Mechanism of the Facile Nitrous Oxide fixation by Homogeneous Ruthenium Hydride Pincer Catalysts

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I. Isomerization Analysis

The initial geometries for the complexes 5, 7 and 8 were obtained from the crystallographic information file provided in the supporting information of the experimental work of D. Milstein and coworkers (J. Am. Chem. Soc. 2018, 140, 7061-7064). In that work, they provided 2 isomers, E1 and E2, of complex 5, the corresponding form E1 of complex 7 and E2 isomer of complex 8 (see Figure S1). Therefore, our first step before starting the study of the catalytic cycle was to determine the relative stability of the two isomers for different species involved in the catalytic cycle A and B (Figure and Tables S1).

![Figure S1. Intermediates 5-8, 10 and 10’ of the PNN-pincer Ru based catalysts involved in the oxidation of CO by N₂O, in two isomeric forms, E1 and E2.](image)

Table S1. Relative Gibbs energies (in kcal/mol) of the intermediates depicted in Figure S1 for the CO oxidation by N₂O homogeneously catalyzed by ruthenium complex, referred to the initial intermediate 6+CO+N₂O E2. All data shown were calculated at T = 70 ºC, using solvent corrections (solvent: THF) and M06-L/cc-pVTZ~sdd//BP86-D3BJ/SVP~sdd level of theory.

| compound | ΔG₁ | ΔG₂ | ΔG₁-ΔG₂ |
|----------|-----|-----|----------|
| 5        | -27.9 | -28.2 | -0.9     |
| 6        | 0.0  | 0.1  | 0.1      |
| 7        | -14.3 | -14.4 | 0.1      |
| 8        | -16.7 | -17.8 | 1.1      |
| 10       | -67.9 | -66.3 | -1.6     |
| 10’      | -69.8 | -71.3 | 1.6      |

We found that, the differences between isomers were smaller than 1 kcal/mol for most of the intermediates. Same results were suggested by the experimental evidences, since in previous work they obtained E1 and E2 X-ray structures. Therefore, we can assume that both isomers will be present in the media during the catalytic process. Moreover, they do not present large structural differences, thus we decided to study the whole process just for the E2 form in order to simplify the study.
II. Complete Reaction Profiles

Figure S2. Reaction profile of the full mechanism for N₂O reduction catalyzed by Ru-H pincer 7 following cycle A (relative Gibbs energies for THF media in kcal/mol and referred to catalyst 6+CO+N₂O, and P = P(tBu₂)). All data shown were calculated at T = 70 °C using M06-L/cc-pVTZ~sdd//BP86-D3BJ/SVP~sdd level of theory.
Figure S3. Reaction profile of the full mechanism for N$_2$O reduction catalyzed by Ru-H pincer 8 following cycle B (relative Gibbs energies for THF media in kcal/mol and referred to catalyst 6+CO+N$_2$O, and P = P(tBu$_2$)). All data shown were calculated at T = 70°C using M06-L/cc-pVTZ~sdd//BP86-D3BJ/SVP~sdd level of theory.
III. Test of other Catalysts and Reaction Conditions

Figure S4. Optimized geometry at the BP86/SVP~sdd level of theory of the intermediate 13+THF.

As we mentioned in the main manuscript, we have experimental results from previous work done by Milstein and coworkers, and we know the TONs for catalysts 2-5 and 15 in toluene at 100 °C. Even the best reactions conditions found experimentally were the ones used for the main study (solvent = THF at 70 °C), the previously mentioned catalyst were not tested in the laboratory using these conditions. Therefore, in order to be coherent with the experimental data we have computed the Gibbs energies of the crucial intermediates of the cycle at these conditions, the results obtained are presented in Table S2.

Figure S5. Classification of different studied catalysts depending on the pincer ligand.

Table S2. Relative energies of the main intermediates and transition states for the CO oxidation by N₂O catalyzed by ruthenium hydride complex. Relative Gibbs energies in kcal/mol and referred to the initial species counterpart of intermediate 6+CO+N₂O, for catalysts 2-5 and 15. All data shown were calculated at T = 100 °C using toluene as solvent.

| catalyst | 7  | 7-9 | 9  | 9-10 | 10 | 11_{inter} | 11_{inter} | 11 | 12 | 12-7 | 7-13 | 13-14 | 14 | 14-15 | 15 |
|----------|----|-----|----|------|----|----------|----------|----|----|------|------|-------|----|--------|----|
| 2        | -17.1 | 17.9 | -4.2 | 19.0 | 21.3 | -71.8 | -67.0 | -40.0 | -70.7 | -31.5 | - | - | - | - | - |
| 3        | -14.1 | 21.1 | 1.3 | 24.7 | 31.5 | -64.8 | -63.5 | -34.1 | -69.7 | -28.6 | - | - | - | - | - |
| 4        | -20.5 | 12.8 | -8.8 | 12.2 | 18.9 | -75.5 | -66.6 | -37.6 | -80.4 | -39.3 | 10.7 | 1.4 | 13.6 | 5.2 | 16.1 | -18.9 |
| 5        | -16.9 | 19.0 | -1.2 | 22.4 | 26.6 | -67.5 | -65.8 | -39.1 | -74.0 | -31.3 | 13.7 | 7.3 | 17.3 | 10.4 | 19.7 | -12.9 |
| 15       | -14.6 | 32.3 | 17.7 | 32.2 | 37.5 | -60.9 | -63.0 | -32.2 | -63.7 | -17.9 | - | - | - | - | - |
Table S3. Relative energies of the main intermediates and transition states for the CO oxidation by \( \text{N}_2\text{O} \) catalyzed by ruthenium hydride complex. Relative Gibbs energies in kcal/mol and referred to the initial species counterpart of intermediate \( 6+\text{CO}+\text{N}_2\text{O} \), for all the catalysts shown in Figure S5. All data shown were calculated at \( T = 70 \, ^\circ \text{C} \) using THF as solvent.

