

ESI for:

Reversible formal insertion of CO₂ into a remote C-H bond of a ligand in a Ru(II) complex at room temperature

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Experimental Section

General information:

All operations were performed using Schlenk/vacuum-line techniques under either dinitrogen, or carbon dioxide, or in a dinitrogen atmosphere glovebox from MBraun. Complex **1** was prepared from a literature procedure.^[1] All glassware was dried overnight in a 180 °C oven prior to use except for J. Young NMR tubes which were dried overnight in a 60 °C oven. Carbon dioxide was purchased from Linde (Grade 4.0), ¹³CO₂ was from Sigma Aldrich and used without further purification. THF, DME, THF-*d*₈ were dried over Na/benzophenone and either distilled under nitrogen or vacuum-transferred before use. Toluene, pentane and hexanes were dried after passing through a Pure Solv Innovative Technology Grubbs'-type solvent purification system, and degassed through three consecutive freeze-pump-thaw cycles. ¹H, and ³¹P spectra were recorded on a Varian 400 MHz NMR spectrometer. All chemical shifts are reported in ppm relative the residual protio-solvent peaks, and ³¹P NMR are referenced externally using 85% H₃PO₄ in a flame-sealed capillary. FT-IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. Elemental analysis was performed by ANALEST at the University of Toronto.

Synthesis and characterization of **2**:

In the glovebox, 107 mg (0.13 mmol) of **1** was suspended and dissolved partially in 20 mL of DME and placed inside a pyrex solvent bomb with re-sealable Teflon valve and removed from the glovebox. The purple mixture was degassed via two freeze-pump-thaw cycles. The mixture inside the bomb was chilled to -30 °C and CO₂ was introduced. After 3h under CO₂ in the cold bath an orange microcrystalline precipitate results, the solution was briefly degassed by opening to vacuum and the bomb was sealed under a partial static vacuum and brought into the glovebox for workup. The orange crystals were quickly collected by filtration, washed with a small amount of DME and pentane and dried under vacuum (61 mg, 50% yield based on (2)•0.75(DME) formula unit). This sample was subjected to NMR studies in THF-*d*₈ (described below) and elemental analysis. Crystals out of DME were subjected X-ray crystallographic analysis, but were not of publication quality since only the connectivity could be determined. Crystals of **2** suitable for X-ray crystallographic analysis were grown under CO₂ from toluene, by allowing CO₂ to diffuse slowly through a glass capillary into a septum-sealed vial containing a toluene solution of **1**.

A 7 mg sample of bright orange **2** was partially dissolved in THF-*d*₈, filtered, and placed in a J. Young tube. After approximately 10 min at R. T. the initially bright orange solution appears brown and the ¹H and ³¹P NMR spectra were recorded, revealing a mixture of **1** and **2** and residual DME (see Figures S1, S2, and S3). The J. Young tube was then degassed via two freeze-pump-thaw cycles, and CO₂ was introduced at R. T. Immediately after introduction of CO₂ the solution appears bright orange and after approximately 10 min the ¹H and ³¹P NMR spectra were recorded revealing only the presence of **2** and residual DME (see Figures S4, S5, S6, S7). ¹³C NMR could not be obtained due to poor solubility of **2** in THF-*d*₈. ¹H NMR under CO₂ (400 MHz, 25 °C, THF-*d*₈): δ 9.27 (s, 1H), 8.06-8.04 (m, 2H), 7.91 (d, J=7.6Hz, 2H), 7.14-6.99 (m, 26H), 6.90 (dd, J=5.0Hz, J=7.7Hz, 2H), 6.62 (dd, J=0.9Hz, J=4.9Hz, 2H), 6.19 (dd, J=5.0Hz, J=7.9Hz, 2H), -12.75 (t, J=19.5Hz, 1H). ³¹P NMR under CO₂ (161.8 MHz, 25 °C, THF-*d*₈): δ 48.67 (s, 2P). IR (nujol mull): ν(Ru-N₂) 2097 cm⁻¹ (s), ν(C=O) 1609 cm⁻¹ (s). Anal. Calcd. For (C₄₈H₃₈N₄O₂P₂Ru)•0.75(C₄H₁₀O₂) (note: ratio of **2** to DME determined from integration of ¹H NMR spectrum after introduction of CO₂): C, 65.62; H, 4.91 ; N, 6.00. Found: C, 65.26; H, 4.51; N, 6.28.

