Supporting Information for

Efficient Base-Free Aqueous Reforming of Methanol Homogeneously Catalyzed by Ruthenium Exhibiting a Remarkable Acceleration by Added Catalytic Thiol

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Note S1. Proposed pathways and potential energy surface

Figure S1. Proposed mechanism including inner-sphere dehydrogenation of water.
Figure S2. Potential energy surface for the pathway including inner-sphere dehydrogenation of water (in MeOH, T = 383.15 K, pressure = 1). Note that Ru-7 with formaldehyde coordinated in a $\kappa^1$-O fashion is 6.0 kcal/mol higher in energy than Ru-7 with $\eta^2$-coordinated C=O, which is presented in this Figure.
Figure S3. Proposed mechanism including inner-sphere dehydrogenation of methandiol.
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Figure S5. Proposed mechanism through thioester formation, excluded by experimental results.
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Figure S8. Potential energy surface for the pathway including outer-sphere dehydrogenation of methanol and methandiol based on ruthenium thiolate complex (in MeOH, T = 383.15 K, pressure = 1).
**Note S2. Control experiments with Ru-4**

Control experiments were carried out using Ru-4 as the catalyst. Interestingly, under the reaction conditions with the addition of 1 equiv thiol, 240 mL gas was collected after 12 h heating at 150 °C (Supporting Figure 9). However, nearly no gas was collected without the addition of thiol.

![Figure S9](image_url)

**Figure S9. Control experiments based on Ru-4.**

To figure out how Ru-4 worked in the reaction system in the presence of thiol, mechanistic studies were conducted heating the biscarbonyl acridine Ru-complex Ru-4 in acetic acid under Ar flow. The utilization of acetic acid is to mimic formic acid in the methanol reforming system, which under the reaction conditions is quite easy to undergo dehydrogenation and thus makes the capture of the key intermediate, ruthenium formate, very difficult. Interestingly, both CO and H₂ were detected by GC during the reaction and the ruthenium acetate complex Ru-16 was generated as the major product (Figure S10).¹ The result proves the lability of the second CO on the ruthenium center and thus in the case of current methanol reforming reaction, it is reasonable to propose that Ru-4 can also react with the intermediate formic acid to release one molecule of CO and H₂ to regenerate monocarbonyl complex Ru-12. The Gibbs energy difference between ruthenium formate complex Ru-12 and Ru-4 is calculated as +10.5 kcal/mol (from Ru-12 to Ru-4, Supporting Figure 7), which can be overcome under the reaction conditions. It is noted the transformation of hydrogen and CO from the condensed phase to the gas phase is not additionally corrected in the free energy quantities.²

Based on the above results, it is proposed that Ru-4 is the off-cycle resting state of the catalyst during most of the reaction time. Even though Ru-4 might be able to catalyze the reaction, it should be very slow as reflected from ref. 1 by the calculated
activation barriers for the dehydrogenation of formic acid (overall kinetic barrier of 41.9 kcal/mol with Ru-4 vs 25.1 kcal/mol with Ru-1 in benzene). Thus in the current methanol reforming system, the monocarbonyl catalysts Ru-1 – Ru-3 are likely still the actual catalysts of the reaction despite the generation of CO.

Figure S10. Control experiments relevant to CO loss from Ru-4.
Note S3. Factors related to the amount of CO generated in the reaction

1. Reaction temperature. Control experiments were carried out heating the reaction at different temperature. While nearly no CO was detected in the collected gas after heating at 120 °C, higher concentration of CO was observed after heating at 135 °C and 150 °C (Supporting Figure S11). Thus, the reaction temperature can affect the generation of CO in the system.\(^3\text{-}^6\) One thing worthwhile to mention is the internal temperature of the system. Since we employed a closed system, the internal temperature of the reaction increased along with the accumulation of the pressure, which might also affect the generation of CO at different stage of the reaction.

\[
\text{MeOH} + \text{H}_2\text{O} \quad \text{Ru-1 (2.5 \, \mu\text{mol})} \quad \text{HexSH (2.5 \, \mu\text{mol})} \quad \text{T \, ^\circ\text{C}, \, X \, \text{h}} \quad \text{CO}_2 + \text{H}_2
\]

| Reaction Temperature | Volume | ppm CO | TOF (H\(_2\)) |
|----------------------|--------|--------|---------------|
| 120 °C, 36 h         | 110 mL | <20 ppm CO | 39 h\(^{-1}\) |
| 135 °C, 24 h         | 150 mL | 154 ppm CO | 76 h\(^{-1}\) |
| 150 °C, 12 h         | 470 mL | 181 ppm CO | 480 h\(^{-1}\) |
| 150 °C, 1 h          | no gas bubbled | |

**Figure S11.** Reaction temperature screening.

2. Generation of Ru-4. The employed catalyst Ru-1 can absorb a little amount of CO to generate a biscarbonyl ruthenium complex Ru-4 (Supporting Figure S12),\(^7\) which is supposed to lower the amount of CO in the collected gas. Note that in addition to the direct coordination by CO, Ru-4 can also be generated by the reaction of Ru-1 either with formic acid (Supporting Table S1), or with CO\(_2\) and H\(_2\) (Supporting Figure S35).

**Figure S12.** Generation of Ru-4 from Ru-1 with CO.
3. Concentration of water in the system. Comparing to the result from 9:1 MeOH:H₂O system, the amount of CO was detected in a very low level in MeOH:H₂O = 4:1 or 6:1 system after 12 h heating, which possibly indicated that the concentration of water in the system might affect the generation of CO (Supporting Figure S13).

\[
\text{MeOH} + \text{H}_2\text{O} \xrightarrow{\text{Ru-1 (2.5 \mu mol)} \quad \text{HexSH (2.5 \mu mol)}} 150^\circ\text{C, 12 h}} \xrightarrow{\text{H}_2} \text{CO}_2 + 3\text{H}_2
\]

![Figure S13. Detailed results of solvent optimization.](image)

In the first 72 h of the long-term reaction (in 3.6 mL MeOH and 0.4 mL H₂O), the amount of CO increased as the reaction continued. For example, while only 0.02% CO was detected in the collected gas of the first cycle (first 12 h), higher amounts of CO were detected in the following 5 cycles (Supporting Figure S14). Considering water was consumed during the reaction, making its concentration continuously decreased, these results also supported the concentration of water in the system could affect the generation of CO.

![Figure S14. Increasing amount of CO during the reaction.](image)
Note S4. Control experiments on the source of CO

1. **Reverse water-gas-shift reaction.** The reverse water-gas-shift reaction\(^8,9\) was tested (See Supporting Figure S15), however, no CO was detected in the resulting gas mixture. The same result was obtained directly starting with Ru-1 as the catalyst without the addition of a catalytic amount of thiol (See Supporting Figure S35).

   \[
   \text{Ru-1 (5 \mu mol)} \\
   \text{HexSH (5 \mu mol)} \\
   \text{CO}_2 + \text{H}_2 \xrightarrow{150 ^\circ C, 36 h} \text{CO} + \text{H}_2\text{O} \\
   \text{6 bar} \quad \text{20 bar} \quad \text{no CO detected by GC}
   \]

**Figure S15.** Test the possibility of reverse water-gashift reaction.

2. **Thermo-decomposition of formic acid.**\(^6\) The dehydrogenation of formic acid was examined under the reaction conditions with or without water (Supporting Table S1). As expected, with Ru-1 as the catalyst, the reactions were very efficient heating at 150 \(^\circ\)C with a TOF (H\(_2\)) more than 10,000 h\(^{-1}\) in 10 minutes. However, no CO was detected after the reaction in the collected gas (entries 1 and 2). Similar results were obtained employing Ru-2 as the catalyst with only trace amount of CO detected in the collected gas (entries 3 and 4, Ru-2 was prepared in situ). The efficiency of Ru-2 is slightly lower than that of Ru-1, which also suggests that Ru-1 is the real catalyst for the dehydrogenation of formic acid step in current methanol reforming reaction.\(^1\) In addition, the biscarbonyl ruthenium complex Ru-4 was also used as the catalyst (entries 5 and 6). Although the reaction rate decreased, still no CO was detected in the collected gas after 20 min heating.

**Table S1. Dehydrogenation of formic acid**

| Entry | [Ru] | H\(_2\)O X mL | t (min) | V (H\(_2\)+CO\(_2\)) (mL) | CO (ppm) | TON (H\(_2\)) | TOF (H\(_2\), h\(^{-1}\)) |
|-------|------|----------------|---------|--------------------------|----------|---------------|-------------------------|
| 1     | Ru-1 | 0.0 mL         | 10      | 410 mL                   | <15      | 1673          | 10040                   |
| 2     | Ru-1 | 0.2 mL         | 10      | 430 mL                   | <15      | 1755          | 10530                   |
| 3     | Ru-2 | 0.0 mL         | 10      | 325 mL                   | 20       | 1327          | 7959                    |
| 4     | Ru-2 | 0.2 mL         | 10      | 370 mL                   | 26       | 1510          | 9061                    |
5 Ru-4 0.0 mL 20 300 mL <15 1224 3673
6 Ru-4 0.2 mL 20 335 mL <15 1367 4102

Conditions: [Ru] (5 \(\mu\)mol), MeOH/H\(_2\)O as indicated, heat in a closed 90 mL Fischer-Porter tube in a 150 °C oil bath; Gas composition of ~1:1 CO\(_2\):H\(_2\) for each case. Detection limit of the GC (<15 ppm); In entries 1-4, the resulting ruthenium species after heating is Ru-4.

3. Thermo-decomposition of formaldehyde.\(^3\)\(^-\)\(^5\) Trioxane (anhydrous formaldehyde surrogate) was tested under the reaction conditions. In order to avoid its further conversion into formic acid, MeOH was used as the only solvent without the addition of water. Moreover, in consideration of internal temperature and atmosphere in the real system, 4 bar H\(_2\) gas was introduced before the reaction in the control experiments (Figure S16). Interestingly, after 24 h heating, 0.28% CO was detected by GC in the collected gas (Note little amount of CO\(_2\) was detected by GC, indicating little amount of water existed in the system). A similar result was also obtained using Ru-1 as the catalyst. These experiments support the generated CO in the developed methanol reforming system mostly comes from the thermo-decomposition of the formaldehyde intermediate.

\[
\begin{align*}
\text{O} & \quad \text{O} \\
3 \text{HCHO} & \quad \text{H}_2 \\
1.2 \text{ mmol} & \\
\text{Ru-1 (5 \(\mu\)mol)} \quad \text{HexSH (5 \(\mu\)mol)} & \quad \text{CO} + \text{H}_2 \\
150 ^\circ\text{C}, 24 \text{ h} & \\
\text{MeOH} = 1.8 & \\
\text{under 4 bar H}_2 & \quad 0.28\%
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{O} \\
3 \text{HCHO} & \quad \text{H}_2 \\
1.2 \text{ mmol} & \\
\text{Ru-1 (5 \(\mu\)mol)} & \quad \text{CO} + \text{H}_2 \\
150 ^\circ\text{C}, 24 \text{ h} & \\
\text{MeOH} = 1.8 & \\
\text{under 4 bar H}_2 & \quad 0.2\%
\end{align*}
\]

**Figure S16.** Decomposition of formaldehyde to CO and H\(_2\).
Supporting Experimental Procedures

1. General considerations

All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmosphere glovebox equipped with a MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All non-deuterated solvents were purified according to standard procedures under argon atmosphere. Deuterated solvents were degassed with argon and directly used. All solvents were degassed with argon and kept in the glove box over 3Å molecular sieves. Water used in this system is deionized water which is further degassed with argon and kept in glovebox. All $^1$H NMR, $^{13}$C NMR or $^{31}$P NMR spectra were recorded on a Bruker AVANCE III 300MHz, 400MHz spectrometer and reported in ppm ($\delta$). Chemical shifts were referenced to the residual solvent peaks ($^1$H NMR, $^{13}$C NMR) or an external standard of phosphoric acid (85% solution in D$_2$O) at 0.0 ppm ($^{31}$P NMR). NMR spectroscopy abbreviations: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. GC analysis was performed on an HP 6890 chromatograph (TCD detector) with helium as the carrier gas.

Complexes Ru-1$^{10}$, Ru-2$^{11}$, Ru-3$^{11}$, Ru-4$^7$ were prepared according to literature procedures.

The scale of the graduated cylinder is 10 mL and the last digit of the volume of collected gas is estimated as 5 or 0.