| catalyst | 7 | 7-9 | 9 | 9-10 | 10 | 11eq | 11axial | 11equatorial | 12 | 12-7 | 7-13 | 13-14 | 14 | 14-8 | 8 |
|----------|---|-----|---|------|----|------|---------|-------------|----|------|------|-------|----|-------|---|
| \( \text{P}(\text{Pr})_3(4) \) | -19.7 | 10.9 | -12.3 | 9.9 | 16.4 | -75.9 | -69.1 | -39.2 | -84.4 | -42.1 | 7.0 | 2.0 | 14.7 | 5.2 | 16.5 | -19.5 |
| \( \text{P}(\text{CH}_3)_3 \) | -20.2 | 10.8 | -12.1 | 9.5 | 16.5 | -75.8 | -68.4 | -40.6 | -84.3 | -43.1 | 6.1 | 2.1 | 15.5 | 7.5 | 17.9 | -20.2 |
| \( \text{P}(\text{CF})_3 \) | -17.2 | 17.1 | -3.9 | 16.6 | 22.4 | -69.9 | -65.1 | -35.1 | -78.3 | -36.6 | 13.9 | 7.7 | 18.9 | 11.2 | 28.1 | -11.8 |
| external \( \sigma \)-CF \( \alpha \) | -15.6 | 16.4 | -3.6 | 17.3 | 24.4 | -68.7 | -67.6 | -41.0 | -75.5 | -34.2 | 6.8 | 3.4 | 12.7 | 4.0 | 13.8 | -24.7 |
| external \( \sigma \)-OMe | -14.6 | 16.9 | -4.3 | 18.7 | 24.3 | -66.6 | -67.4 | -40.7 | -76.3 | -33.4 | 13.2 | 7.6 | 17.0 | 10.0 | 20.2 | -17.4 |
| central \( \sigma \)-CF \( \alpha \) | -14.0 | 18.8 | -2.6 | 19.7 | 24.9 | -66.2 | -66.5 | -39.7 | -74.4 | -32.4 | 12.8 | 9.4 | 19.6 | 11.5 | 23.2 | -14.3 |
| \( \sigma \)-CF \( \alpha \) | -13.8 | 18.7 | -2.8 | 20.0 | 25.2 | -65.7 | -66.4 | -40.0 | -74.4 | -31.9 | 13.1 | 8.7 | 18.5 | 9.4 | 22.1 | -16.0 |
| external \( \sigma \)-OMe | -15.5 | 15.6 | -6.3 | 17.8 | 23.1 | -67.6 | -67.2 | -40.9 | -76.8 | -34.7 | 12.3 | 6.4 | 17.7 | 11.2 | 21.5 | -16.2 |
| central \( \sigma \)-OMe | -14.5 | 16.9 | -3.9 | 18.9 | 26.1 | -67.1 | -67.2 | -40.8 | -76.5 | -33.3 | 11.6 | 8.1 | 18.2 | 10.3 | 20.0 | -19.0 |
| \( \sigma \)-OMe | -14.6 | 16.4 | -4.5 | 18.6 | 24.0 | -67.1 | -67.5 | -41.1 | -76.8 | -33.7 | 12.0 | 7.1 | 16.2 | 9.1 | 18.8 | -19.7 |
| 2 | -18.0 | 15.2 | -6.1 | 15.6 | 18.8 | -73.0 | -69.6 | -43.4 | -76.1 | -34.7 | - - | - - | - - | - - | - - | - - |
| 3 | -14.0 | 18.0 | -2.9 | 19.8 | 27.3 | -66.0 | -66.6 | -36.9 | -72.5 | -32.4 | - - | - - | - - | - - | - - | - - |
| 15 | -15.4 | 27.9 | 11.2 | 28.6 | 34.4 | -63.0 | -66.8 | -34.7 | -66.2 | -21.6 | - - | - - | - - | - - | - - | - - |
| 16 | -14.0 | 18.2 | -3.3 | 19.3 | 25.4 | -66.1 | -66.6 | -37.4 | -73.1 | -32.7 | - - | - - | - - | - - | - - | - - |
Table S4. Gibbs free energy barriers of the main steps for the CO oxidation by N₂O catalyzed by ruthenium hydride complex. Energies in kcal/mol for all the steps shown in Figure S6. All data shown were calculated at T = 70 °C using THF as solvent with the expection of (a) that were calculated at T = 100 °C using toluene as solvent.