NMR data for **1** in THF-*d*₈:

Previously complex **1** was characterized by NMR spectroscopy in C₆D₆,^[1] here the ¹H and ³¹P chemical shifts of **1** in THF-*d*₈ are reported. ¹H NMR (400 MHz, 25 °C, THF-*d*₈): δ 7.89 (d, J=4.4Hz, 1H), 7.41 (d, J=8.2Hz, 1H), 7.27 (dd, J=0.7Hz, J=8.0Hz, 1H), 7.12-6.95 (m, 30H), 6.69 (dd, J=4.5Hz, J=8.0Hz, 1H), 6.56 (dd, J=0.8Hz, J=4.8Hz, 1H), 6.01 (dd, J=4.8Hz, J=8.0Hz, 1H), 5.76 (s, 1H), -12.66 (t, J=19.7Hz, 1H). ³¹P NMR (161.8 MHz, 25 °C, THF-*d*₈): δ 49.06 (s, 2P).

Synthesis and IR characterization of ¹³C-**2**:

¹³C- labelled isotopologue of complex **2** (¹³C-**2**) was synthesized in an analogous way to complex **2**. A J. Young NMR tube containing 0.5 mL of a toluene solution of **1** (20 mg, 0.024 mmol) was degassed, and ¹³CO₂ (~2 atm) was condensed into the J. Young tube and sealed. Within minutes an orange microcrystalline precipitate of ¹³C-**2** formed, workup was done quickly in the glovebox by adding 1 mL of hexanes to the reaction mixture and collecting the product in 20 mL vial, followed by removal of the volatiles under vacuum (16 mg, ~75 % yield). IR (nujol mull): ν(Ru-N₂) 2098 cm⁻¹ (s), ν(C=O) 1574 cm⁻¹ (s).

X-ray Crystallography:

The X-ray diffraction data for structure **2** was collected on a Bruker Kappa Apex II diffractometer, and processed with the Bruker Apex 2 software package.^[2] Data was collected with graphite monochromated Mo Kα radiation (λ = 0.71073 Å), at 150 K controlled by an Oxford Cryostream 700 series low temperature system. The structure was solved by the direct methods and refined using SHELXTL V6.10.^[3] The residual electron density from disordered toluene solvent molecules in the lattice were removed with the SQUEEZE function of PLATON,^[4] and their contributions were excluded in the formula. Disordered phenyl groups were successfully modelled over two positions. Non-hydrogen atoms were refined anisotropically except for disordered portions. The hydride was located directly from the difference Fourier map, while all other hydrogen atoms were calculated using the riding model. The position of the H atom attached to the carboxylic acid group of **2** was calculated to fit with H-bonding patterns.

