

**Supporting Information for:**

**High-Valent Nitridorhenium (V) Complexes containing PNP Ligands: Implications of Ligand Flexibility**

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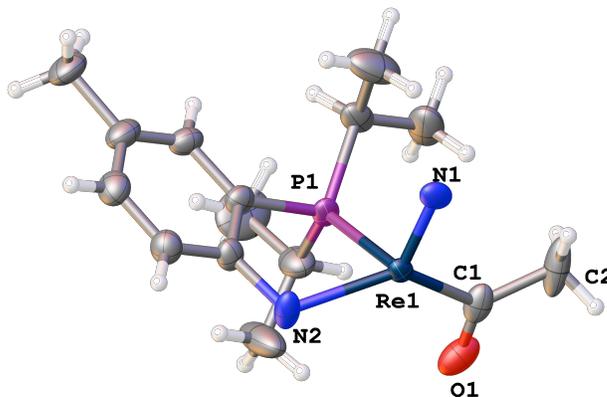
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## I. X-ray Data

### X-ray Crystal Structure of (PNP)(N)Re(C=O)Me, 4.



**Figure S1.** ORTEP structure of (PNP)(N)Re(C=O)Me, 4. Ellipsoids displayed at 50% probability level.

#### Chemical Context

The molecule reported is of interest due to previously reported competency of high valent oxorhenium alkyl complexes to insert carbon monoxide. The choice of the monoanionic tridentate chelate ligand allows for the formation of isoelectronic  $d^2$  rhenium complex containing a nitrido moiety. The stronger trans influence and donor ability of the nitrido ligand should allow for a better stabilization of the resulting acyl product.

#### Structural Commentary

The asymmetric unit of the structure contains the one side of the phosphine ligand and the central nitrogen atom. The other side is generated by symmetry across the mirror plane parallel to the rhenium acyl moiety. The structure exhibits a mild disorder around the isopropyl groups of the phosphine moiety. A significant disorder is observed at the central rhenium atom, which appears to have part time occupancy across two sites. This forces the similar behavior of the acyl ligand. The part time occupancy of these groups was modeled in SHELX using the PART=-1 command and by setting the occupancy of those atoms to 0.5.

#### Supramolecular Features

No significant intermolecular interactions are observed in the structure.

#### Synthesis and Crystallization

The molecule was synthesized by stirring a benzene solution of the (PNP)Re(N)Me precursor under 1 atm of carbon monoxide at room temperature for 48 h. The filtrate was collected and dissolved in dichloromethane. Slow evaporation of dichloromethane afforded X-ray quality crystals suitable for analysis. The molecule was characterized by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy.

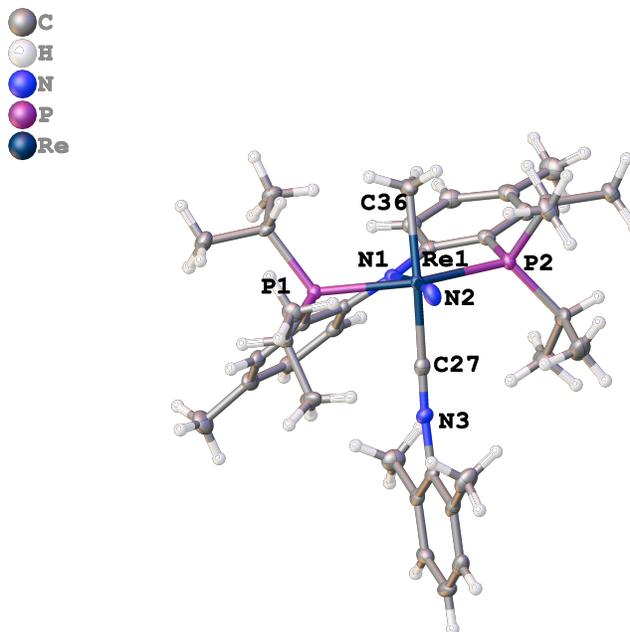
#### Refinement

Crystal data, data collection and structure refinement details are summarized below.

The positional disorder of the rhenium-nitrido-acyl moiety was modeled using the PART command, by assigning those atoms to PART=-1. Other than the PART command, no additional restraints/constraints have been utilized.

## X-ray Crystal Structure Report for (PNP)Re(N)Me(CNR), **6**.

X-ray structure of (PNP)Re(N)Me(CNR) was solved and the parameters of X-ray data collection, integration, absorption correction and refinement are reported.



**Figure S2.** ORTEP structure of (PNP)Re(N)CNR, **6**. Ellipsoids displayed at 50% probability level.

### Structure Description

The structure adopts octahedral geometry with the methyl ligand trans to the isocyanide ligand. The two nitrogen ligands (nitrido and amido) are also positioned trans to each other. The characteristic "twisting" of the PNP aryl rings is also observed in the structure with the torsion angle of  $164^\circ$ . Other bond lengths and angles are consistent with typical values reported.

### Synthesis and Crystallization

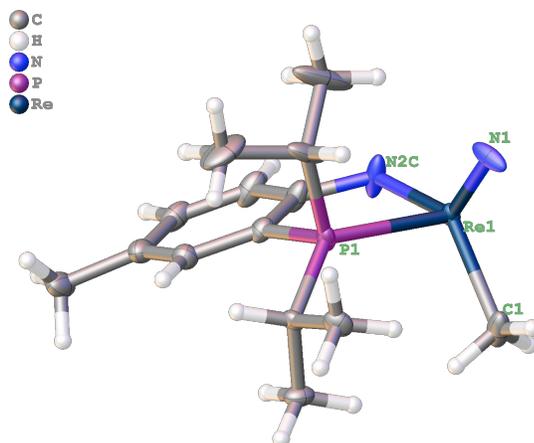
Vapor diffusion of pentane into concentrated benzene solution of complex afforded yellow crystals suitable for analysis. 3 equivalents of isocyanide were used to prevent the equilibration between free Re—Me complex and isonitrile bound complex.

