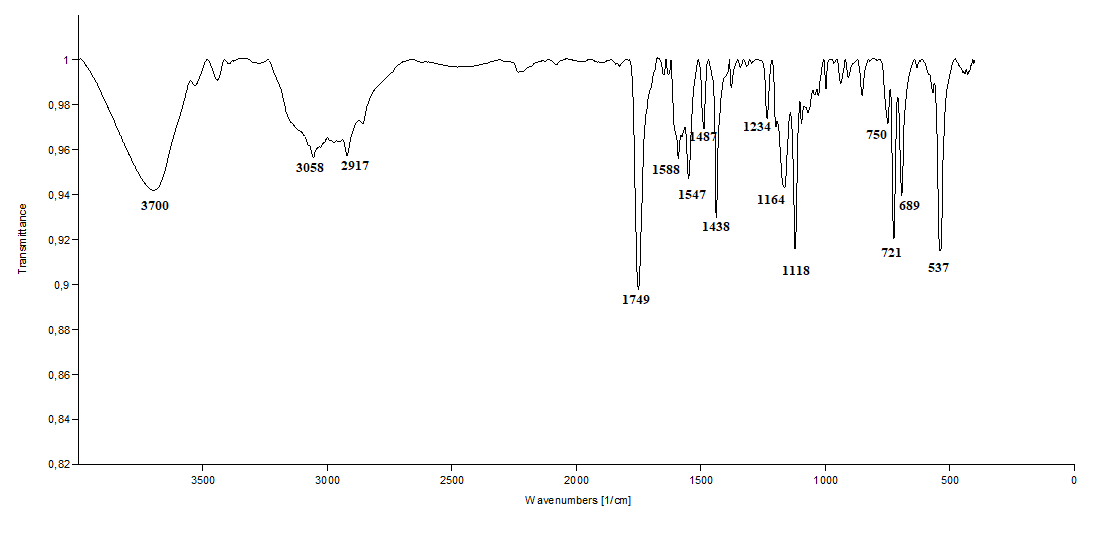
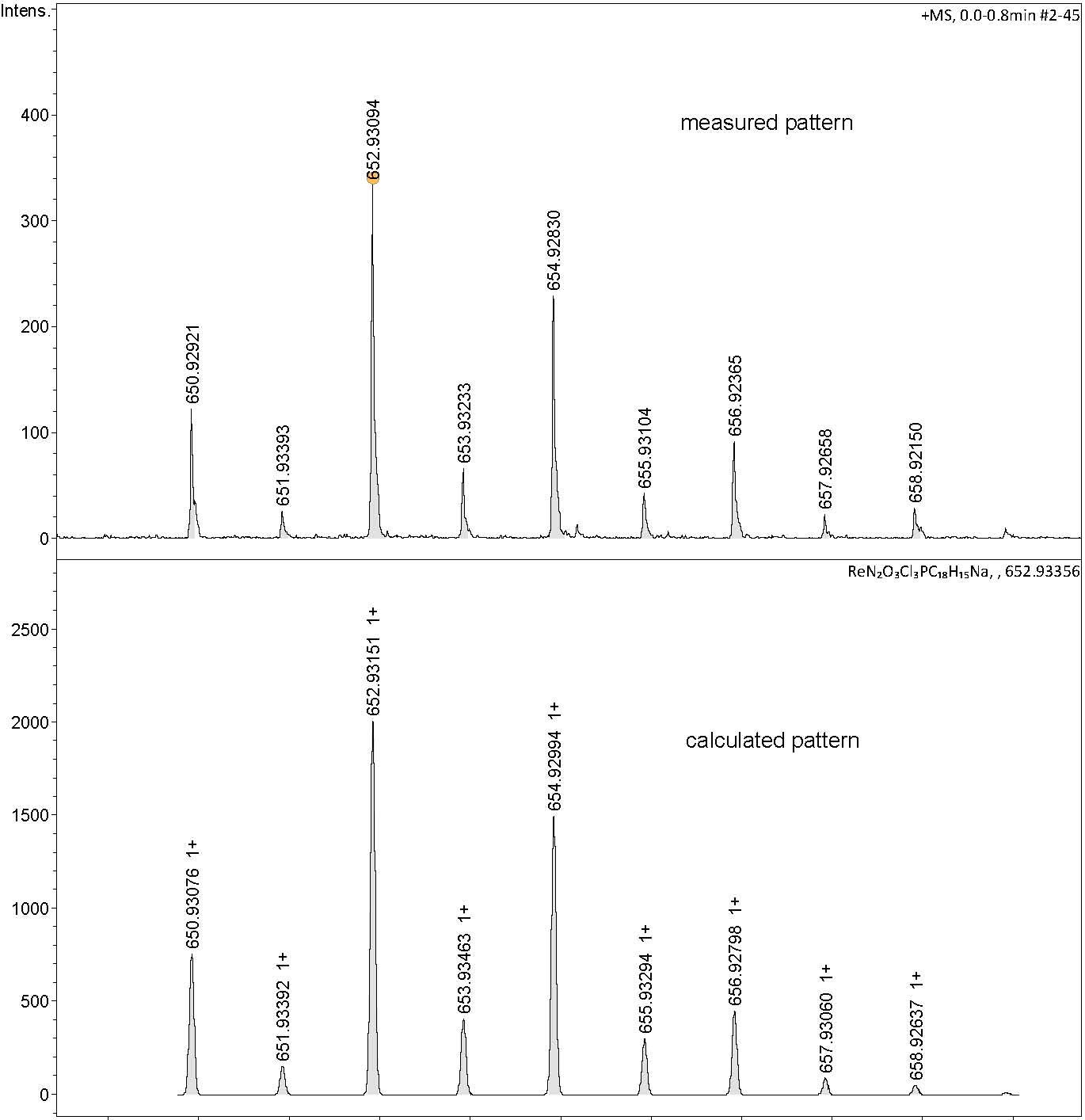