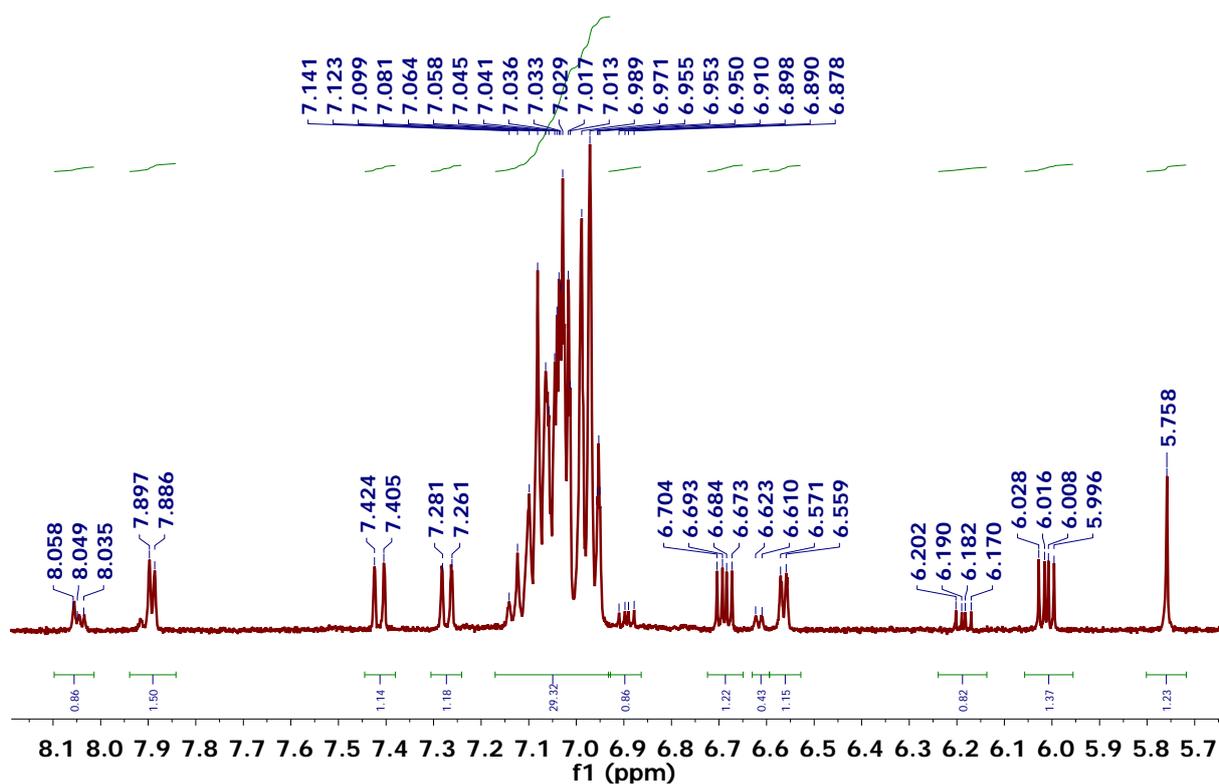


Figure S1. Expansion of aromatic region of ^1H NMR spectrum (400MHz, 25 °C) after dissolving an analytically pure sample of complex $(2)\cdot 0.75(\text{DME})$ in $\text{THF-}d_8$ under N_2 atmosphere.

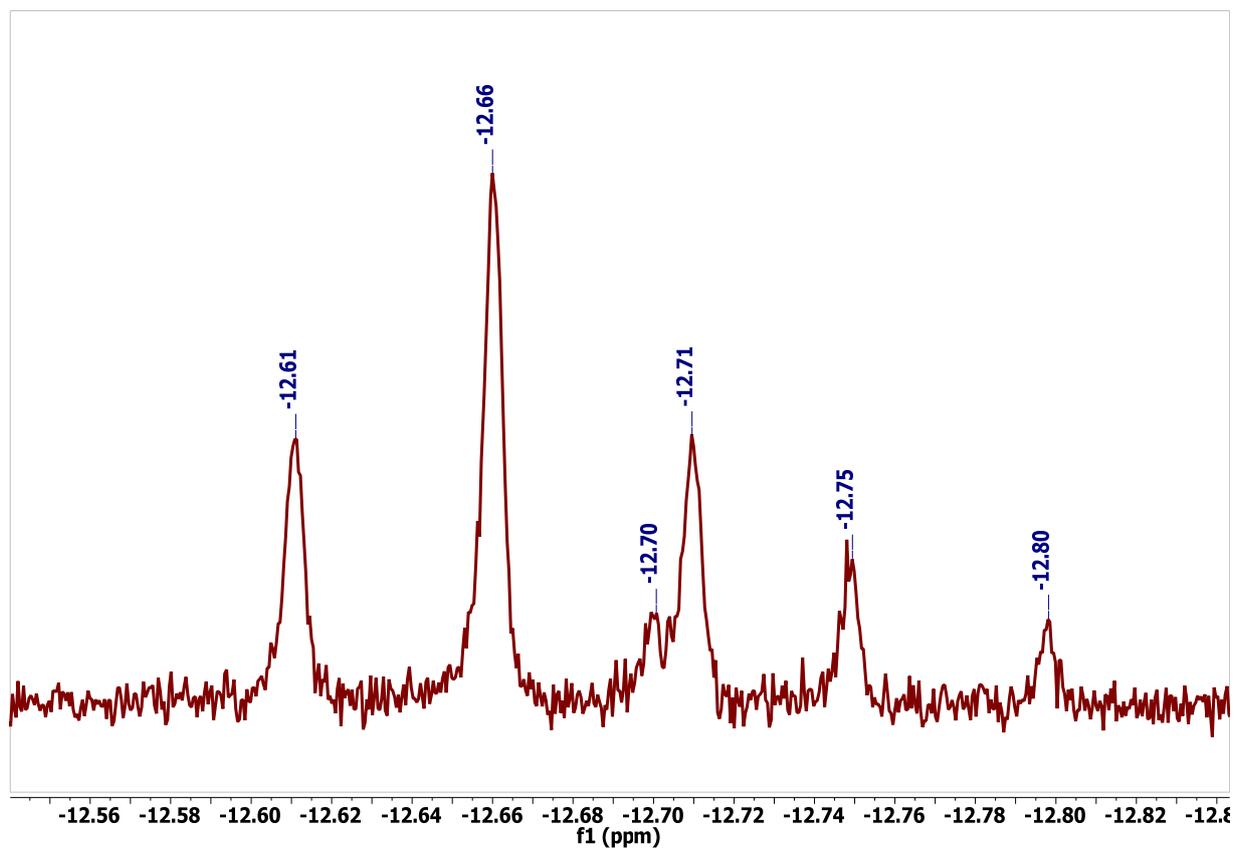


Figure S2. Expansion of hydride region of ^1H NMR spectrum (400MHz, 25 °C) after dissolving an analytically pure sample of $(\mathbf{2})\cdot 0.75(\text{DME})$ in $\text{THF-}d_8$ under N_2 atmosphere. The major species at -12.66 ppm is complex **1**, while the minor species at -12.75 ppm is complex **2**.