### Refinement

Crystal data, data collection and structure refinement details are summarized below in Table S1. No constraints/restraints other than AFIX command for the phenyl rings was employed. The two reflections 0 0 2 and 1 0 2 were omitted as they were blocked by the beam stop.

### X-ray crystal Structure Report for (PNP)Re(N)Me, **3**.

X-ray structure for the representative nitridorhenium methyl complex is described. Data collection. Solution and refinement parameters are described. The asymmetric unit is shown in a figure below.



**Figure S3.** ORTEP structure of (PNP)Re(N)Me, **3**. Ellipsoids displayed at 50% probability level.

#### Structure description

The structure features a typical five coordinate environment around rhenium in a distorted square pyramidal geometry. The rhenium center appears to be disordered across two sites as it is positioned directly at the 2-fold rotation axis. The unit cell consists of two non-superimposable molecules (racemate) further lending evidence to the centrosymmetric nature of the chosen space group.

#### Synthesis and crystallization

The molecule was crystallized by slow evaporation of methylene chloride solution.

#### Refinement

No specific restraints and constraints were necessary to achieve satisfactory refinement. However, the GooF appears to be slightly high due to their twin component we detected during initial assessment of the unit cell parameters. Attempts to refine the structure against two-component twin related by  $180^\circ$  rotation gave unsatisfactory results, with many atoms becoming non-positive definites (NPD). Another possible reason for this behavior is that the crystal is not fully racemic; examination in PLATON revealed the possibility of the Pn as a possible space group against P2/n, however, pursuits of this space group also proved unsatisfactory. Attempts to find higher symmetry (ADDSYMM) were also unsuccessful. Additionally, the presence of a two-fold rotation axis in the proximity of rhenium prompted us to set the occupancy of nitrido fragment (N1), the methyl group (C1) and Re1 to 0.5 in order to account for partial occupancy imposed by this symmetry operation.

## II. NMR Data for (PNP)Re(N) Complexes.

All spectra were obtained in  $\text{CD}_2\text{Cl}_2$  unless otherwise noted.