The turnover number (TON) of H$_2$ was calculated from the amount of gas collected. GC analysis indicate the composition of gas is almost 3:1 H$_2$/CO$_2$ (<0.1% CO is not taken into consideration). Every hydrogen molecule represents one catalyst turnover number. Thus, the TON (H$_2$) value was calculated as:

$$\text{TON (H}_2\text{)} = \frac{V_{\text{gas}} \times (3/4)}{24.5 \div n_{\text{cat}}}$$
2. Preparation of standard curves for CO$_2$, H$_2$ and CO

Figure S17. Standard Curve of H$_2$ in GC.

Figure S18. Standard Curve of CO$_2$ in GC.
Figure S19. Standard Curve of CO in GC.
3. General experimental procedures

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \xrightarrow{\text{cat.}} \text{H}_2O \rightarrow 3\text{H}_2 + \text{CO}_2
\]

In an N\textsubscript{2}-filled glovebox, a 90 mL Fischer-Porter tube was charged with Ru-1 (1.4 mg, 2.5 \(\mu\)mol), HexSH (0.35 \(\mu\)L in 0.1 mL methanol, freshly prepared; 2.5 \(\mu\)mol), methanol (1.7 mL) and a stirring bar, and the mixture was stirred at room temperature for 1 min to allow for the \textit{in situ} generation of Ru-2 (2.5 \(\mu\)mol) in methanol.\textsuperscript{11} \text{H}_2\text{O} (0.2 mL) was then added and the Fischer-Porter tube was sealed and taken out of the glovebox. The reaction mixture was heated to 150 °C (oil bath temperature) and stirred at this temperature for 12 h, at which point the pressure gauge of the Fischer-Porter tube reached \textasciitilde8.5 bar (under heating). Subsequently, the sealed tube was cooled to room temperature and the observed pressure decreased to \textasciitilde5 bar. The Fischer-Porter tube was then connected to an inverted graduated cylinder filled with silicone oil and the tube’s valve was slowly opened to allow the gas to flow into the cylinder and displace the oil. After no more gas bubbles were observed, the valve was closed and the collected gas (470 mL) was analyzed by GC.

Cautions:
(i) The Fischer-Porter tube should be shielded with an iron net and heated behind a shielder.
(ii) Hydrogen is a flammable gas. Reactions associated with H\textsubscript{2} gas should be handled carefully inside proper fume hoods without any flame, spark or static electricity sources nearby.
(iii) Hexanethiol can be smelled when the Fischer-Porter head (adaptor and pressure gauge) is removed, which can also serve as an alarming reagent of leaking.
**Figure S20.** Reaction set-up and gas analysis

**Figure S21.** Details on monitored pressure; Due to accuracy limits of the pressure gauge, the values are approximate.
Long-term reaction with periodic addition of water and methanol: In an N$_2$-filled glovebox, a 90 mL Fischer-Porter tube was charged with Ru-1 (1.4 mg, 2.5 μmol), HexSH (0.35 μL in 0.1 mL methanol, freshly prepared; 2.5 μmol), methanol (3.5 mL) and a stirring bar, and the mixture was stirred at room temperature for 1 min to allow for the in situ generation of Ru-2 (2.5 μmol) in methanol.$^{11}$ H$_2$O (0.4 mL) was then added and the Fischer-Porter tube was sealed and taken out of the glovebox. The reaction mixture was heated to 150 °C (oil bath temperature) and stirred at this temperature, usually for 12 h (1 cycle). After the first heating cycle, the sealed Fischer-Porter tube was cooled to room temperature and connected to an inverted graduated cylinder filled with silicone oil. The tube’s valve was carefully opened and the gas was collected in the inverted cylinder. After no more gas bubbles were observed, the valve was closed and the collected gas was analyzed by GC. The Fischer-Porter tube was then reintroduced into the oil bath and the reaction mixture was stirred at 150 °C for another heating cycle. The above procedure was repeated until ~80% of the water had been consumed (usually within 3 days). At this point, the Fischer-Porter tube was transferred into the glovebox, and both methanol and water were injected into it to restore the solvent ratio to 3.6 mL MeOH/0.4 mL H$_2$O, based on the amounts of solvent that were consumed, as estimated from the volume of collected gas (trace amounts of CO were not taken into consideration). The Fischer-Porter tube was then taken out of the glovebox and the above procedure was repeated. Heating of the reaction mixture continued for a total of 592 h, during which 10930 mL of the H$_2$/CO$_2$ gas mixture were collected.
Figure S22. Long term reaction with overall TON (H2) of 133837 and trace amount of CO, 592 h heating in total.

Figure S23. Long term reaction (counting the resting time); Platform means rest at room temperature; 1167 h in total.
Figure S24. Details of the long-term reaction; MeOH and H$_2$O was injected before the reaction cycle colored in light purple. In order, the following quantities are added: 1. 0.34 mL H$_2$O + 0.77 mL MeOH; 2. 0.34 mL H$_2$O + 0.77 mL MeOH; 3. 0.35 mL H$_2$O + 0.78 mL MeOH; 4. 0.32 mL H$_2$O + 0.73 mL MeOH; 5. 0.35 mL H$_2$O + 0.79 mL MeOH.
Figure S25. $^{31}$P NMR of the resulting species in benzene-$d_6$ after 592 h heating (from the 9:1 system); Considerable amount of Ru-4, the resting state of the catalyst, was detected without the observation of free ligand.
Figure S26. Details of the short continuous reaction in 3.6 mL MeOH and 0.9 mL H₂O.
Figure S27. $^{31}$P NMR of the resulting species in benzene-$d_6$ after 302 h heating (from 6:1 system), indicating the major species is still Ru-4, the resting state of the catalyst.
Figure S28. Details of the short continuous reaction in 7.2 mL MeOH and 1.8 mL H$_2$O with 0.014 mol% Ru-1.
4. Representative GC spectra

Figure S29. GC-gas trace of collected gas $\text{H}_2/\text{CO}_2 = 3$ (3.08):1 with detectable CO (0.0365%).
**Figure S30.** GC trace of collected H\textsubscript{2}/CO\textsubscript{2} = 3 (2.94):1 with CO (20 ppm) around detection limit.
5. Condition screening

\[
\text{MeOH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3 \text{H}_2
\]

\[
\text{Ru (2.5 \mu mol)} \quad \text{HexSH (2.5 \mu mol)}
\]

\[
150 ^\circ \text{C}, 12 \text{ h}
\]

\[
1.8 \text{ mL} \quad 0.2 \text{ mL}
\]

\[
\begin{array}{l}
470 \text{ mL} \\
181 \text{ ppm CO} \\
\text{TOF (H}_2\text{): 480 h}^{-1}
\end{array}
\]

\[
\begin{array}{l}
240 \text{ mL} \\
105 \text{ ppm CO} \\
\text{TOF (H}_2\text{): 245 h}^{-1}
\end{array}
\]

\[
\begin{array}{l}
120 \text{ mL} \\
113 \text{ ppm CO} \\
\text{TOF (H}_2\text{): 122 h}^{-1}
\end{array}
\]

\[
\begin{array}{l}
455 \text{ mL} \\
110 \text{ ppm CO} \\
\text{TOF (H}_2\text{): 464 h}^{-1}
\end{array}
\]

\[
\text{without thiol}
\]

\[
\begin{array}{l}
\text{RuCl}_2(\text{PPh}_3)_3 \\
- \\
-
\end{array}
\]

\[
\begin{array}{l}
\text{replace N}_2 \text{ with} \\
\text{H}_2 \text{ + CO}_2
\end{array}
\]

\[
\text{before the reaction}
\]

**Figure S31.** Catalyst screening.

\[
\text{MeOH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3 \text{H}_2
\]

\[
\text{Ru-1 (2.5 \mu mol)} \quad \text{HexSH (X \mu L)}
\]

\[
\text{1 equiv to cat.}
\]

\[
\text{HexSH} \quad \text{HexSH} \quad \text{HexSH} \quad \text{HexSH} \quad \text{HexSH} \quad \text{HexSH}
\]

\[
\begin{array}{l}
0.0 \mu L \\
0.15 \mu L \\
0.35 \mu L \\
2 \mu L \\
5 \mu L \\
10 \mu L
\end{array}
\]

\[
\begin{array}{l}
<10 \text{ mL} \\
345 \text{ mL} \\
470 \text{ mL} \\
181 \text{ ppm CO} \\
113 \text{ ppm CO} \\
120 \text{ mL}
\end{array}
\]

\[
\text{TOF (H}_2\text{): } <10 \text{ h}^{-1}
\]

\[
\text{TOF (H}_2\text{): 362 h}^{-1}
\]

\[
\text{TOF (H}_2\text{): 362 h}^{-1}
\]

\[
\text{TOF (H}_2\text{): 135 h}^{-1}
\]

**Figure S32.** Effect of amounts of thiol on the reaction.
6. Control experiments

The Fischer-Porter tube was sealed and transferred back to the glove box after the reaction (following the general procedure). The resulting solution was directly measured by $^{31}$P NMR, indicating that a new species was formed. Then the solvent (methanol and water) was directly removed under vacuum and the resulting solid was dissolved in THF for NMR analysis. Both the signals of $^{31}$P NMR and $^1$H NMR (hydride peak) match a biscarbonyl ruthenium acridine complex \textbf{Ru-4}. Note the characterization of \textbf{Ru-2} was done in MeOH-$d4$ directly mixing \textbf{Ru-1} and 1 equiv hexanethiol.$^{11}$
Figure S3. $^{31}$P NMR of resulting species after reaction.

In a N$_2$ glove box, **Ru-1** (2.8 mg, 5 $\mu$mol), HexSH (0.7 $\mu$L, 5 $\mu$mol, by micro-syringe) and toluene-$d_8$ (0.6 mL) were added to a 30 mL steel autoclave fitted with a Teflon sleeve. The autoclave was taken out of the glove box and pressurized with 6 bar CO$_2$ and 20 bar H$_2$ sequentially. After heating at 150 ºC for 36 h with stirring, the steel autoclave was cooled in a cold water bath for 30 min. Then the gas was vented off carefully and analyzed by GC. The resulting solution was analyzed by GCMS and NMR. However, CO and MeOH were not detected.
In a N₂ glove box, Ru-1 (0.012 g, 0.02 mmol) and toluene-d₈ (0.6 mL) were added to a 30 mL steel autoclave fitted with a Teflon sleeve. The autoclave was taken out of the glove box and pressurized with 6 bar CO₂ and 20 bar H₂ sequentially. After heating at 150 °C for 72 h with stirring, the steel autoclave was cooled in a cold water bath for 30 min. Then the gas was vented off carefully and analyzed by GC. No CO was detected. The steel autoclave was transferred back into the N₂ glove box and the resulting solution was directly transferred to a J. Young NMR tube for NMR analysis. Both ³¹P NMR and ¹H NMR indicate two major new species generated, one of which is Ru-4 as signed below. However, after further heating the J. Young NMR tube at 150 °C for 2 h, the other ruthenium species also converted into Ru-4 as indicated by ³¹P NMR. These results indicate Ru-1 can react with CO₂ and H₂ to generate Ru-4. However, Ru-4 is not active enough to conduct further catalysis with CO₂ and H₂.

![Figure S35](image_url)  
Figure S35. ³¹P NMR spectra of the resulting species after heating under CO₂ and H₂.
In a N₂ glove box, Ru-4 (3.0 mg, 5 μmol), dioxane (0.5 mL) and water (0.1 mL) were added to a J. Young NMR tube. The NMR tube was taken out of the box and heated at 135 °C for 24 h, after which it was cooled to room temperature and measured by ³¹P NMR and ¹H NMR. Two species were detected by NMR, one of which was Ru-4 as signed below. The NMR tube was transferred back into the box and dioxane and water was removed under vacuum. Then toluene (0.5 mL) was added and the NMR tube was taken out of the box and measured again. Both ³¹P NMR and ¹H NMR indicated that no Ru-1 was regenerated, eliminating the possibility of water-gas-shift reaction in the system.

**Figure S36.** ³¹P NMR spectra of the resulting species after heating with water.
In a N$_2$ glove box, Ru-1 (2.8 mg, 5 $\mu$mol), HexSH (0 or 0.7 $\mu$L, 0 or 5 $\mu$mol, by micro-syringe), water (0.5 mL) and dioxane (1 mL) were added to a 90 mL Fischer-Porter tube. The tube was taken out of the glove box and evacuated until some bubbling of the solvent was observed. Then it was refilled with CO. After heating at 150 °C for 36 h with stirring, the Fischer-Porter tube was cooled to room temperature. The gauge of Fischer-Porter tube indicated no pressure was generated after heating. The gas inside the tube was analyzed by GC. However, CO$_2$ and H$_2$ were not detected.