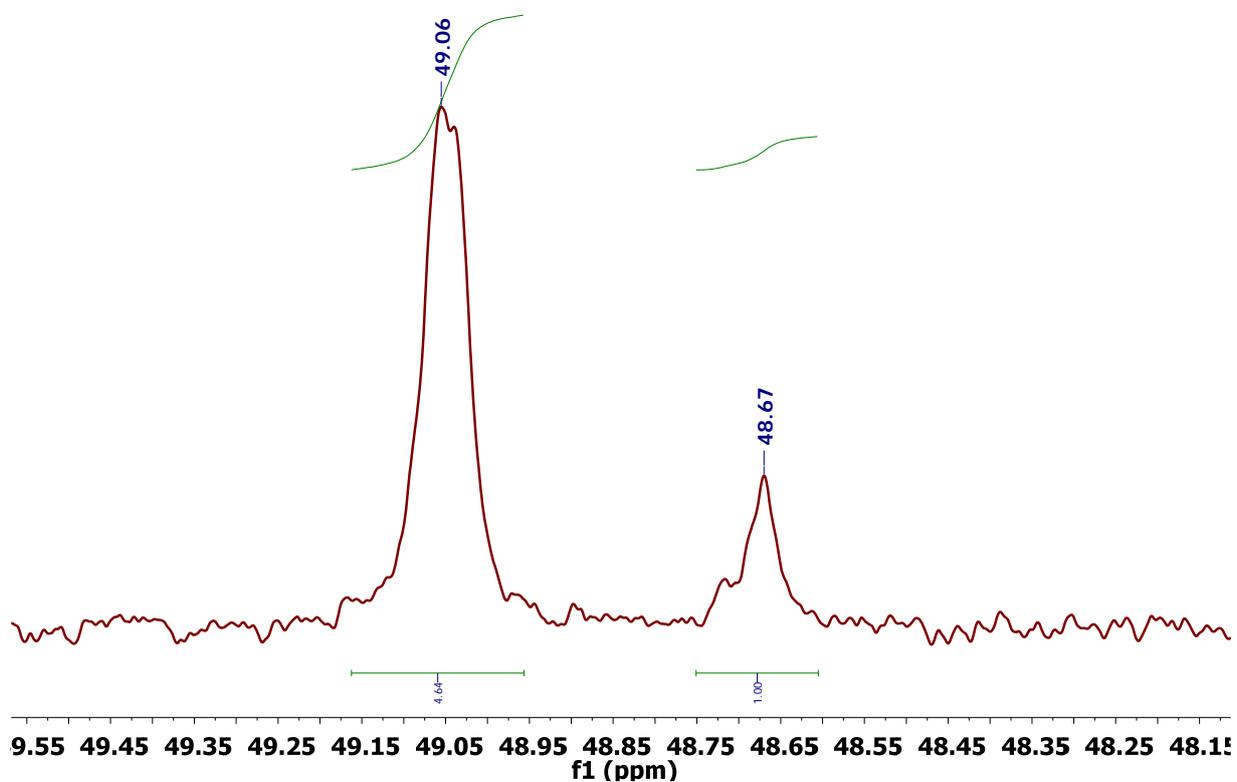


Figure S3. ^{31}P NMR spectrum (161.8 MHz, 25 °C) after dissolving an analytically pure sample of **(2)**•0.75(DME) in THF- d_8 under N_2 atmosphere. The major species at 49.06 ppm is complex **1**, while the minor species at 48.67 ppm is complex **2**.