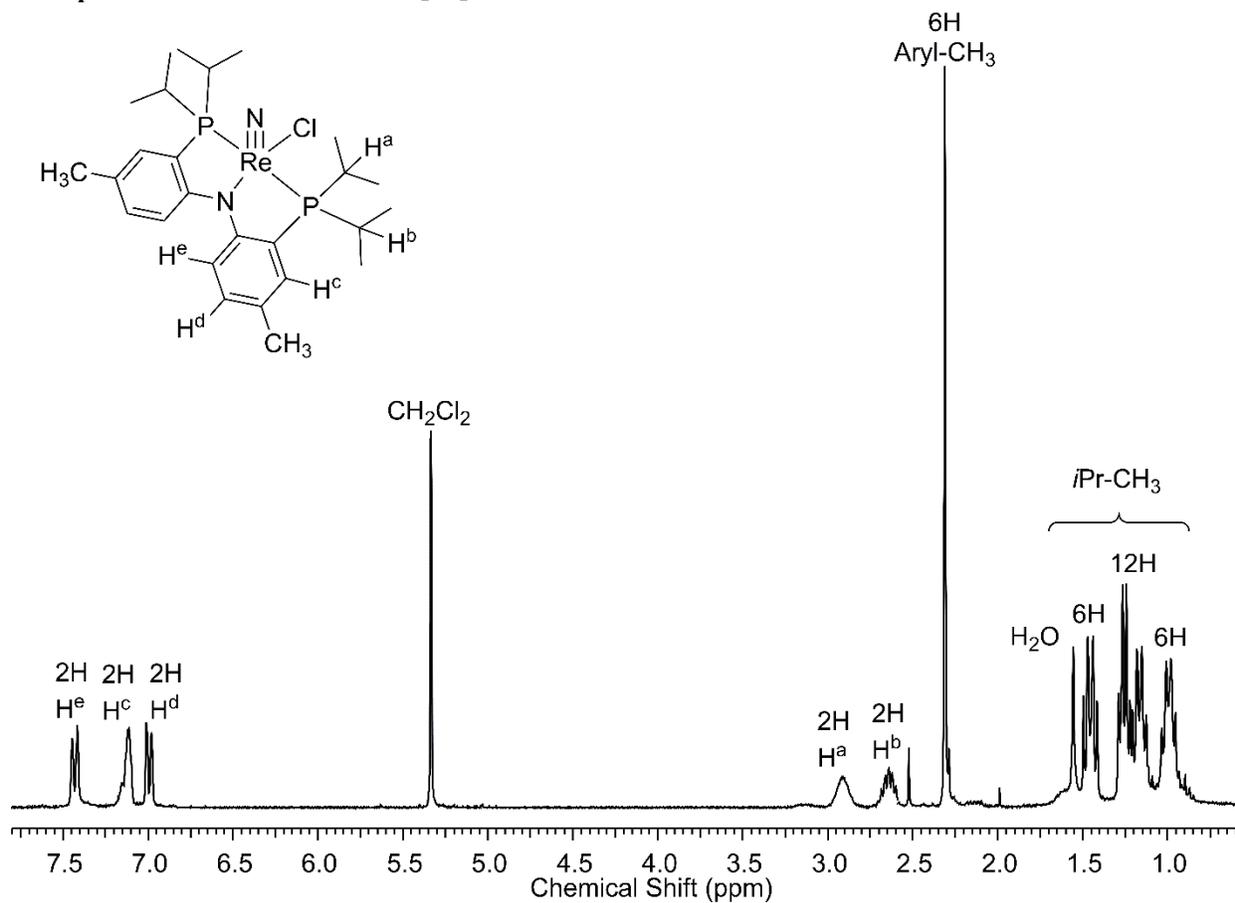
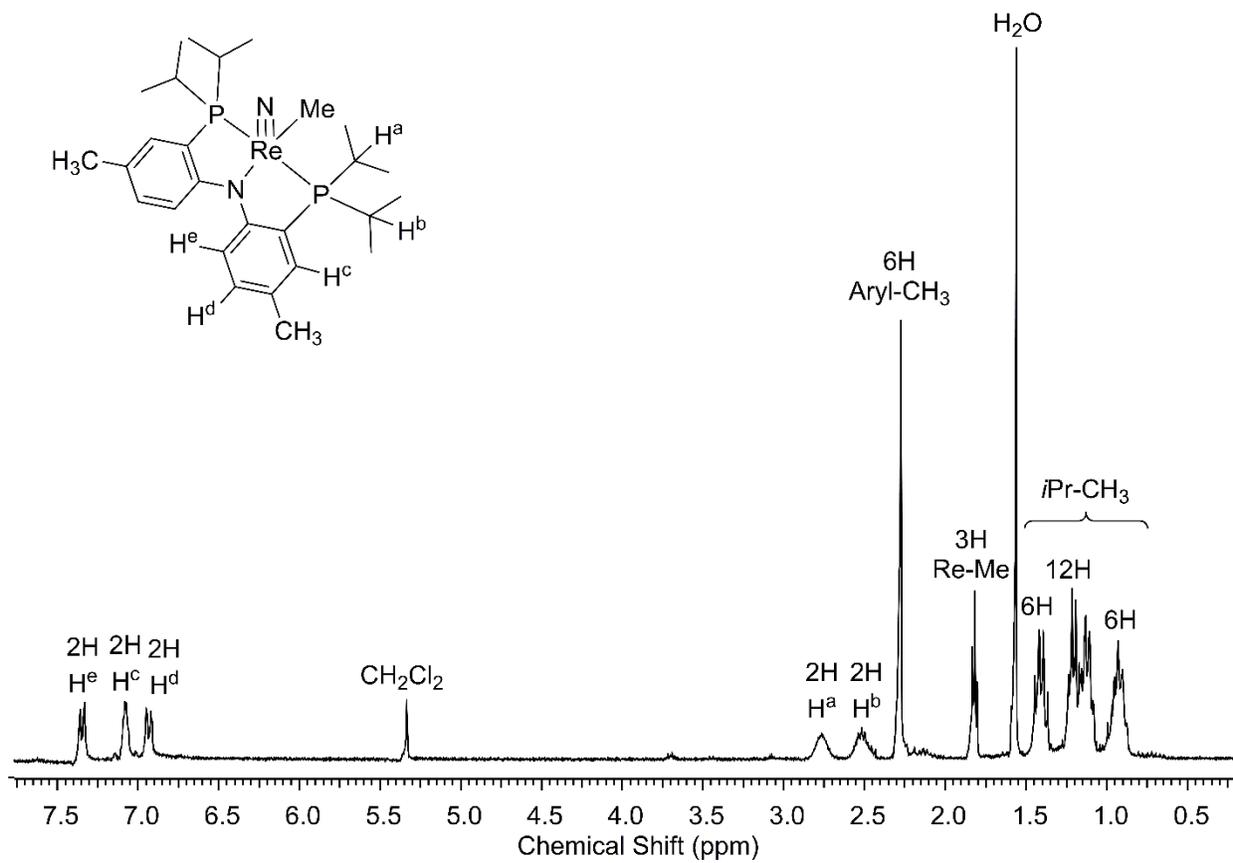
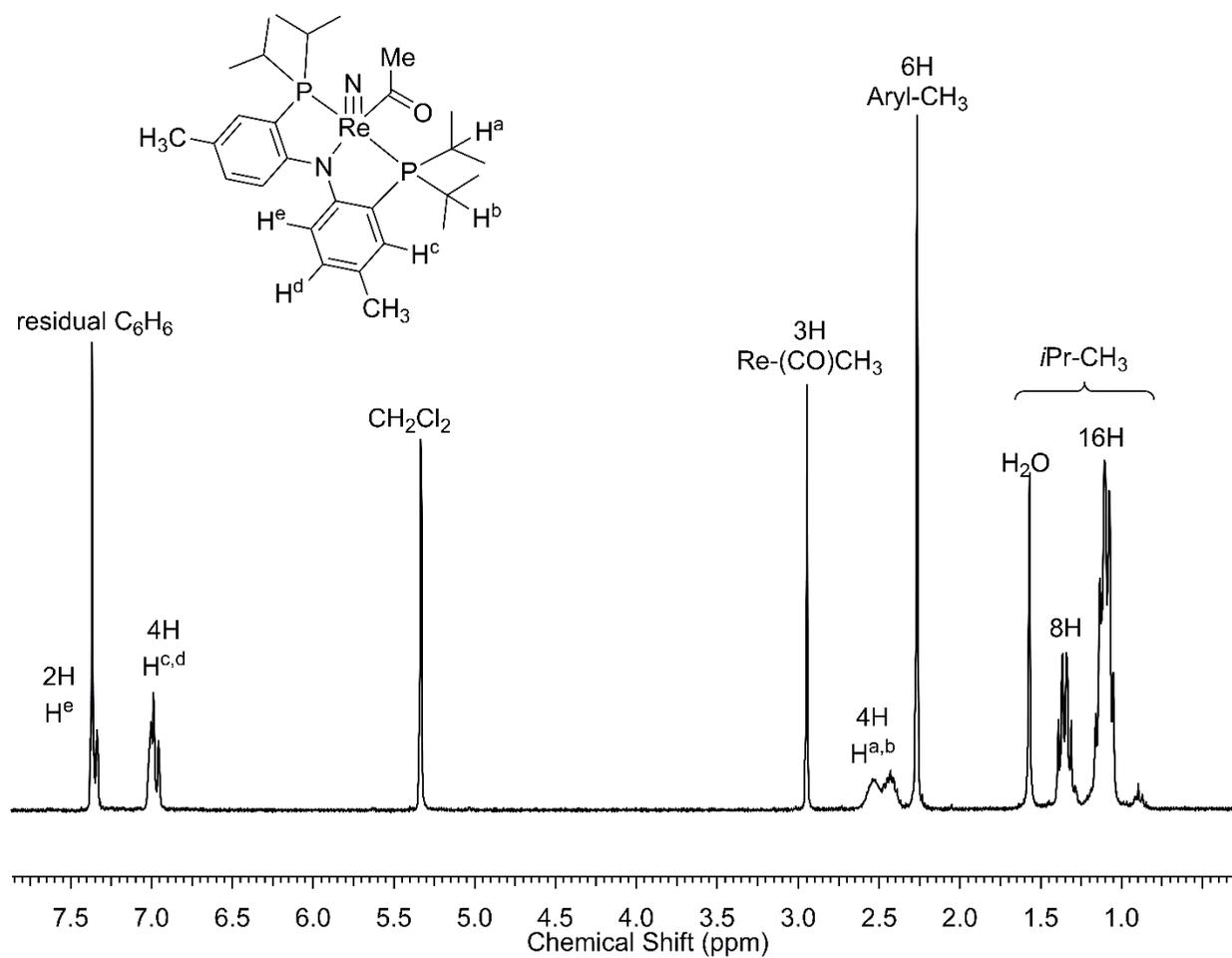