In a N$_2$ glove box, Ru-4 (3.0 mg, 5 $\mu$mol), HexSH (0.7 $\mu$L, 5.0 $\mu$mol, by microsyringe), toluene (0.6 mL) were added to a J. Young NMR tube. The NMR tube was taken out of the box and heated at 150 °C under Ar flow for 18 h, after which it was cooled to room temperature and measured by $^{31}$P NMR and $^1$H NMR, indicating no change of Ru-4.
In a N\textsubscript{2} glove box, Ru-4 (0.012 g, 0.02 mmol), acetic acid (0.5 mL) were added to a J. Young NMR tube. The NMR tube was taken out of the box and heated at 135 °C for 10 min. After cooling down to room temperature, the NMR tube was transferred back to the glove box and the cap of NMR tube was sealed with film. Then the cap was carefully opened and the released gas was directly collected by a micro-syringe for GC analysis. Both CO and H\textsubscript{2} were detected (Figure S38). The NMR tube was taken out of the box and further heated under Ar flow for 18 h, after which it was cooled to room temperature and measured by \textsuperscript{31}P NMR and \textsuperscript{1}H NMR, indicating a major new species generated as shown below (incomplete conversion was observed in a parallel
experiment in closed system). The NMR tube was transferred back into the box and acetic acid was thoroughly removed under vacuum. Then benzene-\textit{d}_6 (0.5 mL) was added and the NMR tube was measured again, indicating the generation of a ruthenium acetate complex. The result proves the lability of the second CO on the ruthenium center. The characteristic data of **Ru-16** is in accordance with the reported one.\textsuperscript{1}

**Figure S38.** $^{31}$P NMR spectra of the resulting species after heating in acetic acid.
Figure S39. GC trace with H$_2$:CO$_2$ = 1(0.6):1, the amount of produced gas was too little which accounts for the deviation error.

Ru-16: $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 7.24 – 7.11 (m, 2H, aryl), 7.05 – 6.94 (m, 4H, aryl), 4.10 (d, $J = 16.0$ Hz, 1H, ArCH$_2$Ar), 3.90 (d, $J = 16.2$ Hz, 1H, ArCH$_2$Ar), 2.80 (t, $J = 10.8$ Hz, 2H, CH$_2$P), 2.55 – 2.39 (m, 2H, CH$_2$P), 2.04 – 1.85 (m, 4H, PCH(CH$_3$)$_2$), 1.55 (s, 3H, COCH$_3$), 1.47 – 1.33 (m, 6H, PCH(CH$_3$)$_2$), 1.17 – 0.93 (m, 18H, PCH(CH$_3$)$_2$). $^{13}$C NMR (101 MHz, C$_6$D$_6$) $\delta$203.06 (t, $J = 15.6$ Hz, Ru-CO), 189.86 (s, COCH$_3$), 153.81 (s, Ar), 129.80 (s, Ar), 127.61 (s, Ar), 126.46 (s, Ar), 122.36 (s, Ar), 118.57 (s, Ar), 34.88 (s, ArCH$_2$Ar), 29.67 (p, $J = 8.9$ Hz, PCH(CH$_3$)$_2$), 28.43 (dt, $J = 18.6$, 9.2 Hz, CH$_3$P), 26.16 (dt, $J = 21.6$, 8.6 Hz, PCH(CH$_3$)$_2$), 24.11 (s,
COCH₃), 20.55 (s, PCH(CH₃)₂), 19.72 (s, PCH(CH₃)₂), 19.09 (s, PCH(CH₃)₂), 18.91 (s, PCH(CH₃)₂). ³¹P NMR (162 MHz, C₆D₆) δ 86.76.

Figure S40. ¹H NMR of crude Ru-16 in benzene-δ₆.

Figure S41. ¹³C NMR of crude Ru-16 in benzene-δ₆.
Figure S42. $^{31}$P NMR of crude Ru-16 in benzene-$d_6$. 
7. Computational details

DFT calculations were performed with Gaussian 16 (C.01 revision)\textsuperscript{12} using Truhlar’s M06-L functional,\textsuperscript{13} the triple-\(\xi\) def2-TZVP basis set,\textsuperscript{14} W06 density fitting,\textsuperscript{15} and Grimme’s D3(0) empirical dispersion correction.\textsuperscript{16} Frequency calculations at this level of theory were run at 383.15K (experimentally determined initial internal reaction temperature) to confirm stationary points and transition states and to obtain thermodynamic corrections. Single point energies of the M06-L optimized structures were computed with ORCA (4.2.1)\textsuperscript{17} using the range-separated meta-GGA hybrid functional \(\omega\)B97M-V of the Head-Gordon group\textsuperscript{18} including dispersion correction,\textsuperscript{19,20} together with the triple-\(\xi\) def2-TZVPP basis set\textsuperscript{14} and the corresponding auxiliary basis sets, def2/J\textsuperscript{15} and def2-TZVPP/C\textsuperscript{21} for RIJCOSX density fitting. The functional and basis set selections are based on recent benchmark studies.\textsuperscript{22} The polarizable continuum model (IEFPCM) was used in all calculations (optimization and single point) with the SMD solvation (Methanol) model of Truhlar and co-workers.\textsuperscript{23}

Gibbs free energies were computed by adding the free energy correction term from the frequency calculation to the single point energy in methanol, according to

\[
G^{\omega B97M-V}_{\text{Methanol,383.15K}} = E^{\omega B97M-V}_{\text{Methanol}} + \text{corr}^{M06-L}_{\text{freq}(\text{Methanol,1 atm,383.15K})}
\]

where \(E^{\omega B97M-V}_{\text{Methanol}}\) is the single point energy; and

where \(\text{corr}^{M06-L}_{\text{freq}}\) is the thermal correction to the Gibbs free energy from the frequency calculation (at \(T = 383.15K\) and \(P = 1\) atm).

Free energy values (\(G^0\)) were then corrected to account for changes in standard states (\(G^0 \rightarrow G\)).

Standard state corrections\textsuperscript{24} were employed such that all species are treated as 1M (using an ideal gas approximation), with the exception of \(H_2\), CO\(_2\), CO (maintained as 1 atm), water (1 atm to 5.5M) and methanol (1 atm to 22M).\textsuperscript{25-27} Other than these standard state corrections, the transformation of hydrogen, CO\(_2\) and CO from the condensed phase to the gas phase is not additionally corrected in the free energy quantities provided.
Ethanethiol were studied as minimal models for hexanethiol in the system.
Directionality of ∆G and ∆G_{TS} values are indicated by the ordering of X,Y and all energies are reported in kcal/mol.

Table S2 Energy data

| Structure | $E^\text{soB97M-V}_\text{MeOH}$ | $G^\text{soB97M-V}_\text{MeOH}$ | Imaginary Frequency | $G_{T=383.15K}$ |
|-----------|---------------------------------|---------------------------------|---------------------|------------------|
| Energy Unit | Hartree | Hartree | cm$^{-1}$ | kcal |
| mer Ru-1 | -1999.28346 | -1998.751253 | - | -1254213.976 |
| fac Ru-1 | -1999.270686 | -1998.734105 | - | -1254203.216 |
| fac Ru-2 | -2477.298617 | -2476.693754 | - | -1554122.895 |
| Ru-3 | -2476.110273 | -2475.521106 | - | -1553387.059 |
| Ru-4 | -2112.668395 | -2112.129625 | - | -1325358.904 |
| Ru-5 | -2115.024487 | -2114.439602 | - | -1326808.415 |
| Ru-6 | -2113.816693 | -2113.262898 | - | -1326070.033 |
| Ru-7 | -2113.817184 | -2113.252456 | - | -1326063.48 |
| Ru-8 | -2075.73643 | -2075.17787 | - | -1302171.678 |
| Ru-9 | -2074.538698 | -2073.997816 | - | -1301431.194 |
| Ru-10 | -2189.090472 | -2188.518229 | - | -1373292.753 |
| Ru-11 | -2189.100084 | -2188.53336 | - | -1373302.248 |
| Ru-12 | -2187.938354 | -2187.388297 | - | -1372583.721 |
| Ru-13 | -2187.913267 | -2187.364281 | - | -1372568.651 |
| Ru-15 | -2190.277381 | -2189.690626 | - | -1374028.433 |
| TS_{2,3} | -2477.277135 | -2476.674399 | -799.9086 | -1554110.75 |
| TS_{3,4} | -2591.814004 | -2591.183875 | -432.5953 | -1625965.446 |
| TS_{4,5} | -2667.079178 | -2666.445477 | -784.5237 | -1673192.102 |
| TS_{5,6} | -2114.984669 | -2114.04952 | -1283.1892 | -1326786.672 |
| TS_{6,7} | -2113.817771 | -2113.25254 | -409.6517 | -1326063.533 |
| TS_{8,9} | -2075.701105 | -2075.146419 | -1149.2154 | -1302151.942 |
| TS_{9,10} | -2190.236516 | -2189.654216 | -124.1641 | -1374005.585 |
| TS_{10,11} | -2189.081706 | -2188.517223 | -608.7270 | -1373292.122 |
| TS_{11,12} | -2189.092849 | -2188.530098 | -1206.7272 | -1374005.858 |
| TS_{12,13} | -2187.897814 | -2187.354255 | -344.4940 | -1372562.36 |
| TS_{13,14} | -2190.236516 | -2189.654216 | -1422.1539 | -1374005.585 |
| TS_{14,15} | -2190.240271 | -2189.654652 | -1127.4550 | -1374005.859 |
| H$_2$O | -76.44592285 | -76.44951685 | - | -47968.3383 |
| EtSH | -477.9872272 | -477.9478982 | - | -299909.8707 |
| MeOH | -115.7259917 | -115.7053527 | - | -72600.31985 |
| Chemical  | First Value   | Second Value  | Difference | Final Value |
|-----------|---------------|---------------|------------|-------------|
| HCHO      | -114.5117968  | -114.5135018  | -          | -71854.78694|
| HOCH$_2$OH | -190.9818141  | -190.9586491  | -          | -119824.1168|
| HCOOH     | -189.7986995  | -189.7975065  | -          | -119095.4999|
| hydrogen  | -1.161258141  | -1.167228141  | -          | -732.4356587 |
| CO$_2$    | -188.6177062  | -188.6345492  | -          | -118368.1796|
| CO        | -113.3293545  | -113.3499765  | -          | -71127.11022|
### Cartesian Coordinates

**mer Ru-1**

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| Ru   | -0.240225  | 6.307933   | 1.352731   |
| P    | -1.850357  | 7.509768   | 0.173570   |
| P    | 1.679411   | 5.967394   | 2.632795   |
| O    | -2.105920  | 5.415163   | 3.484014   |
| N    | 0.972914   | 6.122066   | -0.508069  |
| C    | -1.365209  | 5.829090   | 2.671698   |
| C    | -1.661386  | 10.101667  | 1.254831   |
| C    | -3.225217  | 8.513471   | 2.391300   |
| C    | -2.622652  | 8.940461   | 1.062134   |
| C    | -4.065093  | 7.452908   | -1.617497  |
| C    | -2.987689  | 5.253264   | -1.041240  |
| C    | -3.325142  | 6.656310   | -0.556063  |
| C    | 3.499795   | 4.192877   | 3.917809   |
| C    | 1.157803   | 3.350946   | 3.491058   |
| C    | 2.283448   | 4.255521   | 3.010600   |
| C    | 0.733571   | 6.602650   | 5.200755   |
| C    | 1.908427   | 8.428848   | 3.968930   |
| C    | 1.837554   | 6.928923   | 4.208356   |
| C    | 0.371835   | 6.184855   | -1.776885  |
| C    | 2.209471   | 5.452769   | -0.497248  |
| C    | -0.911573  | 8.298111   | -1.189745  |
| C    | -0.462736  | 7.262280   | -2.163354  |
| C    | -0.942430  | 7.331640   | -3.468564  |
| C    | -0.655335  | 6.362306   | -4.415424  |
| C    | 0.108194   | 5.272152   | -4.028696  |
| C    | 0.597470   | 5.172611   | -2.736121  |
| C    | 1.346791   | 3.972866   | -2.269279  |
| C    | 2.485945   | 4.420994   | -1.420600  |
| C    | 3.737401   | 3.830370   | -1.498942  |
| C    | 4.754566   | 4.207257   | -0.636033  |
| C    | 4.478889   | 5.164913   | 0.326312   |
| C    | 3.237065   | 5.787495   | 0.419097   |
| C    | 2.989638   | 6.698525   | 1.569384   |
| H    | -0.777316  | 9.800954   | 1.821011   |
| H    | -1.326318  | 10.531454  | 0.312261   |
| H    | -2.151193  | 10.896763  | 1.819481   |
| H    | -3.840353  | 9.316846   | 2.799746   |
| H    | -3.856302  | 7.628047   | 2.307745   |
| H    | -2.443131  | 8.297529   | 3.121666   |
| H    | -3.430765  | 9.273000   | 0.402903   |
| H    | -4.994328  | 6.947981   | -1.881740  |
| H    | -4.328119  | 8.457604   | -1.287567  |
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H -0.9201740000 6.9737010000 1.0649970000
H -2.3405070000 7.7641340000 0.3745970000
C -0.7860170000 9.0987160000 0.9931630000