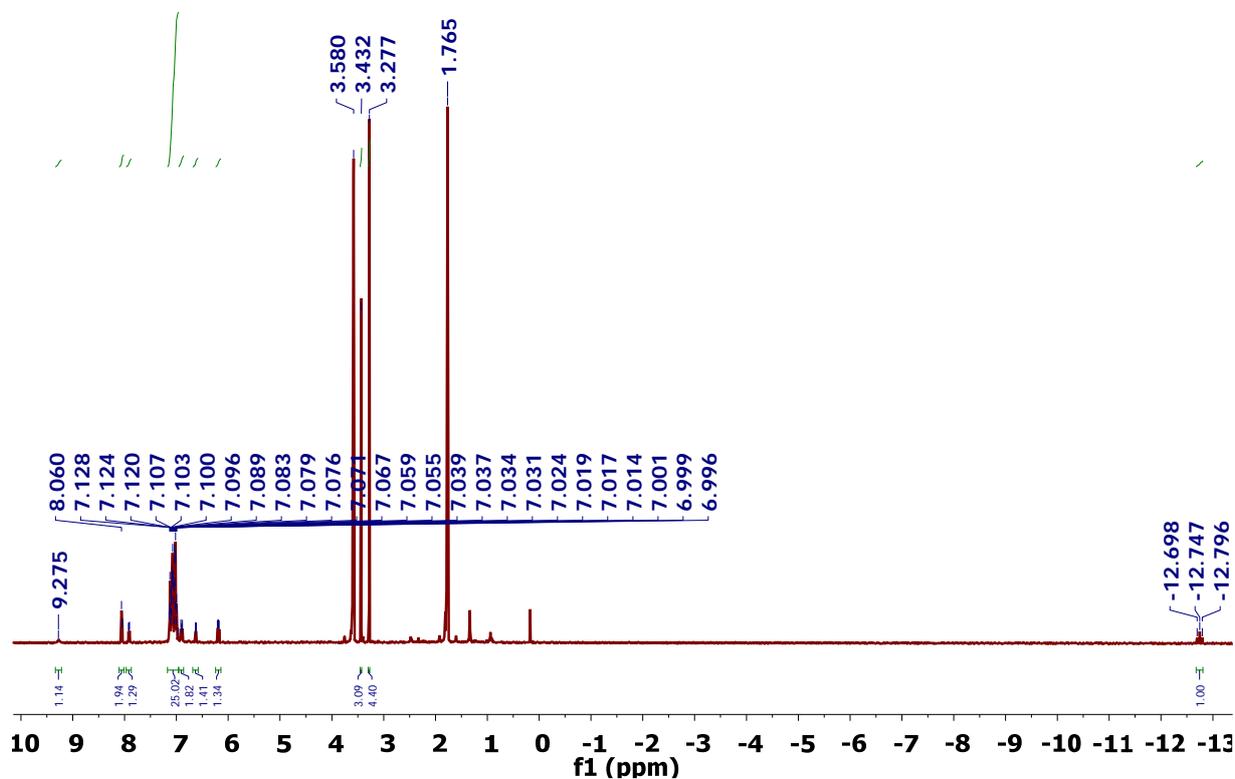


Figure S4. ^1H NMR spectrum (400MHz, 25 °C) of complex (2)•0.75(DME) in THF- d_8 under CO_2 atmosphere. Note peaks at 3.58 and 1.76 are *protio*-THF, and peaks at 3.43 and 3.27 are DME.