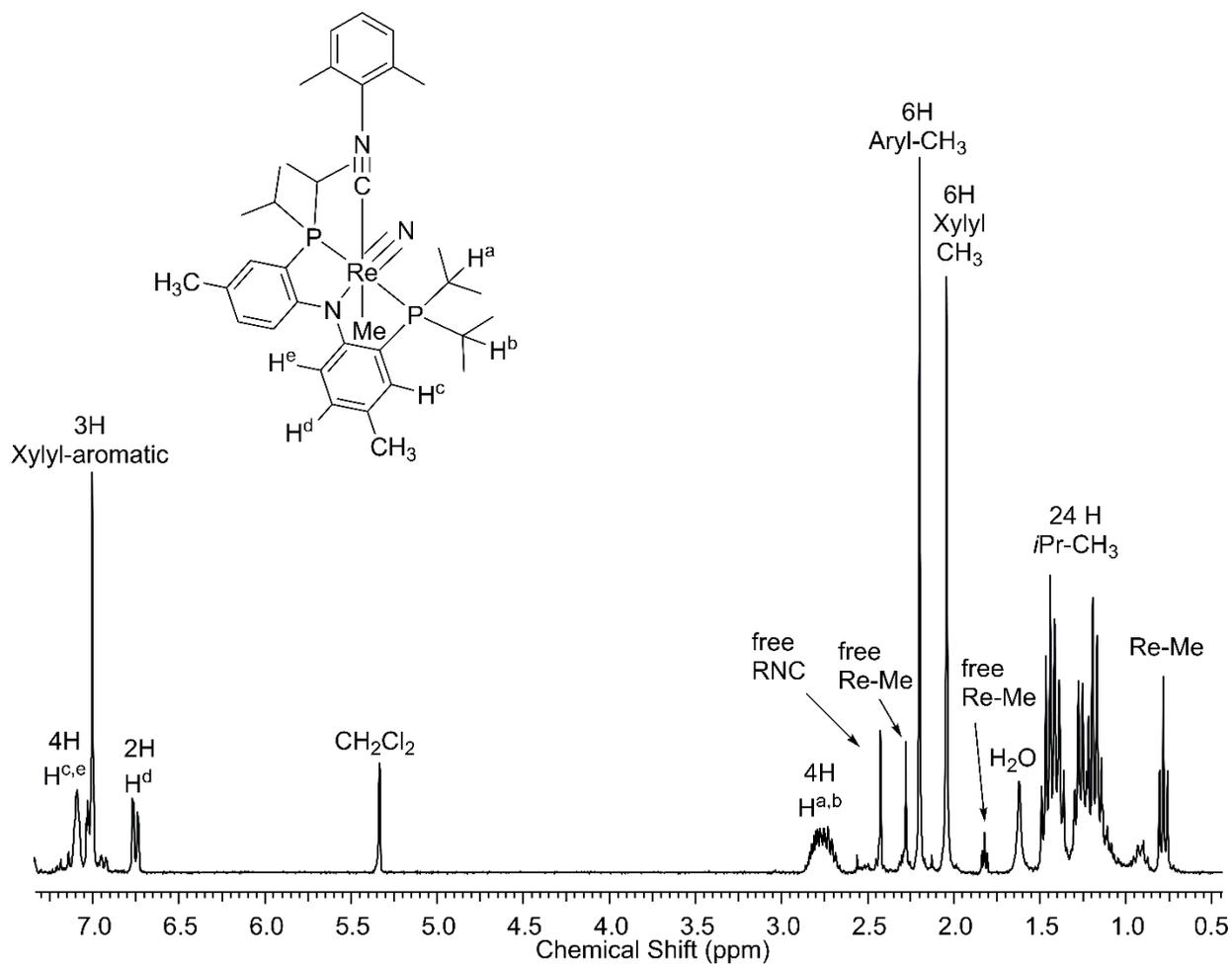
Figure S4.  $^1\text{H}$  NMR spectrum of complex 2.