S45
| Element | X       | Y       | Z       |
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| C       | -1.1585830000 | 10.0562490000 | 0.0554960000 |
| H       | -2.0558360000 | 9.8857300000 | -0.5306330000 |
| C       | -0.3878200000 | 11.1881910000 | -0.1675780000 |
| H       | -0.6844640000 | 11.9142630000 | -0.9138220000 |
| C       | 0.7758270000 | 11.3688630000 | 0.5695420000 |
| H       | 1.3959330000 | 12.2436160000 | 0.4025280000 |
| C       | 1.1527070000 | 10.4551970000 | 1.5419060000 |
| C       | 0.3707040000 | 9.3064040000 | 1.7787610000 |
| C       | 2.3599520000 | 10.6529080000 | 2.4069360000 |
| H       | 3.0786260000 | 11.3272400000 | 1.9381740000 |
| H       | 2.0501340000 | 11.1520410000 | 3.3382390000 |
| C       | 2.9861430000 | 9.3390660000 | 2.7610220000 |
| C       | 3.4469640000 | 9.1844160000 | 2.9798170000 |
| H       | 5.0057680000 | 10.0319380000 | 2.8201380000 |
| C       | 4.8632320000 | 7.9755470000 | 3.4304310000 |
| H       | 5.9250750000 | 8.6546100000 | 3.6105960000 |
| C       | 4.0009050000 | 6.9096880000 | 3.6511520000 |
| H       | 4.3914800000 | 5.9586900000 | 3.9981580000 |
| C       | 2.6369660000 | 7.0235540000 | 3.4071600000 |
| C       | 2.1125200000 | 8.2550850000 | 2.9602760000 |
| C       | 1.7202650000 | 5.8625430000 | 3.6023760000 |
| H       | 2.2885030000 | 4.9541930000 | 3.8046010000 |
| H       | 1.1164080000 | 5.6861950000 | 2.7066780000 |
| C       | -3.4785280000 | 6.2516120000 | 2.6492890000 |
| H       | -4.2945830000 | 6.5865760000 | 2.0035610000 |
| C       | -4.0595750000 | 5.8708190000 | 4.0017820000 |
| H       | -3.2825550000 | 5.5544260000 | 4.6995260000 |
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| H       | -4.5955740000 | 6.6990340000 | 4.4656620000 |
| C       | -2.7978760000 | 5.0813150000 | 1.9527070000 |
| H       | -2.6225510000 | 5.2837740000 | 0.8972660000 |
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| H       | -1.8352450000 | 4.8245240000 | 2.3975280000 |
| C       | -3.4505270000 | 9.2086390000 | 2.8307260000 |
| H       | -2.7739510000 | 9.9779390000 | 2.4412900000 |
| C       | -3.8669670000 | 9.6381640000 | 4.2287940000 |
| H       | -4.4598150000 | 8.8772000000 | 4.7378800000 |
| H       | -4.4784830000 | 10.5408230000 | 4.1744910000 |
| H       | -3.0050940000 | 9.8635380000 | 4.8568090000 |
| C       | -4.6441540000 | 9.1188500000 | 1.8945180000 |
| H       | -4.3741900000 | 8.7707720000 | 0.8969820000 |
| H       | -5.1042570000 | 10.1022570000 | 1.7827000000 |
| H       | -5.4113120000 | 8.4493280000 | 2.2867080000 |
| C       | 1.5924660000 | 6.1796570000 | 6.4548550000 |

S46
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 C -1.5854520000 7.8810530000 1.1784000000
 H -1.0136730000 6.9482970000 1.1365060000
 H -2.4795490000 7.7472390000 0.5693000000
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 C 2.7064240000 10.3679440000 1.2943300000
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Ru-4

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C 21.5248970000 -1.0312070000 6.1552370000
C 20.4471440000 0.0984850000 8.3180920000
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H 20.1643580000 -3.3898400000 4.8973580000
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H 23.0845320000 4.6176300000 6.2416940000
H 24.2577270000 4.2228750000 7.4903760000
H 24.4388370000 1.7917150000 8.3513540000
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H 21.2526590000 3.2401730000 3.0256560000
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H 23.3202580000 2.7094910000 4.2376370000
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Ru-5

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C 1.2471820000 10.2432670000 1.2724010000
C 0.466475000 9.1182720000 1.6184060000
C 2.4962990000 10.4928000000 2.0657850000
H 3.2069120000 11.1001450000 1.5021770000
H 2.2386770000 11.0959920000 2.9511570000
C 3.1157130000 9.2091670000 2.5281500000
C 4.5769250000 9.0739150000 2.7635780000
H 5.1342440000 9.9085560000 2.5414420000
C 4.9961930000 7.9049700000 3.3058430000
H 6.0574810000 7.8144890000 3.4998890000
C 4.1377740000 6.8504000000 3.5921030000
H 4.5297530000 5.9246570000 4.0013840000
C 2.7768960000 6.9432030000 3.3096300000
C 2.2452840000 8.1427080000 2.8096130000
C 1.8552110000 5.7954270000 3.5486760000
H 2.4037270000 4.8839050000 3.7934390000
H 1.2853840000 5.6078190000 2.6356140000
C -3.4748620000 6.3502980000 3.0767770000

S53
H -2.8300070000 5.5430000000 3.4219170000
C -4.1061080000 5.8849030000 1.7742320000
H -4.7323720000 6.6461880000 1.3115360000
H -4.7416350000 5.0185930000 1.9699000000
H -3.3587640000 5.5756360000 1.0441460000
C -4.5124600000 6.5760780000 4.1671770000
H -4.0701100000 6.9532540000 5.0908020000
H -5.0098890000 5.6337710000 4.4041400000
H -5.2845080000 7.2791380000 3.8549980000
C -3.3281090000 9.3379730000 2.8359770000
H -2.5736220000 10.0468530000 2.4795840000
C -3.8239110000 9.8553300000 4.1791290000
H -4.6774410000 9.2888270000 4.5487090000
H -4.1507340000 10.8925040000 4.0763630000
H -3.0500740000 9.8319880000 4.9445100000
C -4.4514060000 9.3098840000 1.8109210000
H -4.1249610000 8.9562560000 0.8333000000
H -4.8495920000 10.3177980000 1.6738740000
H -5.2808590000 8.6810450000 2.1353110000
C 1.6114280000 5.9965100000 6.3941370000
H 2.4478250000 6.6502900000 6.1174910000
C 0.9613890000 6.5833230000 7.6355570000
H 0.6968880000 7.6306100000 7.5039860000
H 1.6569460000 6.5239680000 8.4746460000
H 0.0615490000 6.0395400000 7.9255890000
C 2.1685610000 4.6110760000 6.6860400000
H 1.4003210000 3.9446240000 7.0808360000
H 2.9491020000 4.6833870000 7.4451170000
H 2.6109820000 4.1332580000 5.8119970000
C -0.3698020000 4.4919060000 4.8060430000
H 0.3132670000 3.7373150000 5.2030700000
C -0.7137570000 4.0898600000 3.3750640000
H -1.0067050000 4.9392150000 2.7548210000
H -1.5400630000 3.3769280000 3.3659500000
H 0.1322190000 3.6142830000 2.8811170000
C -1.5785940000 4.5633080000 5.7259000000
H -1.2873870000 4.7166940000 6.7654290000
H -2.1497050000 3.6343940000 5.6785850000
H -2.2498120000 5.3789460000 5.4552510000
C -0.3705310000 11.2848030000 5.1702650000
H -0.9965930000 11.0015460000 6.0137230000
H 0.6765910000 11.1617110000 5.4537570000
C -1.3747880000 8.0028730000 5.9557350000
Ru -0.3771280000 8.0817400000 4.4455230000
Ru-6
Ru -0.3364660000 -0.1829860000 0.5825190000
P -1.3223740000 1.6428180000 -0.2809670000
P -0.7434650000 -1.9797680000 -0.8948940000
O 0.6489420000 1.0036710000 2.0215530000
O -2.7989970000 -0.7917020000 2.1644360000
N 1.4432500000 0.2141090000 -0.6767200000
C -0.1645200000 2.3216350000 -1.5372000000
H -0.1282560000 1.5699920000 -2.3317460000
H -0.5876610000 3.2340910000 -1.9570980000
C 1.1968390000 2.5765200000 -0.9799310000
C 1.7120910000 3.8639930000 -0.8837000000
H 1.1025830000 4.6990000000 -1.2129210000
C 2.9961820000 4.0865180000 -0.4047390000
H 3.3914370000 5.0929440000 -0.3502270000
C 3.7679440000 3.0048970000 0.0054360000
H 4.7664340000 3.1685400000 0.3980100000
C 3.2683210000 1.7125110000 -0.0452010000
C 1.9766610000 1.4820370000 -0.5529010000
C 0.6400380000 -2.0470570000 -2.1055000000
H 0.5364370000 -2.3931200000 -2.7259680000
H 0.5078510000 -1.1731020000 -2.7494010000
C 1.9785130000 -1.9981110000 -1.4493830000
C 2.8747570000 -3.0564250000 -1.5429340000
H 2.5710450000 -3.9542130000 -2.0714260000
C 4.1536740000 -2.9602800000 -1.0111340000
H 4.8477070000 -3.7858320000 -1.1053830000
C 4.5396550000 -1.7869470000 -0.3730630000
H 5.5417970000 -1.6950510000 0.0332610000
C 3.6554010000 -0.7285330000 -0.2267670000
C 2.3522990000 -0.8287370000 -0.7515600000
C 4.0099700000 0.5309620000 0.5069790000
H 5.0885190000 0.7003500000 0.5009490000
H 3.7391050000 0.4147690000 1.5670820000
C -2.9578430000 1.4767970000 -1.1313500000
H -2.8989490000 0.4643740000 -1.5303930000
C -3.1574630000 2.4220070000 -2.3080380000
H -4.1240920000 2.2133580000 -2.7699380000
H -2.3976460000 2.2967760000 -3.0775670000
H -3.1626020000 3.4684760000 -2.0047710000
C -4.1441390000 1.5185990000 -0.1795080000