Figure S 19. FTIR complex **4** as solid KBr pellet.

Figure S20. HR-ESI complexes **2** and **3**. Detection of **3** (solvent CH3CN + NaOH)

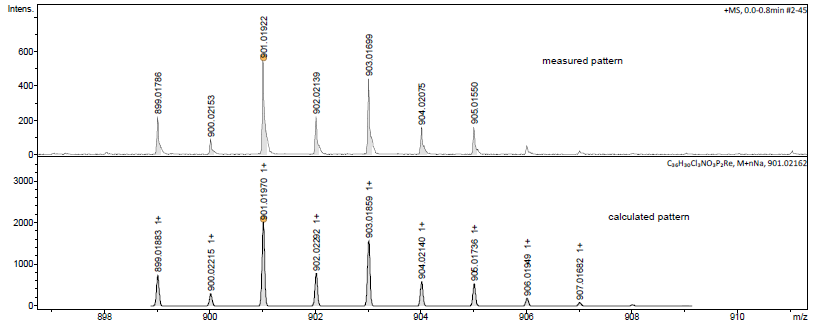
|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Analysis Info** | |  | |  | Acquisition Date | | 4/11/2014 10:36:27 AM | | |
| Analysis Name | | D:\Data\Service\6042alhres.d | |  |  | |  | | |
| Method | tune\_low\_modified\_09\_01\_14\_pos.m | | |  | Operator | ust | |  | |
| Sample Name | [Re(NO)2Cl3(OPPh3)] | | |  | Instrument | maXis | | 255552.00033 | |
| Comment | Solvent: MeCN + NaOH | | |  |  |  | |  | |
| Client: Grieco | | | |  |  | | | | |
| **Acquisition Parameter** | | | |  |  | | | | |
| Source Type | ESI | | Ion Polarity | Positive | Set Nebulizer | | | | 0.3 Bar |
| Scan Begin | 50 m/z | | Set Capillary | 3000 V | Set Dry Heater | | | | 180 °C |
| Scan End | 3000 m/z | | Set End Plate Offset | -500 V | Set Dry Gas | | | | 4.0 l/min |



HR-ESI-MS (Bruker maXis)

Figure S20. HR-ESI complexes **2** and **3**. Detection of **2** (solvent CH3CN + NaOH)