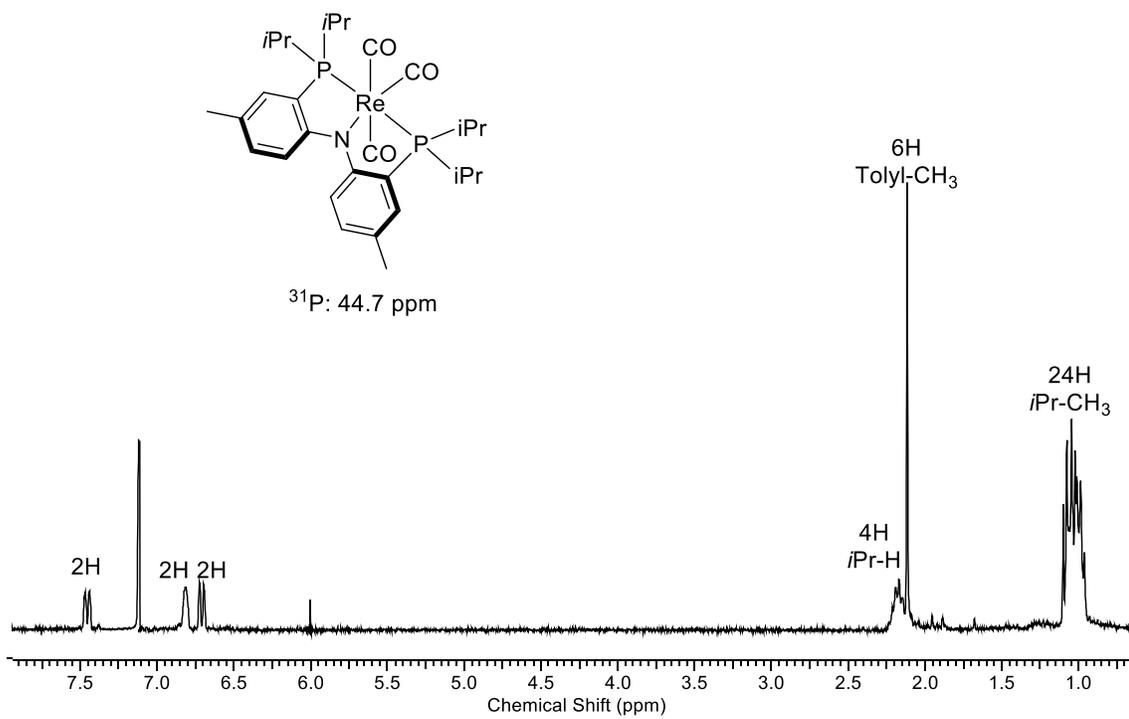
**Figure S5.** <sup>1</sup>H NMR spectrum of complex 3.



**Figure S6.**  $^1\text{H}$  NMR spectrum of complex 4.

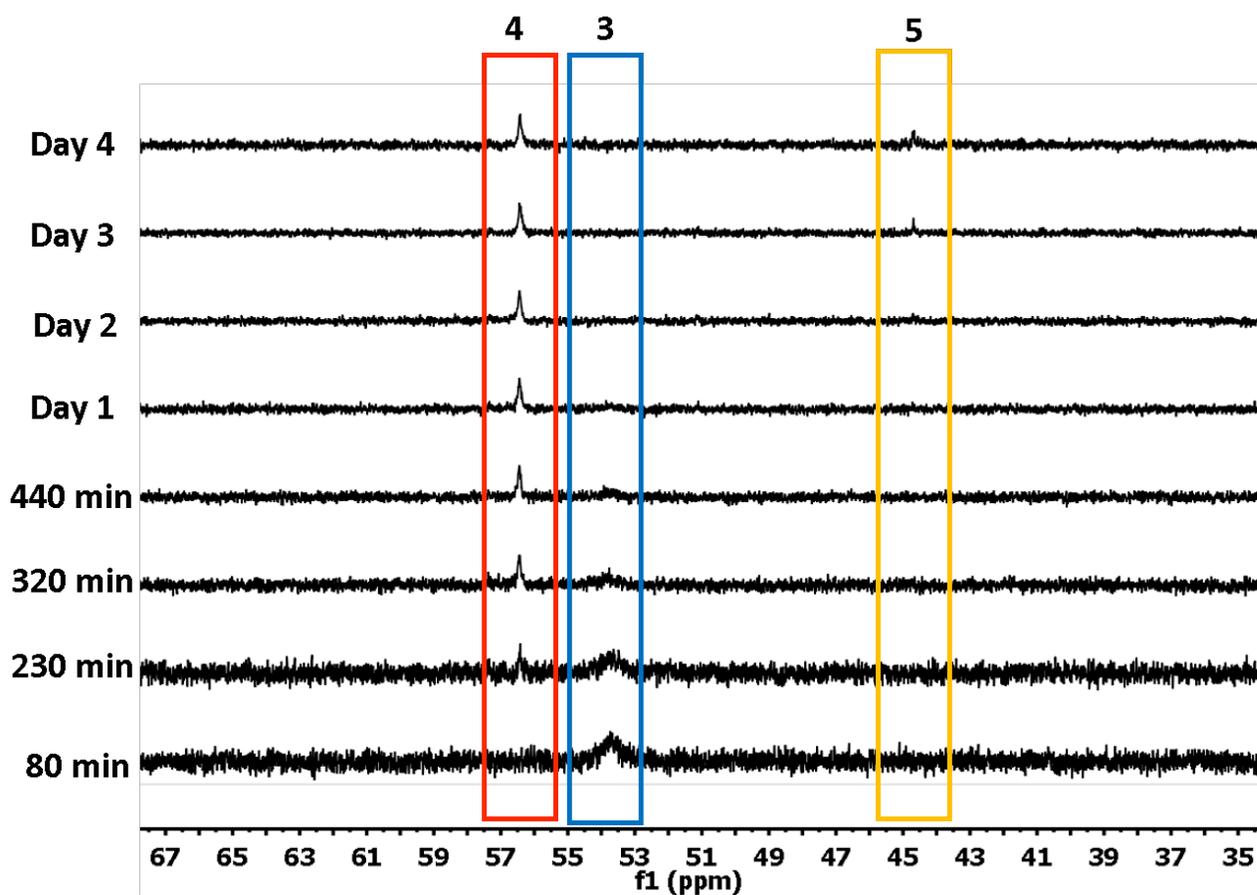
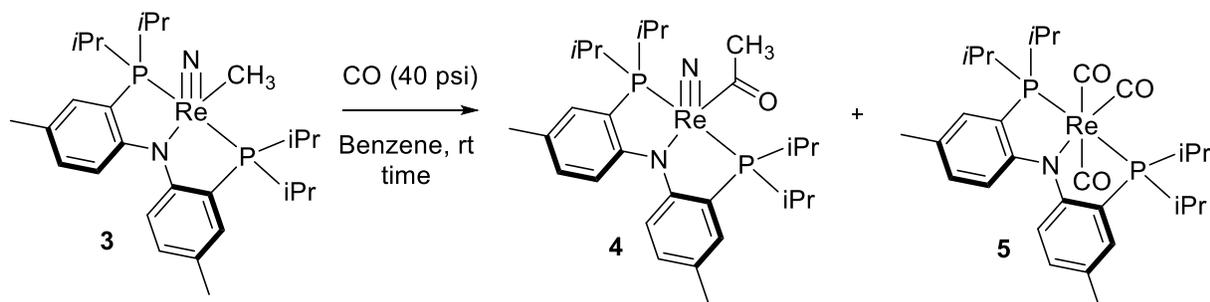