S55
Ru-7
Ru -0.3357970000 -0.3189950000 0.7704930000
P -1.4224240000 1.6656010000 -0.2195100000
P -0.6563350000 -2.1432460000 -0.6247140000
O 0.5343170000 1.1316710000 2.1866110000
O -2.7331410000 -0.9884770000 2.4192250000
N 1.4593860000 0.1908030000 -0.4826470000
C -0.2358410000 2.2484750000 -1.4964520000
H -0.1793250000 1.4388740000 -2.2307880000
H -0.6330110000 3.1295430000 -2.0011410000
C 1.1139390000 2.5424560000 -0.9295640000
C 1.5818640000 3.8521780000 -0.9048310000
H 0.9379510000 4.6395650000 -1.2823580000
C 3.2092260000 5.1797570000 -0.4472340000
C 3.6706890000 3.1267190000 0.0013600000
H 4.6710310000 3.3435150000 0.3624230000
C 3.2234290000 1.8142830000 0.0227240000
C 1.9301640000 1.4961710000 -0.4414240000
C 0.7725330000 -2.1855230000 -1.7697140000
H 0.7162760000 -3.1025580000 -2.3592160000
H 0.6121030000 -1.3419540000 -2.4458580000
C 2.0997810000 -2.0420310000 -1.1100260000
C 3.0296900000 -3.0733190000 -1.1235100000
H 2.7516740000 -4.0219500000 -1.5716520000
C 3.3091160000 -2.8887560000 -0.6157770000
H 5.0309610000 -3.6951210000 -0.6425750000
C 4.6560690000 -1.6496890000 -0.0938940000
H 5.6571880000 -1.4846020000 0.2915040000
C 3.7356850000 -0.6117990000 -0.0314460000
C 2.4300970000 -0.8017210000 -0.5185190000
C 4.0692780000 0.7121420000 0.5868600000
H 5.1314130000 0.9396570000 0.4705050000
H 3.9100590000 0.6587480000 1.6733820000
C -3.0669010000 1.5475020000 -1.0698010000
H -3.0478560000 0.5432690000 -1.4909940000
C -3.2757740000 2.5109770000 -2.2277110000
H -4.2611120000 2.3382380000 -2.6650850000
H -2.5424370000 2.3661100000 -3.0201620000
H -3.2370120000 3.5550440000 -1.9199760000
C -4.2193190000 1.5888760000 -0.0770430000
H -4.3994000000 2.5984640000 0.2914340000
H -4.0527710000 0.9413220000 0.7847770000
H -5.1357400000 1.2543180000 -0.5661970000
C -1.4644100000 3.0873200000 0.9678050000
H -0.3976070000 3.1876120000 1.1934320000
C -2.1787210000 2.7881010000 2.2782120000
H -1.9144940000 3.5460000000 3.0179230000
Ru-8
O 1.1596540000 9.4098330000 5.6041730000
P 2.3535220000 7.8817160000 2.8695240000
P 0.3693660000 6.0619010000 4.8681670000
O 1.6084620000 7.9904190000 6.6599810000
N 0.7127030000 8.3683330000 2.6466370000
C 1.6239340000 8.0447350000 1.1889340000
H 1.0013980000 7.1552910000 1.0673470000
H 1.3828687000 7.9925090000 0.4535080000
C 0.7895770000 9.2618850000 1.0002310000
C 1.1360390000 10.2578720000 0.0966200000
C -0.6124050000 4.5861580000 5.0010640000
H -1.4273930000 4.7775850000 4.3046260000
C -1.2338530000 4.3927000000 6.3765870000
H -0.4947420000 4.0942510000 7.1193170000
H -1.9762330000 3.5945290000 6.3237510000
H -1.7406450000 5.2836550000 6.7435870000
H 0.0989100000 3.3252470000 4.5305580000
C 0.4126690000 3.3870830000 3.4899180000
H 0.5884730000 2.4811580000 4.6113220000
H 0.9741500000 3.0884770000 5.1342540000
H -1.7080970000 7.8934270000 5.8329430000
Ru -0.5754400000 8.1190540000 6.2557670000
H 0.6447770000 9.4403610000 6.2557670000

Ru-10
Ru 10.4526630000 3.6499870000 2.5158250000
O 11.7809570000 4.1125720000 4.1398860000
P 9.3395570000 2.0411020000 3.6793300000
P 9.7352170000 3.4245630000 0.3082590000
O 8.2603360000 5.5884510000 3.1248670000
N 11.9652620000 2.0603180000 1.9913320000
C 10.2519810000 0.4568840000 3.4774030000
H 9.7635990000 -0.3155010000 4.0709860000
H 10.1407950000 0.1903130000 2.4220010000
C 11.6918520000 0.5787570000 3.8490800000
C 12.2250850000 -0.1143120000 4.9294000000
H 11.5725760000 -0.7488020000 5.5199700000
C 13.5764810000 -0.0284530000 5.2360900000
H 13.9837830000 -0.5864390000 6.0696820000
C 14.4007710000 0.7807340000 4.4617910000
H 15.4558480000 0.8664350000 4.7017150000
C 13.8914580000 1.5115240000 3.3990980000
C 12.5260150000 1.4086300000 3.0721530000
C 14.7209850000 2.4859610000 2.6154690000
H 14.6740940000 3.4655530000 3.1143740000
H 15.7767360000 2.2070040000 2.6280360000
C 14.2161660000 2.6344470000 1.2106820000
C 12.8388260000 2.4478770000 0.9910210000
C 15.0381130000 2.9930910000 0.1523310000
H 16.0986530000 3.1346560000 0.3346260000
C 14.5204680000 3.1941600000 -1.1224480000
H 15.1705010000 3.4885030000 -1.9367030000
C 13.1640550000 2.9964110000 -1.3454810000
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| H    | 9.883592| 6.415704| 0.000000|
| C    | 9.129673| 4.844131| 2.894636|
| C    | 12.131431| 5.348319| 1.091550|
| O    | 11.849274| 6.206710| 1.965520|
| H    | 13.113634| 6.146463| 4.048719|
| Ru   | 0.109232| 11.162280| 4.613228|
| O    | 1.119027| 10.174111| 4.838560|
| H    | 0.985343| 8.733058| 5.099179|
| P    | -2.318852| 7.815303| 2.867874|
| P    | 0.493240| 6.253526| 4.859008|
| O    | -1.999168| 8.242837| 6.870955|
| N    | 0.827971| 7.963810| 4.242075|
| C    | -1.680421| 7.975277| 1.153815|
| H    | -1.089431| 7.068410| 0.990144|
| H    | -2.514455| 7.960348| 0.451169|
| C    | -0.838399| 9.185967| 0.934659|
| C    | -1.281103| 10.221027| 0.121040|
| H    | -2.272864| 10.153892| -0.315067|
| C    | -0.465129| 11.306998| -0.167466|
| H    | -0.819035| 12.105051| -0.807699|
| C    | 0.824049| 11.334932| 0.347766|
| H    | 1.487162| 12.158850| 0.102803|
| C    | 1.287516| 10.331538| 1.188610|
| H    | 0.439272| 9.263142| 1.537333|
| C    | 2.668323| 10.380346| 1.773412|
| H    | 3.375483| 10.789814| 1.045246|
| H    | 2.686827| 11.098957| 2.606283|
| C    | 3.131002| 9.043590| 2.265267|
| C    | 4.479317| 8.769849| 2.449514|
| H    | 5.207659| 9.528294| 2.179630|
| C    | 4.903666| 7.563563| 2.991066|
| H    | 5.958126| 7.367816| 3.138843|
| C    | 3.956064| 6.609339| 3.335952|
| H    | 4.269371| 5.655521| 3.747755|
| C    | 2.604022| 6.838353| 3.135534|
| C    | 2.166548| 8.076251| 2.608560|
| C    | 1.591931| 5.788165| 3.459338|
| H    | 2.085795| 4.843977| 3.689964|
| H    | 0.917305| 5.617264| 2.614176|

**Ru-II**

O 1.092323000 11.162280000 4.6132280000
H 1.119027000 10.1741110000 4.8385600000
H 0.9853430000 8.7330580000 5.0991790000
P -2.3188520000 7.8153030000 2.8678740000
P 0.4932400000 6.2535260000 4.8590080000
O -1.9991680000 8.2428370000 6.8709550000
N 0.8279710000 7.9638100000 4.2420750000
C -1.6804210000 7.9752770000 1.1538150000
H -1.0894310000 7.0684100000 0.9901440000
H -2.5144550000 7.9603480000 0.4511690000
C -0.8383990000 9.1859670000 0.9346590000
C -1.2811030000 10.2210270000 0.1210400000
H -2.2728640000 10.1538920000 -0.3150670000
C -0.4651290000 11.3069980000 -0.1674660000
H -0.8190350000 12.1050510000 -0.8076990000
C 0.8240490000 11.3349320000 0.3477660000
H 1.4871620000 12.1588500000 0.1028030000
C 1.2875160000 10.3315380000 1.1886100000
H 0.4392720000 9.2631420000 1.5373330000
C 2.6683230000 10.3803460000 1.7734120000
H 3.3754830000 10.7898140000 1.0452460000
H 2.6868270000 11.0989570000 2.6062830000
C 3.1310020000 9.0435900000 2.2652670000
C 4.4793170000 8.7698490000 2.4495140000
H 5.2076590000 9.5282940000 2.1796300000
C 4.9036660000 7.5635630000 2.9910660000
H 5.9581260000 7.3678160000 3.1388430000
C 3.9560640000 6.6093390000 3.3359520000
H 4.2693710000 5.6555210000 3.7477550000
C 2.6040220000 6.8383530000 3.1355340000
C 2.1665480000 8.0762510000 2.6085600000
C 1.5919310000 5.7881650000 3.4593380000
H 2.0857950000 4.8439770000 3.6899640000
H 0.9173050000 5.6172640000 2.6141760000
Ru-12
Ru 8.7192150000 12.3981460000 13.1372780000
P 7.7315180000 14.1885710000 12.1137510000
P 8.3621890000 10.6173260000 11.7127640000
O 9.7486020000 13.5699330000 14.7825430000
O 10.2089880000 11.4147160000 14.6737180000
O 6.2123630000 11.8196930000 14.6654000000
N 10.5389150000 12.8135620000 11.9614140000
C 8.9422960000 14.8508730000 10.8988380000
H 9.0412370000 14.0767970000 10.1315100000
H 8.5286930000 15.7407000000 10.4246510000
C 10.2663850000 15.1554210000 11.5209000000
C 10.7585330000 16.4569600000 11.5713480000
H 10.1513140000 17.2610750000 11.1738690000
C 12.0208290000 16.7220950000 12.0832570000
H 12.3982890000 17.7365840000 12.1015980000
C 12.7997330000 15.6738430000 12.5604780000
H 13.7886690000 15.8719020000 12.9612830000
C 12.3239760000 14.3714270000 12.5567980000
C 11.0438220000 14.0985770000 12.0385630000
C 9.7975720000 10.5334490000 10.5709820000
H 9.7104180000 9.6320800000 9.9621490000
H 9.6892650000 11.3961670000 9.9082060000
C 11.1169630000 10.5963670000 11.2640860000
C 12.0191150000 9.5400770000 11.2286300000
H 11.7308930000 8.6188880000 10.7327750000
C 13.2883540000 9.6695910000 11.7772650000
H 13.9886160000 8.8451490000 11.7323420000
C 13.6593420000 10.8740380000 12.3647770000
H 14.6549550000 10.9898240000 12.7808760000
C 12.7663400000 11.9318930000 12.4516920000
C 11.4717600000 11.7923800000 11.9207780000
C 13.0969610000 13.2239400000 13.1394970000
H 14.1708660000 13.4199840000 13.1140160000
H 12.8495030000 13.1338070000 14.2080320000
C 6.1020840000 14.0935760000 11.2389410000
H 6.1198910000 13.0894630000 10.8183200000
C 5.9467300000 15.0658880000 10.0786280000
H 4.9713100000 14.9108940000 9.6141380000
H 6.6998440000 14.9134620000 9.3070090000
H 5.9928290000 16.1070700000 10.3954710000