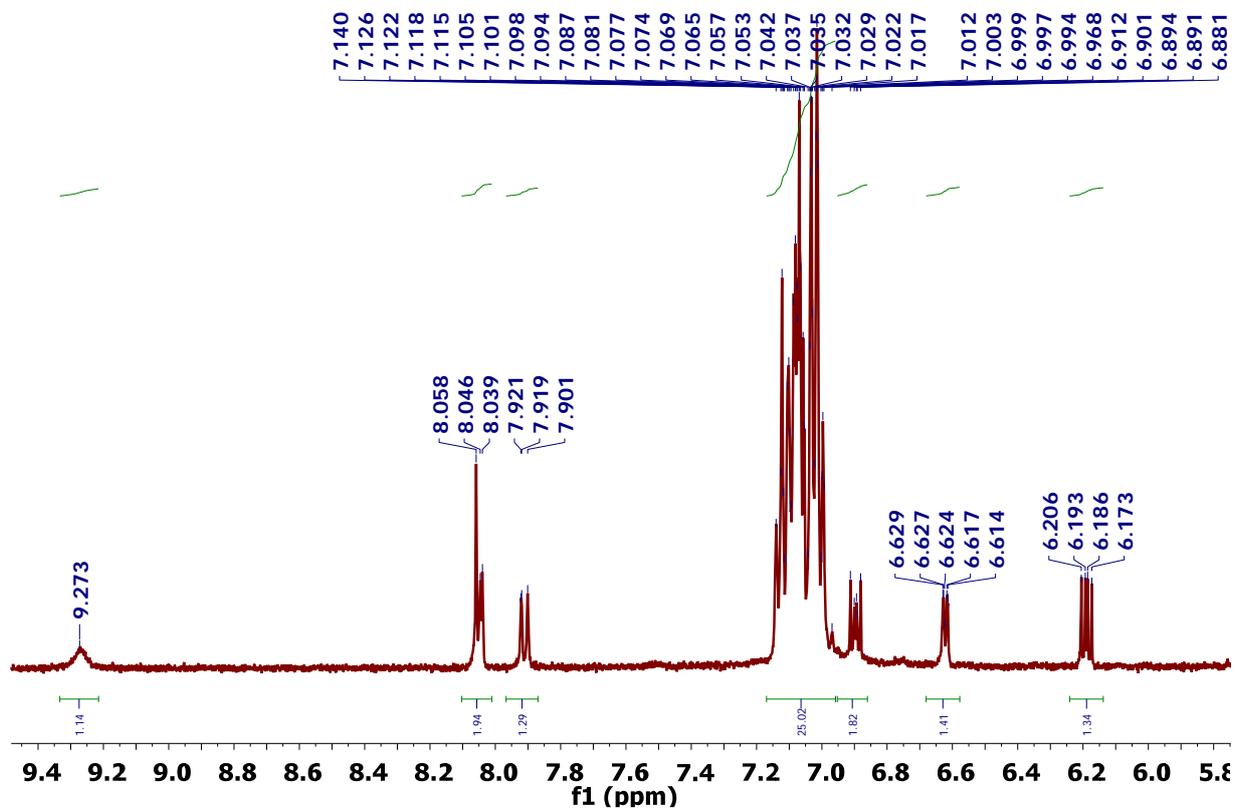


Figure S5. Expansion of aromatic region of ^1H NMR spectrum (400MHz, 25 °C) for complex (2)•0.75(DME) in THF- d_8 under CO_2 atmosphere.

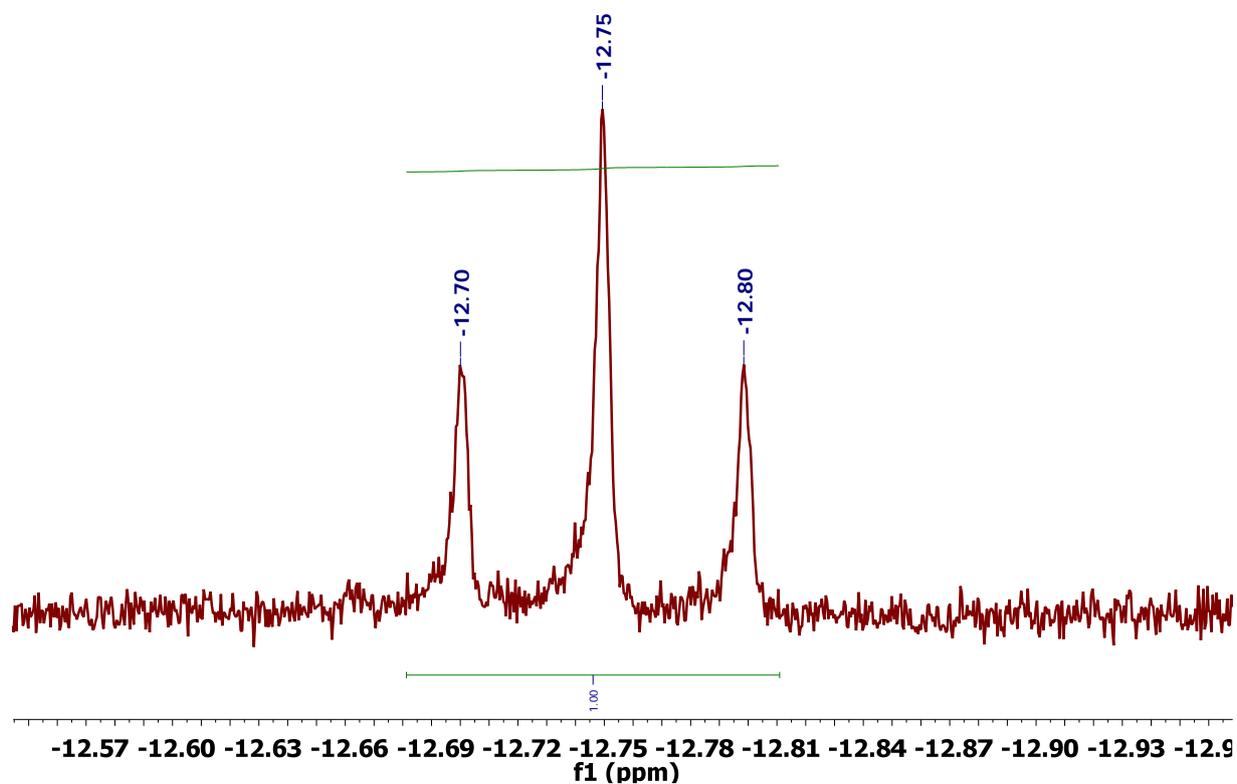


Figure S6. Expansion of hydride region of ^1H NMR spectrum (400MHz, 25 °C) for complex **(2)**•0.75(DME) in THF- d_8 under CO_2 atmosphere.