**Figure S7.** <sup>1</sup>H NMR spectrum of complex **6**. The NMR solution shows an equilibrium between the free and bound isonitrile species.

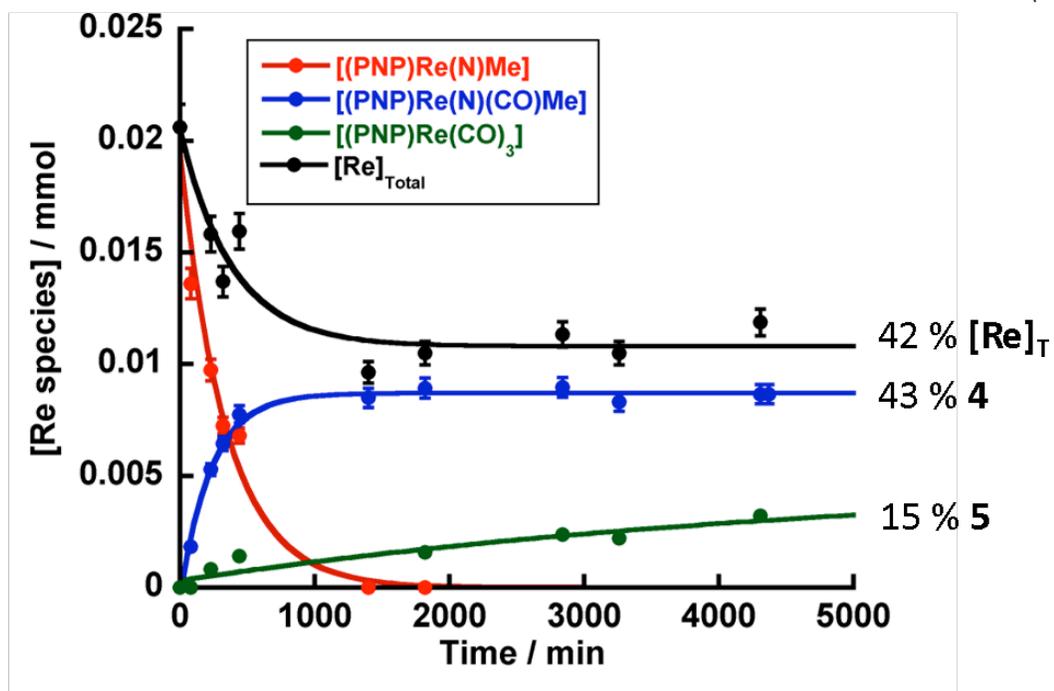
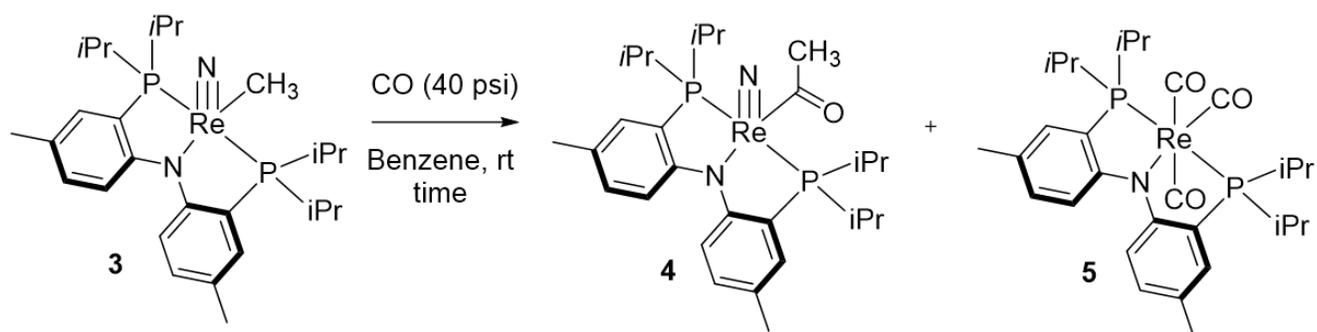


**Figure S8.**  $^1\text{H}$  NMR spectrum of complex **5**. The NMR solution shows an equilibrium between the free and bound isonitrile species.