S66
Ru-13
Ru 8.7236490000 12.3812320000 13.1057190000
P 7.7737110000 14.2024490000 12.1727170000
P 8.3392700000 10.6083460000 11.6447040000
O 11.0536710000 13.5979310000 16.3286270000
Ru-15
O -0.7354370000 10.4458900000 4.0739290000
H -0.1413760000 10.6811820000 3.3428000000
H 0.9980320000 8.5044510000 5.2654490000
P -2.2972550000 7.7965130000 2.9493440000
P 0.5825290000 6.0808670000 4.8569120000
O -2.0422070000 7.9394210000 6.9238770000
N 0.8906360000 8.2118180000 2.5919840000
C -1.5785950000 7.7146630000 1.2518390000
H -0.9758560000 6.8011170000 1.2358750000
H -2.3683150000 7.6088080000 0.5072740000
C -0.7375930000 8.9106780000 0.9452910000
C -1.1435540000 9.8224630000 -0.0230020000
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | -2.0819560000 | 9.6469630000 | -0.5385360000 |
| C    | -0.3642980000 | 10.9205350000 | -0.3601190000 |
| H    | -0.6929320000 | 11.6097710000 | 0.0488970000 |
| C    | 0.8430430000 | 11.1353700000 | 2.9670270000 |
| C    | 3.1287660000 | 9.2106050000 | 2.5524630000 |
| C    | 4.4886730000 | 9.0739710000 | 2.7948200000 |
| H    | 5.1478400000 | 9.9079460000 | 2.5756790000 |
| C    | 5.0042600000 | 7.9045640000 | 3.3393550000 |
| H    | 6.0644830000 | 7.8130700000 | 3.5386130000 |
| C    | 4.1434870000 | 6.8505460000 | 3.6203610000 |
| H    | 4.5325320000 | 5.9239950000 | 4.0305680000 |
| C    | 2.7840920000 | 6.9448090000 | 3.3523080000 |
| C    | 2.2556610000 | 8.1452030000 | 2.8297380000 |
| C    | 1.8606990000 | 5.7973680000 | 3.5635070000 |
| H    | 2.4072980000 | 4.8849140000 | 3.8090130000 |
| H    | 1.2945790000 | 5.6121100000 | 2.6476840000 |
| C    | -3.4703700000 | 6.3589060000 | 3.0700830000 |
| H    | -2.8276640000 | 5.5494110000 | 3.4142760000 |
| C    | -4.1002520000 | 5.8981350000 | 1.7652540000 |
| H    | -4.7250320000 | 6.6614510000 | 1.3039820000 |
| H    | -4.7369560000 | 5.0319080000 | 1.9573890000 |
| H    | -3.3521790000 | 5.5902970000 | 1.0352880000 |
| C    | -4.5090800000 | 6.5849770000 | 4.1594610000 |
| H    | -4.0670680000 | 6.9586170000 | 5.0846730000 |
| H    | -5.0097250000 | 5.6436220000 | 4.3933520000 |
| H    | -5.2785100000 | 7.2911810000 | 3.8479690000 |
| C    | -3.3191770000 | 9.3468310000 | 2.8364980000 |
| H    | -2.5642680000 | 10.0538870000 | 2.4782080000 |
| C    | -3.8123820000 | 9.8672880000 | 4.1797240000 |
| H    | -4.6721270000 | 9.3080480000 | 4.5465740000 |
| H    | -4.1283440000 | 10.9078070000 | 4.0778910000 |
| H    | -3.0409340000 | 9.8357450000 | 4.9474120000 |
| C    | -4.4434190000 | 9.3202990000 | 1.8123820000 |
| H    | -4.1177900000 | 8.9666770000 | 0.8345100000 |
| H    | -4.8400210000 | 10.3289120000 | 1.6759790000 |
| H    | -5.2737610000 | 8.6926250000 | 2.1366410000 |
| C    | 1.6060850000 | 5.9963850000 | 6.4080020000 |
| H    | 2.4431100000 | 6.6509330000 | 6.1350150000 |
H 3.0739950000 5.0029340000 7.3385500000
H 2.6865520000 4.3811230000 5.7376770000
C -0.3568310000 4.6197650000 4.8715130000
H 0.3837420000 3.8961660000 5.2207170000
C -0.8042580000 4.1720810000 3.4809730000
H -1.1175940000 4.9995580000 2.8428190000
H -1.6433410000 3.4778660000 3.5513900000
H 0.0007050000 3.6597390000 2.9561520000
C -1.4700660000 4.6738860000 5.9077330000
H -1.0687890000 4.7844140000 6.9152550000
H -2.0543560000 3.7523780000 5.8878660000
H -2.1575110000 5.5041930000 5.7443440000
C -0.7130120000 11.4715380000 5.7308200000
H -1.7319810000 11.2665100000 6.0587070000
H -0.0422800000 10.8907970000 6.3631630000
C -0.4011530000 12.9445400000 5.7638300000
H -1.0859720000 13.5171100000 5.1379320000
H 0.6151120000 13.1440670000 5.4264240000
H -0.4902600000 13.3179440000 6.7843420000
C 2.3694450000 9.6575290000 5.6001280000
H 1.0835760000 8.7829660000 5.1205050000
H 3.0160150000 8.8582790000 5.1979340000
C -1.3541950000 8.2751240000 5.9295670000
Ru -0.4109260000 8.2905880000 4.3756250000
H 2.0631940000 9.5036370000 6.6508200000

TS
S -0.6486560000 10.8099450000 3.9828500000
H 0.7057820000 10.9710020000 4.0075520000
O 2.2666600000 10.7879550000 4.9610900000
P -2.3506110000 7.8964820000 3.0456550000
P 0.5091130000 6.2446130000 4.7796280000
O -2.0282060000 8.3609040000 6.8838990000
N 0.7468690000 8.3328010000 2.4524240000
C -1.7421190000 7.6788130000 1.3241430000
H -1.1102380000 6.7859560000 1.3454000000
H -2.5833700000 7.4792530000 0.6602150000
C -0.9624070000 8.8583320000 0.8435280000
C -1.4399690000 9.6606580000 -0.1863770000
H -2.4109690000 9.4372120000 -0.6155570000
C -0.6798240000 10.7057210000 -0.6928900000
H -1.0585900000 11.3138410000 -1.5045010000
C 0.5796160000 10.9497550000 -0.1590420000
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C 2.2380030000 | 4.9077770000 | 6.5857010000 |
| H 1.5304860000 | 4.1781400000 | 6.9820130000 |
| C 3.0139300000 | 5.0424780000 | 7.3408630000 |
| C 2.7140040000 | 4.4731630000 | 5.7074220000 |
| C -0.3952660000 | 4.6307130000 | 4.8271680000 |
| H 0.3538780000 | 3.9142030000 | 5.1728410000 |
| C -0.8123310000 | 4.1888590000 | 3.4239190000 |
| H -1.1216730000 | 5.0134800000 | 2.7812680000 |
| H -1.6450340000 | 3.4854970000 | 3.4751090000 |
| H 0.0083910000 | 3.6872420000 | 2.9134080000 |
| C -1.5189950000 | 4.6476300000 | 5.8576510000 |
| H -1.1238100000 | 4.5893200000 | 6.8712570000 |
| H -2.1784870000 | 3.7895500000 | 5.7172740000 |
| C -2.1335630000 | 5.5471210000 | 5.8076570000 |
| C -0.8749290000 | 11.5554360000 | 5.6383810000 |
| H -1.9203050000 | 11.3907330000 | 5.8962120000 |
| H -0.2689820000 | 10.9834790000 | 6.3402960000 |
| C -0.5228350000 | 13.0201570000 | 5.6473620000 |
| H -1.1379870000 | 13.5867130000 | 4.9490700000 |
| H 0.5227120000 | 13.1804850000 | 5.3847240000 |
| H -0.6824350000 | 13.4324020000 | 6.6441200000 |
| C 2.2556480000 | 9.6548240000 | 5.5121710000 |
| H 1.1120980000 | 8.9435110000 | 5.1434230000 |
| H 2.9448340000 | 8.8635790000 | 5.1739620000 |
| C -1.3986200000 | 8.3410610000 | 5.9019910000 |
| Ru -0.4356310000 | 8.3371780000 | 4.3562920000 |
| O 2.2057720000 | 9.6028400000 | 6.9042700000 |
| H 1.8560050000 | 10.4569100000 | 7.1986070000 |

**TS_{S,6}**

| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| O -0.2062540000 | 10.7741490000 | 3.8223680000 |
| P -2.0613490000 | 7.8741260000 | 3.0433720000 |
| P 0.8063950000 | 6.5409090000 | 4.9414160000 |
| O -1.6531950000 | 8.7178020000 | 6.8916110000 |
| N 0.9666180000 | 8.3580700000 | 2.4071240000 |
| C -1.5143070000 | 7.6956640000 | 1.2976200000 |
| H -0.8999470000 | 6.7889270000 | 1.2994150000 |
| H -2.3811450000 | 7.5050380000 | 0.6645210000 |
| C -0.7217830000 | 8.8489580000 | 0.7717440000 |
| C -1.1488230000 | 9.5865720000 | -0.3272620000 |
| H -2.1015810000 | 9.3434130000 | -0.7851090000 |
| C -0.3563950000 | 10.5858510000 | -0.8757010000 |
| H -0.6999640000 | 11.1412910000 | -1.7391400000 |
TS$_{6,7}$
Ru -0.3481240000 0.2738470000 0.6965800000
P -1.4187380000 1.6575960000 -0.3193380000
P -0.6602880000 -2.0938270000 -0.6936440000
O 0.6625380000 0.9844890000 2.2038640000
O -2.7869450000 -0.9397920000 2.2872280000
N 1.4502330000 0.2222460000 -0.5516680000
C -0.2412550000 2.2553290000 -1.5993240000
H -0.1775050000 1.4485830000 -2.3361830000
H -0.6498130000 3.1331380000 -2.1003570000
C 1.1056280000 2.5640280000 -1.0328700000
C 1.5757720000 3.8734090000 -1.0300070000
H 0.9361790000 4.6551600000 -1.4260350000
C 2.8470150000 4.1832340000 -0.5707340000
H 3.2037960000 5.2051250000 -0.5917040000
C 3.6583230000 3.1612880000 -0.0942890000
H 4.6557800000 3.3845340000 0.2707130000
C 3.2079890000 1.8508260000 -0.0503270000
C 1.9184550000 1.5276100000 -0.5210790000

TS$_{5,7}$
Ru -0.1912130000 0.8072020000 7.0991510000
H 2.8514410000 5.6332140000 6.7017920000
H 0.2405280000 5.0570090000 5.8636350000
C -0.1912130000 5.0487260000 5.4007990000
C 2.8514410000 5.6332140000 6.7017920000
C -0.7163090000 5.1321010000 6.8270860000
H -1.0429810000 5.1233470000 4.7221010000
H -0.7325100000 4.9403860000 7.5538290000
H -1.4883930000 4.3765900000 6.9808390000
H -1.1556420000 6.1011050000 7.0629330000
C 0.4746410000 3.7061820000 5.1323430000
H 0.7206910000 3.5682680000 4.0810070000
C -0.1912130000 5.0487260000 5.4007990000
C 1.1056280000 2.5640280000 -1.0328700000
C 1.5757720000 3.8734090000 -1.0300070000
H 0.9361790000 4.6551600000 -1.4260350000
C 2.8470150000 4.1832340000 -0.5707340000
H 3.2037960000 5.2051250000 -0.5917040000
C 3.6583230000 3.1612880000 -0.0942890000
H 4.6557800000 3.3845340000 0.2707130000
C 3.2079890000 1.8508260000 -0.0503270000
C 1.9184550000 1.5276100000 -0.5210790000

S79
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | -1.8791| 0.0000| -0.87999690000 |
| C    | -2.10537| -2.264723| 0.87996900000 |
| H    | -2.031977| -3.279565| -5.02863900000 |
| C    | -3.414401| -2.153844| 0.87996900000 |
| H    | -3.506412| -1.201159| 3.06422900000 |
| C    | -3.513698| -2.228987| -0.31840200000 |
| H    | -3.261052| -2.238827| 0.17426500000 |
| C    | -1.994629| -1.298585| -0.00465800000 |
| H    | -2.967642| -1.610950| 0.34789960000 |
| H    | -1.310373| -1.673260| -0.76420400000 |
| C    | -2.031977| -0.312769| 2.70901200000 |
| H    | 1.005958| -0.240512| 2.47607000000 |
| C    | -0.580780| 0.1986070| -1.16735990000 |
| H    | -0.551533| 0.768047| 3.28609100000 |
| O    | 0.855703| 9.568584| 5.53889200000 |
| P    | -2.302698| 7.787492| 2.89497200000 |
| P    | 0.348488| 6.048815| 4.83701800000 |
| O    | -2.520088| 7.785863| 6.72508400000 |
| N    | 0.747360| 8.344292| 2.69400800000 |
| C    | -1.577240| 8.012210| 1.22291400000 |
| H    | -0.939100| 7.137976| 1.07066300000 |
| H    | -2.383266| 7.970125| 0.48810700000 |
| C    | -0.766260| 9.253040| 0.10721080000 |
| C    | -1.128452| 10.266668| 0.19393800000 |
| H    | -2.059392| 10.17713| -0.35624700000 |
| C    | -0.297398| 11.35983| -0.01487300000 |
| H    | -0.582487| 12.13758| 0.67192200000 |
| C    | 0.910183| 11.43802| 2.66859000000 |
| H    | 1.571427| 12.28324| 0.50686800000 |
| C    | 1.279557| 10.461274| 1.58255200000 |
| C    | 0.433517| 9.361632| 1.80616400000 |
| H    | 2.529252| 10.552256| 0.40643300000 |
| H    | 3.299085| 11.13348| 1.89497800000 |
| C    | 3.040812| 9.196623| 1.57969300000 |
| C    | 4.386639| 8.937757| 3.00154900000 |
| H    | 5.102321| 9.741208| 2.86072200000 |
| C    | 4.820104| 7.685971| 3.42014800000 |
| H    | 5.871569| 7.502158| 3.60062400000 |
H 0.4357010000 3.2385400000 3.5581950000
H -0.5137180000 2.34813700000 4.7355410000
H 1.0357860000 3.03037400000 5.2030860000
C -1.7882210000 7.92957100000 5.8308480000
Ru -0.6387530000 8.13986100000 4.4264790000
H -0.1985380000 9.93746200000 4.7229830000
H 1.6349060000 9.53231700000 4.9676660000
H -0.9705970000 9.90419400000 4.1760850000