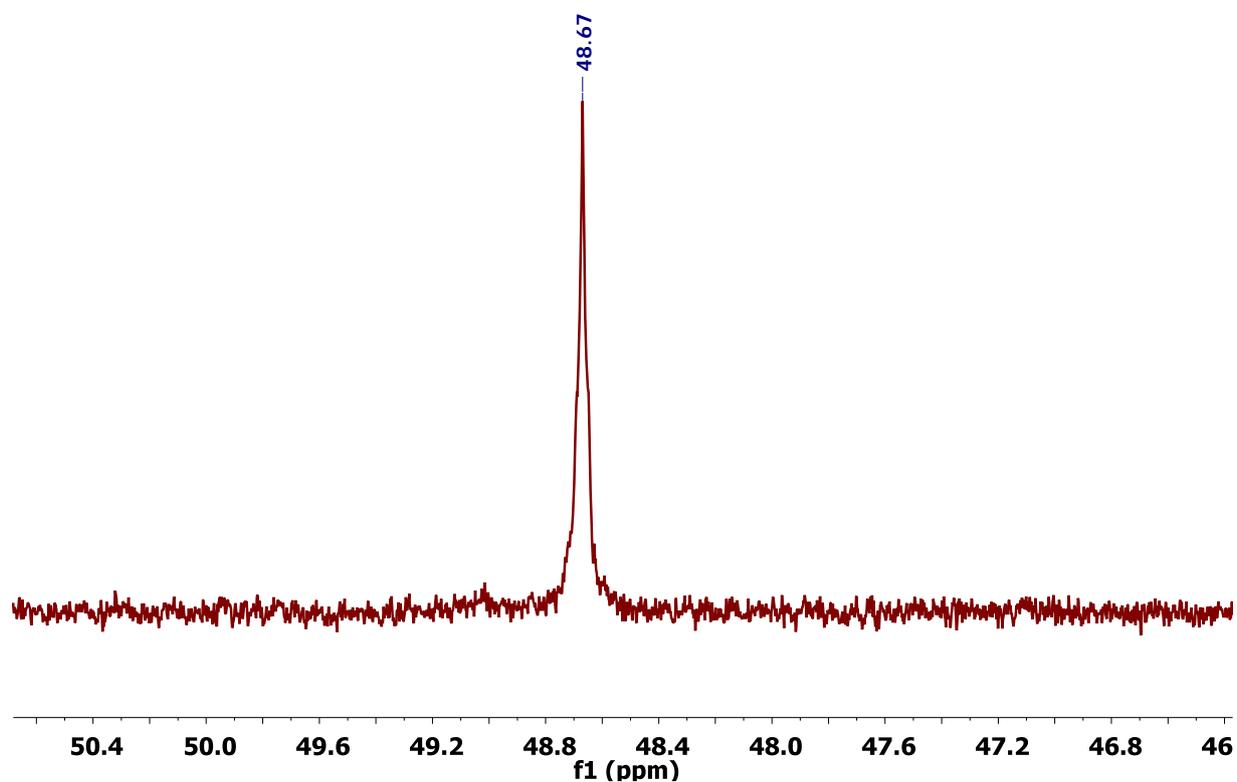


Figure S7. ^{31}P NMR spectrum (161.8 MHz, 25 °C) for complex (2)•0.75(DME) in THF- d_8 under CO_2 atmosphere.