### III. Additional Kinetic Data.

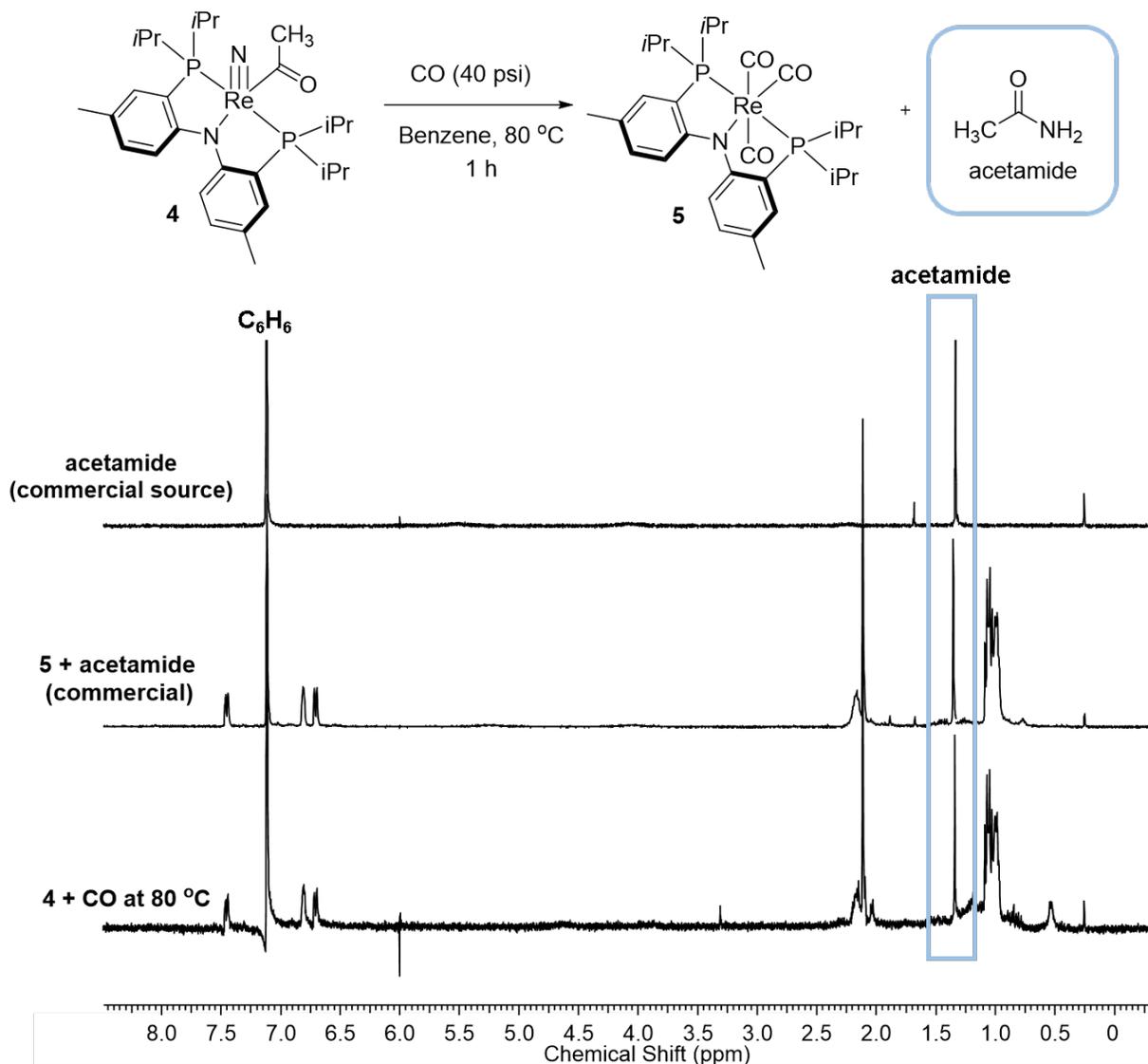


**Figure S9.** <sup>31</sup>P NMR spectrum of reaction of **3** with CO at room temperature. Slow formation of tricarbonyl complex **5** as well as acetamide product was detected by <sup>31</sup>P NMR spectroscopy (44.8 ppm, yellow box) and <sup>1</sup>H NMR spectroscopy respectively.



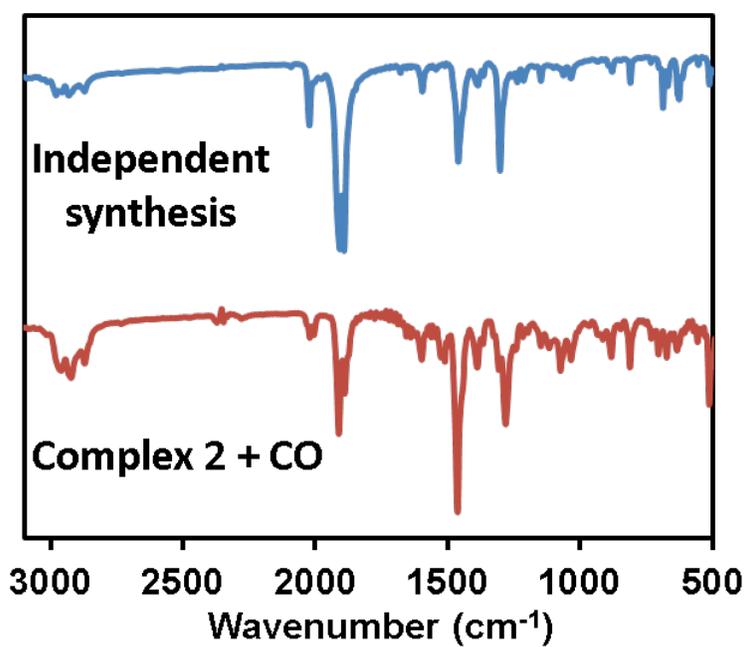
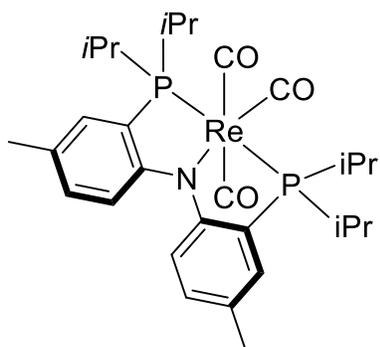
**Figure S10.** Time profile of reaction of **3** with CO at room temperature over several days. Slow formation of tricarbonyl complex **5** is observed. Conditions:  $[\mathbf{3}] = 0.02$  mmol,  $p_{\text{CO}}$  (40 psi) in J. Young tube with mesitylene as internal standard (0.02 mmol). Conversions determined by  $^1\text{H}$  NMR spectroscopy.