TS_{9,10}
O 0.6877310000 8.79039700000 5.7015470000
P -2.1779870000 7.19554200000 2.7313620000
P 0.4058650000 5.69938100000 4.8413900000
O -2.6825870000 6.98511700000 6.5695830000
N 0.7906620000 8.05095000000 2.8614430000
C -1.3427770000 7.61785400000 1.1499270000
H -0.5972700000 6.83204700000 1.0003800000
H -2.0668690000 7.54868300000 0.3365310000
C -0.6692110000 8.94829900000 1.1681530000
C -1.0636780000 9.98648200000 0.3329100000
H -1.9269820000 9.84556300000 -0.3093100000
C -0.3413790000 11.17158700000 0.2798520000
H -0.6489030000 11.96838100000 -0.3855100000
C 0.7925070000 11.31787200000 1.0718820000
H 1.3721850000 12.23411200000 1.0245880000
C 1.1852920000 10.31692200000 1.9476530000
C 0.4398320000 9.12652400000 2.0209070000
C 2.3504850000 10.45579800000 2.8829730000
H 3.0857080000 11.16529900000 2.4984580000
H 1.9912920000 10.88625000000 3.8292730000
C 2.9771450000 9.12383800000 3.1784320000
C 4.3204490000 8.97019600000 3.4853130000
H 4.9718360000 9.83766700000 3.4527560000
C 4.8314580000 7.73223300000 3.8613610000
H 5.8801950000 7.62564100000 4.1081470000
C 3.9857100000 6.63215300000 3.9149390000
H 4.3759010000 5.65927500000 4.1947020000
C 2.6417310000 6.74704500000 3.5795300000
C 2.1228610000 8.00626900000 3.2144980000
C 1.7314160000 5.56309400000 3.5753660000
H 2.2901840000 4.64180300000 3.7384170000
H 1.2086380000 5.47449100000 2.6179750000
C -3.0257680000 5.60926400000 2.3196190000

S83
H -3.7417150000 5.8836680000 1.5406130000
C -3.8212530000 5.0719930000 3.5009520000
H -3.2215010000 4.9560760000 4.4036470000
H -4.2432820000 4.0955070000 3.2584360000
H -4.6510530000 5.7324680000 3.7515310000
C -2.0455030000 4.6125890000 1.6986290000
H -1.9305550000 4.7920540000 0.6307930000
H -2.4080900000 3.5910040000 1.8227880000
H -1.0458060000 4.6584700000 2.1322390000
C -3.5164550000 8.4935880000 2.7726220000
H -2.9404070000 9.4018320000 2.5606200000
C -4.1998930000 8.6885130000 4.1172150000
H -4.6890710000 7.7812020000 4.4722300000
H -4.9719220000 9.4541960000 4.0215500000
H -3.5086830000 9.0244140000 4.8874050000
C -4.5482180000 8.3234180000 1.6659770000
H -4.1046240000 8.1560410000 0.6849870000
H -5.1566140000 9.2265450000 1.5960670000
H -5.2570640000 7.4953960000 1.8753590000
C 1.3910680000 5.7935060000 6.4102890000
H 2.0298970000 6.6571450000 6.1928390000
C 0.6043510000 6.1109930000 7.6740650000
H -0.1035750000 6.9290620000 7.5492920000
H 1.2981110000 6.3993050000 8.4653890000
H 0.0456700000 5.2506500000 8.0380190000
C 2.2934420000 4.5864180000 6.6340680000
H 1.7204630000 3.6949550000 6.8891570000
H 2.9613070000 4.7897300000 7.4731400000
H 2.9184700000 4.3523600000 5.7741200000
C -0.5244910000 4.0986420000 4.8096010000
H -1.3207430000 4.3081670000 4.0984630000
C -1.1880680000 3.7594540000 6.1362050000
H 0.4645520000 3.4233780000 6.8780750000
H -1.8952590000 2.9426030000 5.9828700000
H -1.7434430000 4.5949710000 6.5594230000
C 0.2706300000 2.9201830000 4.2661270000
H 0.6237670000 3.0895570000 3.2501290000
H -0.3735160000 2.0392270000 4.2430650000
H 1.1318650000 2.6763720000 4.8875560000
C -1.8961320000 7.2496390000 5.7497940000
Ru -0.6697740000 7.6513460000 4.4615430000
H 0.6388550000 8.4979720000 6.6189360000
O -1.2109380000 10.2770190000 4.5657480000
C -0.7101830000 10.3465020000 5.6922640000
H 0.0390720000 11.1160760000 5.9381870000
H -1.1945110000 9.8882470000 6.5710590000

TS_{18,11}
Ru 10.6826510000 3.6825120000 2.3871710000
O 12.0469010000 4.2692880000 4.0764870000
P 9.4272670000 2.1176510000 3.6804400000
P 10.0837350000 3.4545920000 0.1899780000
O 8.6929480000 5.8773040000 2.7566660000
N 12.1630190000 2.0161920000 2.0847590000
C 10.3915330000 0.5551750000 3.7091000000
H 9.8959790000 -0.1632420000 4.3648200000
H 10.3343830000 0.1692800000 2.6876840000
C 11.8189790000 0.7390810000 4.0981200000
C 12.3170430000 0.1807570000 5.2698390000
H 12.0450680000 -0.2042930000 6.4882950000
C 14.5325660000 0.8835720000 4.6974000000
H 15.5943060000 0.9317100000 4.9175960000
C 14.0604280000 1.4871780000 3.5411550000
C 12.6869090000 1.4424030000 3.2327710000
C 14.9641560000 2.2459330000 2.6161410000
H 15.0515330000 3.2827660000 2.9730090000
H 15.9817520000 1.8505480000 2.6524780000
C 14.4393650000 2.2489160000 1.2108000000
C 13.0443790000 2.1753460000 1.0292540000
C 15.2745610000 2.3689800000 0.1095300000
H 16.3470130000 2.4219490000 0.2681140000
C 14.7584380000 2.4432060000 -1.1786000000
H 15.4194050000 2.5482230000 -2.0295510000
C 13.3845980000 2.3674250000 -1.3623030000
H 12.9678450000 2.3988100000 -2.3636440000
C 12.5224550000 2.2112110000 -0.2831320000
C 11.0535340000 2.0497950000 -0.4916650000
H 10.6824860000 1.1624620000 0.0308150000
H 10.8282970000 1.9331270000 -1.5518680000
C 9.4828160000 2.6274100000 5.4686910000
C 10.5546680000 2.5394260000 5.6820190000
C 9.0813070000 4.0713370000 5.7278430000
H 9.7120320000 4.7781520000 5.1916320000
H 9.1785500000 4.2912740000 6.7926000000
H 8.0440870000 4.2675200000 5.4538800000
C 8.7364370000 1.6825080000 6.3984720000
H 7.6565970000 1.8192270000 6.3225590000
H 9.0128080000 0.6317220000 6.2090240000
C 7.6988660000 1.5353300000 3.3758900000
H 7.4040780000 1.0349590000 4.3021700000
C 6.7586470000 2.7092720000 3.1532040000
H 6.3517220000 3.3730700000 4.0132420000
H 5.7407310000 2.3530810000 2.9867060000
H 7.0448980000 3.3058010000 2.2864140000
C 7.6431590000 0.4959750000 2.2622960000
H 8.2164600000 0.7825460000 1.3796890000
H 6.6105760000 0.3429130000 1.9446520000
H 8.0288810000 -0.4666840000 2.5940950000
C 8.3222220000 3.1239700000 -0.2893180000
H 7.9695990000 2.5266760000 0.5517280000
C 7.4775780000 4.3893700000 -0.3233290000
H 7.6042320000 5.0050630000 0.5665250000
H 6.4217410000 4.1199020000 -0.3849640000
H 7.7033710000 5.0060760000 -1.1928090000
C 8.1314900000 2.2876150000 -1.5459810000
H 8.5090170000 2.7861500000 -2.4408230000
H 7.0648010000 2.1126710000 -1.6991710000
C 8.3699690000 1.3121170000 -1.4707490000
C 10.7173900000 4.8684160000 -0.8367160000
H 11.7980590000 4.7405240000 -0.6974380000
H 12.0424301000 4.7480850000 -2.3252630000
H 10.6842990000 3.7719660000 -2.7327320000
H 11.0079130000 5.4918160000 -2.8709350000
H 9.3751720000 4.9385340000 -2.5508220000
C 10.3609660000 6.2521550000 -0.3162110000
H 9.2921100000 6.4567640000 -0.3661560000
H 10.8613570000 7.0074310000 -0.9248170000
H 10.6844050000 6.3991620000 0.7134110000
H 9.4638240000 5.0143500000 2.6101840000
C 12.5155730000 5.0355170000 3.1798300000
H 11.8888210000 4.7007960000 1.7638780000
H 13.5045970000 4.8381890000 2.7434660000
O 12.2392990000 6.3662070000 3.3176690000
H 12.7391540000 6.8653850000 2.6569080000

**TS**\(\text{II,12}\)
O 1.1206120000 10.9995480000 4.8676790000

S86
TS_{13,14}
Ru 8.7541810000 12.3374990000 13.1169950000
P 7.6925680000 14.2584430000 12.0652810000
P 8.4643750000 10.4996450000 11.7981530000
O 9.9785530000 13.4065440000 14.8329410000
O 9.9413830000 11.4228620000 15.9823570000
O 6.2345940000 11.7201390000 14.6210770000
N 10.5477520000 12.8178500000 11.9163170000

S88
| C    | 8.8932630000 | 14.8530500000 | 10.8040820000 |
|------|--------------|---------------|----------------|
| H    | 8.9684620000 | 14.0478520000 | 10.0666500000 |
| H    | 8.4971400000 | 15.7339210000 | 10.2986890000 |
| C    | 10.2254700000| 15.1589300000 | 11.4060280000 |
| C    | 10.7024500000| 16.4659060000 | 11.4180970000 |
| H    | 10.0847610000| 17.2478530000 | 10.9893700000 |
| C    | 11.9534230000| 16.7726250000 | 11.9315600000 |
| H    | 12.3162320000| 17.7924640000 | 11.9164880000 |
| C    | 12.7363930000| 15.7532490000 | 12.4584870000 |
| C    | 13.7161340000| 15.9764340000 | 12.8682100000 |
| C    | 12.2778240000| 14.4454760000 | 12.4939780000 |
| C    | 11.0122700000| 14.1256910000 | 11.9608830000 |
| C    | 9.8962880000 | 10.4303090000 | 10.6555330000 |
| H    | 9.8388290000 | 9.4966170000  | 10.0929000000 |
| H    | 9.7404970000 | 11.2550680000 | 9.9559200000  |
| C    | 11.2161470000| 10.5858210000 | 11.3268500000 |
| C    | 12.1553020000| 9.5626860000  | 11.3433780000 |
| H    | 11.9000190000| 8.6095630000  | 10.8917120000 |
| C    | 13.4156670000| 9.7608800000  | 11.8919780000 |
| H    | 14.1456140000| 8.9614270000  | 11.8870780000 |
| C    | 13.7327200000| 10.9987250000 | 12.4367320000 |
| H    | 14.7151070000| 11.1672780000 | 12.8658570000 |
| C    | 12.8005680000| 12.0267240000 | 12.4696520000 |
| C    | 11.5228670000| 11.8277060000 | 11.9215960000 |
| C    | 13.0679240000| 13.3429390000 | 13.1332140000 |
| H    | 14.1346410000| 13.5750420000 | 13.1358380000 |
| H    | 12.7844560000| 13.2697590000 | 14.1937110000 |
| C    | 6.0314580000 | 14.2283900000 | 11.2411840000 |
| H    | 6.0062100000 | 13.2404950000 | 10.7798370000 |
| C    | 5.8443550000 | 15.2474900000 | 10.1276500000 |
| H    | 4.8466240000 | 15.1303500000 | 9.7008010000  |
| H    | 6.5593850000 | 15.1082170000 | 9.3178920000  |
| H    | 5.9274630000 | 16.2749880000 | 10.4792710000 |
| C    | 4.8961560000 | 14.2778400000 | 12.2532700000 |
| H    | 4.7831170000 | 15.2710820000 | 12.6868970000 |
| H    | 5.0296930000 | 13.5678590000 | 13.0693890000 |
| H    | 3.9560440000 | 14.0321300000 | 11.7568850000 |
| C    | 7.7371200000 | 15.6283160000 | 13.3179440000 |
| H    | 8.8170950000 | 15.7031490000 | 13.4927400000 |
| C    | 7.0959120000 | 15.2797030000 | 14.6532480000 |
| H    | 7.2848410000 | 16.0850480000 | 15.3652910000 |
| H    | 7.5082420000 | 14.3665550000 | 15.0805380000 |
| H    | 6.0157570000 | 15.1699950000 | 14.5822790000 |
| C    | 7.2575120000 | 16.9750000000 | 12.7982140000 |
H 6.1749910000 16.9957340000 12.6707850000
H 7.7136780000 17.2469190000 11.8467870000
H 7.5125570000 17.7565600000 12.6707850000
C 8.6301130000 8.9056560000 12.7304900000
H 9.7047670000 8.9132730000 12.9538280000
C 7.8874800000 8.8458700000 14.0546870000
H 6.8071370000 8.9145870000 12.9538280000
H 8.2010440000 9.6308200000 14.7402810000
H 8.0929470000 7.8891700000 14.5300300000
C 8.3284170000 7.6819050000 11.8790930000
H 8.6645520000 6.7850550000 12.4008400000
H 8.0289240000 7.7007100000 10.9111070000
H 7.2574750000 7.5698630000 11.7047510000
C 7.0171870000 10.3142020000 10.6705380000
H 7.0886930000 9.2856010000 10.3058880000
C 7.5040550000 10.4610470000 11.4208240000
H 5.7878400000 11.4575520000 11.8475040000
H 5.6169180000 9.7432390000 12.2365780000
H 4.8682970000 10.2945100000 10.7438600000
C 7.1329410000 11.2421740000 9.4664090000
H 6.1639790000 11.3457880000 8.9760330000
H 7.8332580000 10.8551700000 8.7280210000
H 7.4717670000 12.2439270000 9.7362000000
C 9.8314850000 12.2201210000 15.0964400000
H 9.7772580000 11.2123780000 13.7590700000
C 7.2110780000 11.9536650000 14.0363160000