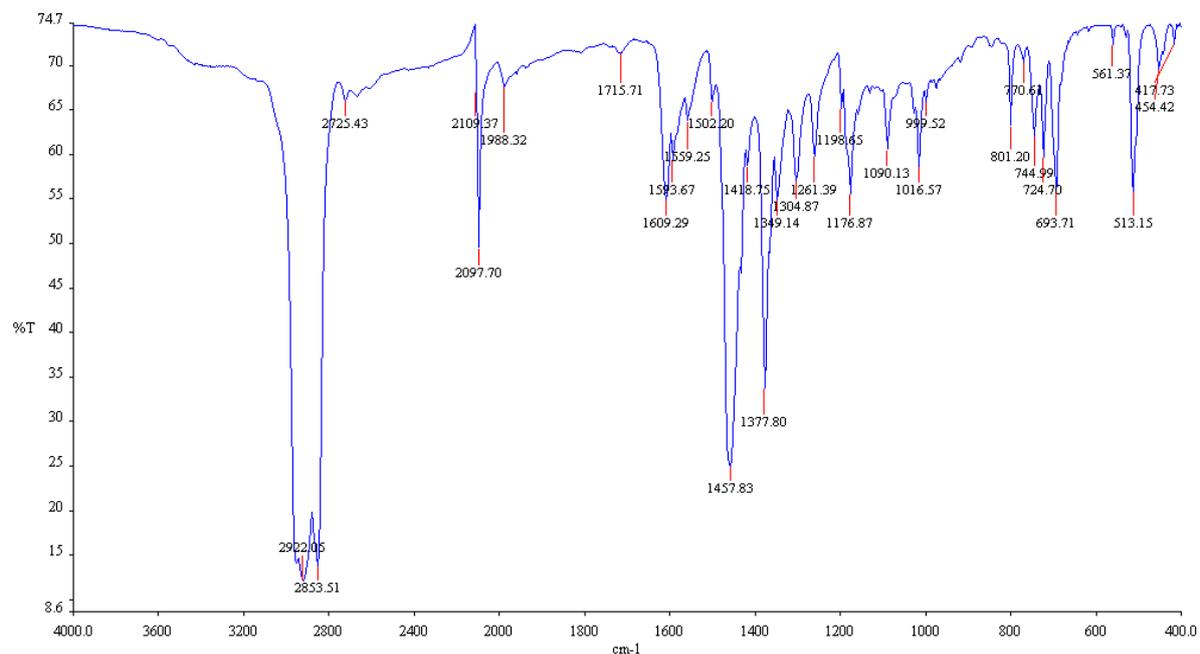


Figure S8. FT-IR spectrum of (2)•0.75(DME) as a nujol mull.

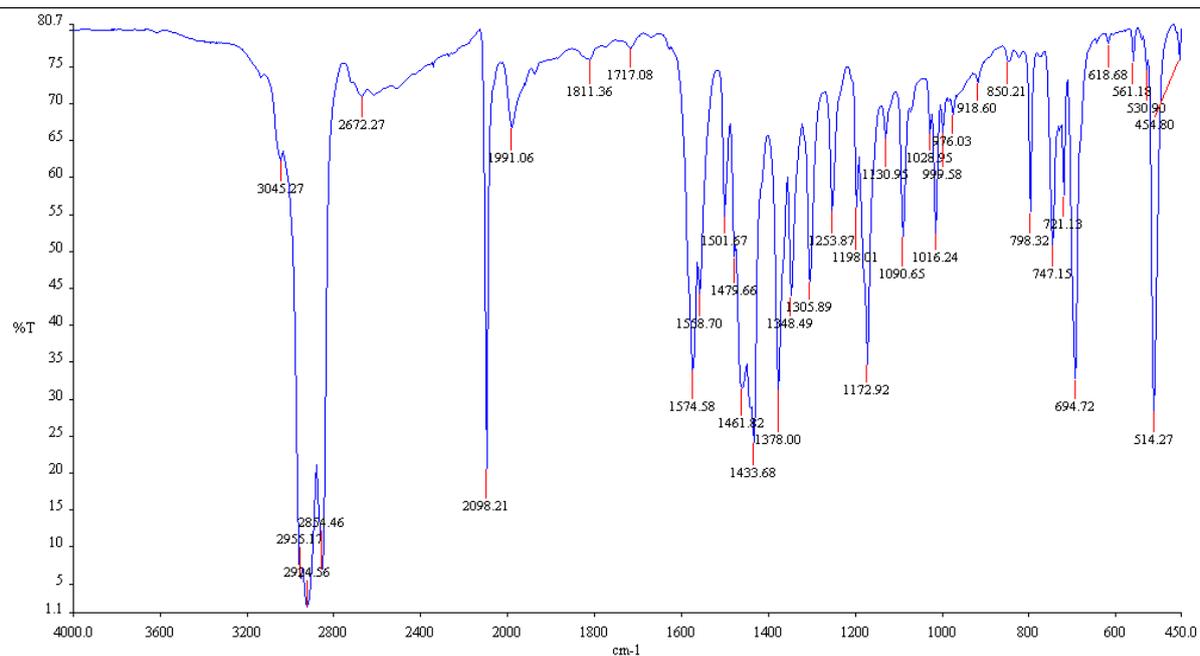


Figure S9. FT-IR spectrum of (¹³C-2) as a nujol mull.

References:

- [1] E. Stepowska, H. Jiang, D. Song, *Chem. Commun.* **2010**, 46, 556-558.
- [2] Apex 2 Software Package; Bruker AXS Inc. **2008** .
- [3] G. M. Sheldrick, *Acta Crystallogr. , Sect. A: Found. Crystallogr.* **2008**, 64, 112.
- [4] A. L. Spek, *J. Appl. Crystallogr.* **2003**, 36, 7.