#### IV. Additional NMR Data.

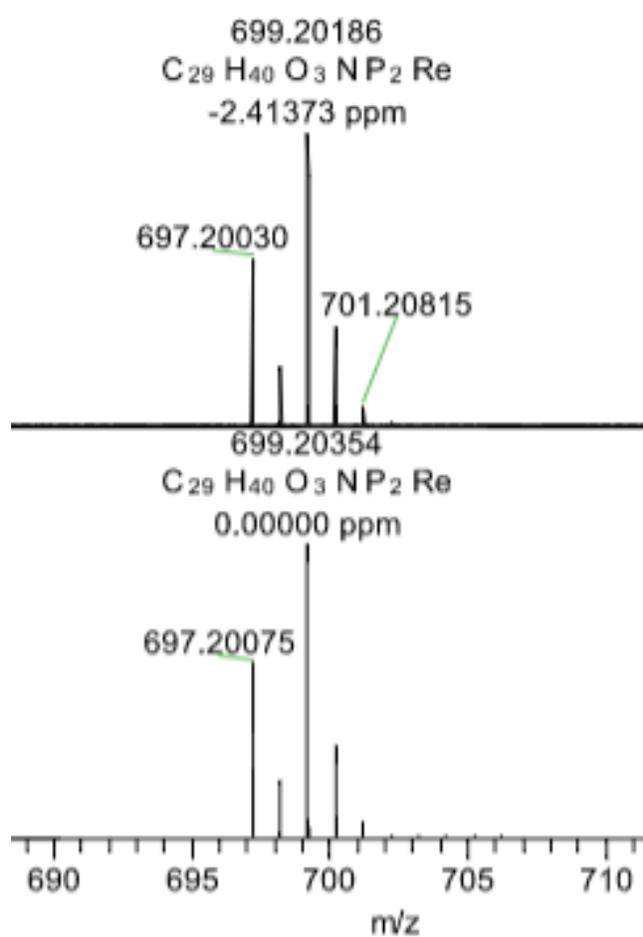


**Figure S11.**  $^1\text{H}$  NMR spectral overlay of crude reaction mixture (**4** + CO at  $80^\circ\text{C}$ , bottom spectrum), externally prepared complex **5** with commercial acetamide (middle spectrum) and commercially obtained acetamide (top spectrum) in benzene. Quantitative formation of acetamide resulting from reduction of acyl complex **4** is observed, leading to observation of tricarbonyl species **5**.

## V. IR and Mass Spectrometry Data for Complex 5.

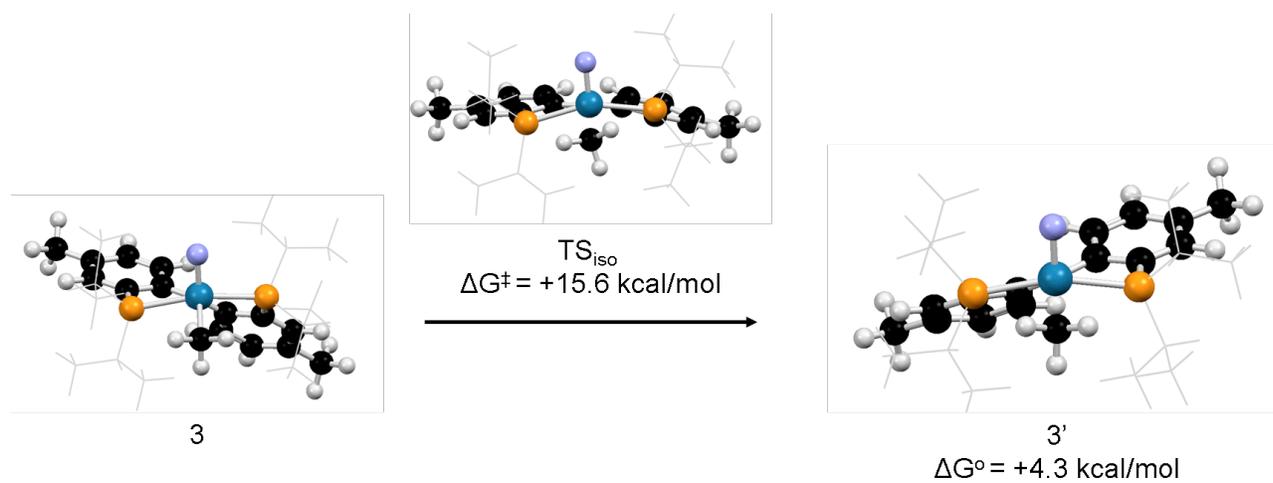


**Figure S12.** FTIR spectrum of complex 5 (KBr pellet). The presence of two sets of dicarbonyl stretches indicates the formation of two isomers.



**Figure S13.** High-resolution mass spectrometry data for complex **5**.

## VI. Additional Computational Data



**Figure S14.** Calculated isomerization pathway from **3** to **3'**. Isopropyl groups are depicted in wireframe for clarity. Legend: nitrogen = purple; rhenium = blue; phosphorus = orange; carbon = black; hydrogen = white.

## VII. References

### Full Gaussian09 Citation

Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.