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Analysis Info** | |  | |  | Acquisition Date | | 4/11/2014 10:36:27 AM | | |
| Analysis Name | | D:\Data\Service\6042alhres.d | |  |  | |  | | |
| Method | tune\_low\_modified\_09\_01\_14\_pos.m | | |  | Operator | ust | |  | |
| Sample Name | [Re(NO)Cl3(OPPh3)2] | | |  | Instrument | maXis | | 255552.00033 | |
| Comment | Solvent: MeCN + NaOH | | |  |  |  | |  | |
| Client: Grieco | | | |  |  | | | | |
| **Acquisition Parameter** | | | |  |  | | | | |
| Source Type | ESI | | Ion Polarity | Positive | Set Nebulizer | | | | 0.3 Bar |
| Scan Begin | 50 m/z | | Set Capillary | 3000 V | Set Dry Heater | | | | 180 °C |
| Scan End | 3000 m/z | | Set End Plate Offset | -500 V | Set Dry Gas | | | | 4.0 l/min |

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HR-ESI-MS (Bruker maXis)

**Table S22**. Infrared data of the mixture of the complexes **2** and **3**.

|  |  |  |
| --- | --- | --- |
| **Band position (1/cm)** | **Assignment** | |
| 1881 | ν (NO+) complex **3** |
| 1792 | ν (NO+) complex **3** |
| 1762 | ν (NO) complex **2** |
| 1589 | ν (C—C) in the plane complex **3** |
| 1485 | ν (C—C) in the plane complex **2** |
| 1438 | ν (P—C6H5) complexes **2** and **3** |
| 1391 | ν (NO‒) complex **3** |
| 1378 | ν (NO‒) complex **3** |
| 1193 | ν (O=P) complex **2** and **3** |
| 1122 | δ (C—CH) in the plane complexes **2** and **3** |
| 1087 | δ (C—CH) in the plane complexes **2** and **3** |

**DFT CALCULATIONS EXCLUDING THE HYPOTHESIS OF DIMERS OF COMPLEX 3**

Considering the dimeric complex **D1** as the reference, the structures that are highest in calculated energy are the ones in which the NOs are in trans position to each other or are bridging the two Re centres. In this way it is possible to exclude the presence of the dimeric complexes **D4**, **D5**, **D6**, **D7** and **D8** due to their high energies. The possible structures left are **D2** and **D3**. A lower energy is associated with the dimeric complex **D2**, probably because all the NO ligands are placed in way to do not electronically interfere with each other. For instance,Rattat and Berke prepared dimeric rhenium complexes whose FTIR spectra were not distinguishable.**1** Further calculations were carried out to understand whether η2 NO structures of **3** would be the possible intermediates in the NHC attack (Scheme 6). These calculations revealed that **B2** is energetically favoured when compared with the **B1** taking the latter as the energetic reference with a value of zero. The lower calculated energy shown by **B2** is probably due to the fact that in the latter structure a TTPO ligand is located trans to the NO, while in the complex **B1** there is a strong trans labilizing ligand as the Cl in this position. The complex **3** does probably not give rise to dihapto NO complexes, since the corresponding energies are more than 22 kcal/mol higher than the energy of the complex **B1**, and consequently more than 26 kcal/mol higher than the one of complex **B2** (Scheme 6). Considering the geometry of the complex **B1** as the reference, we can see that the isomer that corresponds to the solid- state structure of the complex **3**, has a lower energetic difference (-4.3 kcal/mol). We conclude that the η2 isomers show too high calculated energies that make their formation in solution unlikely to happen.



Scheme S23. Possible dimeric structures of complex 3 calculated by means of DFT calculations. Here are shown the isomeric dimeric structures that could form after loss of a TPPO of the complex 3.



Scheme S24. Potential η2 Re—NO intermediates in solution evaluated by gas phase DFT calculations.

1. D. Rattat, A. Verbruggen and H. Berke, *Zeitschrift für Anorganische und Allgemeine Chemie*, 2006, **632**(7), 1351‒1355.

**Table S25** - Conditions employed in the nitrosylation of complex **1**. The procedure followed was the one described in “Synthesis of the mixture of **2** and **3**”.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Entry | NO (g) | AcOH (µL) | Temp.(°C) | Time (h) | Yield |
| 1 | Saturated solution | 150 | RT | 3 | **2**+**3**+**S.Mat** |
| 2 | Saturated solution | 150 | 50°C | 3 | **2**+**3**+**S.Mat** |
| 3 | Saturated solution | 150 | 80°C | 3 | **2**+**3** |
| 4 | Saturated solution | 300 | 80°C | 3 | **2**+**3** |
| 5 | Saturated solution | 450 | 80°C | 3 | **2**+**3** |
| 6 | Saturated solution | 450 | 80°C | Overnight | **2**+**3+indefinite products** |