ts15.10
O -0.1092920000 10.8865580000 3.8090260000
P -2.0852960000 7.8565060000 3.0095680000
P 0.8206840000 6.5960920000 4.9412960000
O -1.6469100000 8.7776550000 6.8552550000
N 0.9425290000 8.3580520000 2.3684540000
C -1.5385430000 7.6355480000 1.2700400000
H -0.9145370000 6.7357720000 1.2951580000
H -2.4010510000 7.4204760000 0.6387420000
C -0.7582520000 8.7865330000 0.7214230000
C -1.1957600000 9.4928590000 -0.3940980000
H -2.1439930000 9.2231840000 -0.8464790000
C -0.4196680000 10.492110000 -0.9644610000
H -0.7710100000 11.0217430000 -1.8408680000
C 0.8191960000 10.7915470000 -0.4102910000
H 1.4378960000 11.5675900000 -0.8491260000
C 1.2767540000 10.1204960000 0.7127330000
C 0.4902540000 9.1073040000 1.2942770000

S90
TS1_{10}
P -2.3070720000 7.8123510000 2.9385760000
P 0.3886180000 6.0992120000 4.9208950000
O -2.3589510000 7.7896260000 6.8915490000
O 0.8026160000 8.3745680000 2.7423090000
N -1.5683350000 8.1047340000 1.2836150000
C -0.9339580000 7.2312020000 1.1099710000
H -2.3616770000 8.0919140000 0.5338290000
C -0.7390220000 9.3368220000 1.1679700000
C -1.1131140000 10.3806870000 0.3322460000
H -2.0674050000 10.3229190000 0.1817140000
C -0.2672530000 11.4604710000 0.1115180000
H -0.5647360000 12.2637290000 0.6506470000
C 0.9788780000 11.4779470000 0.7246710000
H 1.6637560000 12.2991490000 0.5378830000
C 1.3656030000 10.4687450000 1.5963910000
C 0.4898020000 9.3998890000 1.8654610000
C 2.6845220000 10.5023310000 2.3112960000
H 3.4442160000 10.9977720000 1.7017470000
H 2.5978300000 11.1285090000 3.2122440000
C 3.1352390000 9.1308180000 2.7149720000
C 4.4766170000 8.8335280000 2.9077140000

S92
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H -1.7030130000 5.2741870000 6.8380430000
C -0.0106760000 3.2902760000 4.5317380000
H 0.2729490000 3.3683550000 3.4830790000
H -0.7277860000 2.4705760000 4.6111810000
H 0.8733890000 3.0015510000 5.0987790000
C -1.6638240000 7.9303730000 5.9621750000
Ru -0.5721240000 8.1544480000 4.5350520000
O -1.1493610000 10.3029150000 4.2697600000
C 0.6869840000 11.1920960000 3.9945390000
H 0.2234160000 11.1584830000 4.6107560000
O 0.4329090000 10.7749420000 5.9810850000
C 0.8044050000 8.6034410000 5.5039040000
H 0.5953770000 9.6235920000 5.7774030000
H -0.5854010000 12.1783050000 4.8069280000
H -0.2710850000 10.8028900000 6.6505270000

H$_2$O
O -8.2271840000 -1.6389100000 6.2520390000
H -7.2656790000 -1.5897450000 6.2468220000
H -8.5010740000 -0.7210590000 6.1546430000

EtSH
C -9.9558530000 -0.0967600000 0.0308470000
C -8.4496880000 -0.0716910000 -0.0235610000
H -10.3926520000 0.3558640000 -0.8596280000
H -10.3343650000 0.4422600000 0.8987270000
H -10.3160800000 -1.1251750000 0.0889650000
S -7.7348850000 1.6032440000 -0.0839600000
H -8.0712110000 -0.6414900000 -0.8714220000
H -8.0148030000 -0.5157750000 0.8719590000
H -8.3215440000 1.9804240000 -1.2302140000

MeOH
C -5.9167870000 -0.7878820000 -0.0046620000
O -4.4998440000 -0.7990150000 -0.0172300000
H -6.3343220000 -1.7399890000 0.3358800000
H -6.3371480000 -0.5568560000 -0.9879490000
H -6.2297140000 -0.0106690000 0.6906760000
H -4.2185740000 -1.4904380000 -0.6253810000
HCHO
O -7.5825790000 -3.0691900000 -0.0036400000
C -8.7844630000 -3.0691900000 -0.0036400000
H -9.3756140000 -2.5971430000 0.8060190000
H -9.3756140000 -3.5412370000 -0.8132990000

HOCH₂OH
O -8.4385830000 -1.6737050000 6.0570180000
C -7.0901240000 -1.5488890000 6.4289100000
H -8.8455630000 -0.8003000000 6.1144750000
H -6.7193580000 -2.5700330000 6.5484220000
H -6.9844290000 -1.0086630000 7.3731880000
O -6.3278170000 -0.8313960000 5.4928590000
H -6.2574030000 -1.3673100000 4.6934440000

HCOOH
C -2.2568410000 1.8748520000 -1.4042650000
O -2.6976030000 1.8590950000 -0.2827730000
H -2.6487290000 2.4986220000 -2.2196580000
O -1.2349090000 1.1492920000 -1.8409640000
H -0.8990080000 0.6022550000 -1.1098350000

Hydrogen
H -5.8399560000 -0.7818910000 0.0000000000
H -5.0987590000 -0.8556050000 0.0000000000

CO₂
C -1.9561880000 1.8306030000 -1.1426770000
O -1.0102470000 1.8620690000 -1.8108040000
O -2.9021180000 1.7991350000 -0.4745340000

CO
C -6.8316010000 1.0855950000 0.0000000000
O -6.1699660000 0.1736850000 0.0000000000
Supporting References

1. Kar, S.; Rauch, M.; Leitus, G.; Ben-David, Y.; Milstein, D. Highly Efficient Additive-Free Dehydrogenation of Neat Formic Acid. Nat. Catal. 2021, 4, 193-201.

2. Rauch, M.; Luo, J.; Avram, L.; Ben-David, Y.; Milstein, D. Mechanistic Investigations of Ruthenium Catalyzed Dehydrogenative Thioester Synthesis and Thioester Hydrogenation. ACS Catal. 2021, 11, 2795-2807.

3. Heim, L. E.; Konnerth, H.; Prechtl, M. H. G. Future Perspectives for Formaldehyde: Pathways for Reductive Synthesis and Energy Storage. Green Chem. 2017, 19, 2347-2355.

4. Bone, W. A.; Smith, H. L. XCIV.-The Thermal Decomposition of Formaldehyde and Acetaldehyde. J. Chem. Soc. Trans. 1905, 87, 910-916.

5. Jenner, G.; Nahmed, E. M.; Libs-Konrath, S. Formaldehyde and Formates as Sources of Synthesis Gas via Ruthenium-Catalyzed Decomposition Reactions. J. Mol. Catal. 1991, 64, 337-347.

6. Nelson, W. L.; Engelder, C. J. The Thermal Decomposition of Formic Acid. J. Phys. Chem. 1926, 30, 470-475.

7. Xie, Y.; Ben-David, Y.; Shimon, L. J. W.; Milstein, D. Highly Efficient Process for Production of Biofuel from Ethanol Catalyzed by Ruthenium Pincer Complexes. J. Am. Chem. Soc. 2016, 138, 9077-9080.

8. Zhu, M.; Ge, Q.; Zhu, X. Catalytic Reduction of CO2 to CO via Reverse Water Gas Shift Reaction: Recent Advances in the Design of Active and Selective Supported Metal Catalysts. Trans. Tianjin Univ. 2020, 26, 172-187.

9. Ebrahimi, P.; Kumar, A.; Khraisheh, M. A Review of Recent Advances in Water-Gas Shift Catalysis for Hydrogen Production. Emergent mater. 2020, 3, 881-917.

10. Zou, Y-Q.; von Wolff, N.; Anaby, A.; Xie, Y.; Milstein, D. Ethylene Glycol as an Efficient and Reversible Liquid Organic Hydrogen Carrier. 2019, Nat. Catal. 2, 415-422.
11. Luo, J.; Rauch, M.; Avram, L.; Ben-David, Y.; Milstein, D. Formation of Thioesters by Dehydrogenative Coupling of Thiols and Alcohols with H₂ Evolution. *Nat. Catal.* 2020, 3, 887-892.

12. Frisch, M. J. et al. *Gaussian 16, Revision C.01*; (Gaussian, Inc., Wallingford CT, 2016).

13. Zhao, Y.; Truhlar, D. G. A New Local Density Functional for Main-Group Thermochemistry, Transition Metal Bonding, Thermochemical Kinetics and Noncovalent Interactions. *J. Chem. Phys.* 2006, 125, 194101/1-18.

14. Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* 2005, 7, 3297-3305.

15. Weigend, F. Accurate Coulomb-Fitting Basis Sets for H to Rn. *Phys. Chem. Chem. Phys.* 2006, 8, 1057-1065.

16. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements HPu. *J. Chem. Phys.* 2010, 132, 154104/1-19.

17. Neese, F. Software Update: The ORCA Program System, Version 4.0. *WIREs Comput. Mol. Sci.* 2018, 8, e1327-e1332.

18. Mardirossian, N.; Head-Gordon, M. ωB97X-V: A 10-Parameter, Range-Separated Hybrid, Generalized Gradient Approximation Density Functional with Nonlocal Correlation, Designed by a Survival-Of-The-Fittest Strategy. *Phys. Chem. Chem. Phys.* 2014, 16, 9904-9924.

19. Vydrova, O. A., and Voorhis, T. V. (2010). Nonlocal van der Waals density functional: The simpler the better. *J. Chem. Phys.* 2017, 133, 244103/1-9.

20. Hujo, W., and Grimme, S. (2011). Performance of the van der Waals Density Functional VV10 and (hybrid)GGA Variants for Thermochemistry and Noncovalent Interactions. *J. Chem. Theory Comput.* 2017, 7, 3866-3871.

21. Hellweg, A.; Hattig, C.; Hoefener, S.; Klopper, W. Optimized Accurate Auxiliary Basis Sets for RI-MP2 and RI-CC2 Calculations for the Atoms Rb to Rn. *Theor. Chem. Acc.* 2007, 117, 587-597.
22. Iron, M. A.; Janes, T. Evaluating Transition Metal Barrier Heights with the Latest Density Functional Theory Exchange-Correlation Functionals: The MOBH35 Benchmark Database. *J. Phys. Chem. A* **2019**, *123*, 3761-3781.

23. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113*, 6378-6396.

24. Cramer, C. J. Essentials of Computational Chemistry: *Theories and Models in 2nd Edition*. (John Wiley, and Sons Ltd: West Sussex, England, 2014).

25. Sparta, M.; Riplinger, C.; Neese, F. Mechanism of Olefin Asymmetric Hydrogenation Catalyzed by Iridium Phosphino-Oxazoline: A Pair Natural Orbital Coupled Cluster Study. *J. Chem. Theory and Computation* **2014**, *10*, 1099-1108.

26. Hopmann, K. H. How Accurate is DFT for Iridium-Mediated Chemistry?. *Organometallics* **2016**, *35*, 3795-3807.

27. Gusev, D. G. Revised Mechanisms of the Catalytic Alcohol Dehydrogenation and Ester Reduction with the Milstein PNN Complex of Ruthenium. *Organometallics* **2020**, *39*, 258-270.