| catalyst     | 7-9   | 7-10+H₂O | 9-10+H₂O | 7-10 | 9-10-11 | 11-11 | 11-11 | 11-11-6 | 12-6 | 12-7 | 12-13 | 13-14 | 14-8 |
|--------------|-------|----------|----------|------|---------|-------|-------|---------|------|------|-------|-------|------|
| 5 (cycle A) | 31.4  | 33.5     | 22.7     | 40.3 | 29.5    | 15.3  | 5.6   | 26.5    | 35.7 | 42.5 | 27.2  | 33.5  | 10.3 |
| 5 (cycle B) | 33.9  | 32.5     | 25.0     | 42.0 | 34.6    | 19.8  | 5.9   | 25.9    | 41.8 | 40.5 | -     | -     | -    |
| P(Pr)₂ (4)  | 30.7  | 29.6     | 22.2     | 36.2 | 28.8    | -     | -     | 30.0    | 45.3 | 42.3 | 26.8  | 34.4  | 12.7 |
| P(CH₃)₂     | 31.0  | 29.6     | 21.5     | 36.6 | 28.5    | -     | -     | 27.8    | 43.7 | 41.3 | 26.3  | 35.6  | 13.4 |
| P(CF₃)₂     | 34.3  | 33.8     | 20.5     | 39.7 | 26.4    | -     | -     | 30.0    | 43.2 | 41.8 | 31.1  | 36.1  | 11.2 |
| external o-CF₃ | 32.0  | 32.9     | 20.9     | 40.0 | 28.0    | -     | -     | 26.6    | 34.5 | 41.3 | 22.4  | 28.3  | 9.3  |
| central p-CF₃ | 32.1  | 33.7     | 23.0     | 39.4 | 28.7    | -     | -     | 27.0    | 35.7 | 43.2 | 27.4  | 32.4  | 9.7  |
| p-CF₃       | 31.0  | 33.3     | 24.1     | 38.6 | 29.4    | -     | -     | 26.3    | 35.9 | 42.1 | 27.8  | 33.2  | 11.3 |
| external o-OMe | 31.0  | 33.3    | 23.0     | 38.9 | 28.6    | -     | -     | 26.6    | 35.6 | 42.8 | 27.8  | 31.6  | 9.4  |
| central p-OMe | 31.4  | 33.4     | 22.8     | 40.6 | 30.0    | -     | -     | 26.4    | 35.8 | 43.2 | 26.2  | 32.7  | 10.1 |
| p-OMe       | 31.0  | 33.2     | 23.1     | 38.5 | 28.5    | -     | -     | 26.4    | 35.7 | 43.1 | 26.5  | 30.8  | 9.1  |
| 2           | 33.3  | 33.7     | 21.7     | 36.8 | 24.9    | -     | -     | 26.2    | 32.7 | 41.5 | -     | -     | -    |
| 3           | 32.0  | 33.8     | 22.7     | 41.3 | 30.1    | -     | -     | 29.7    | 35.7 | 40.1 | -     | -     | -    |
| 15          | 43.3  | 44.0     | 17.4     | 49.8 | 23.2    | -     | -     | 32.1    | 31.6 | 44.6 | -     | -     | -    |
| 16          | 32.2  | 33.3     | 22.6     | 39.4 | 28.7    | -     | -     | 29.2    | 35.7 | 40.3 | -     | -     | -    |
| 2 (a)       | 35.0  | 36.1     | 23.2     | 38.4 | 25.5    | -     | -     | 27.0    | 30.7 | 39.2 | -     | -     | -    |
| 3 (a)       | 35.2  | 38.8     | 23.4     | 45.6 | 30.2    | -     | -     | 29.4    | 35.6 | 41.1 | -     | -     | -    |
| P(Pr)₂ (4)  | 33.4  | 32.7     | 21.0     | 39.4 | 27.7    | -     | -     | 29.0    | 42.8 | 41.1 | 31.2  | 34.1  | 12.1 |
| 5 (cycle A) | 35.9  | 39.3     | 23.7     | 43.5 | 27.9    | -     | -     | 26.7    | 34.9 | 42.7 | 30.6  | 34.1  | 9.9  |
| 15 (a)      | 46.8  | 46.8     | 14.5     | 52.1 | 19.9    | -     | -     | 30.7    | 31.5 | 45.8 | -     | -     | -    |
Figure S7. Comparison of the key steps in the CO oxidation by N₂O catalyzed by different Ru-H pincer catalysts, substituted with -OME and -CF₃ (relative Gibbs energies for THF media at 70°C in kcal/mol and referred to the complex equivalent to catalyst 6+CO+N₂O, and P = P(tBu₂)).
Figure S8. Comparison of the isomerization process from 7 to 8 using different -OMe and -CF$_3$ substituted Ru-H pincer catalysts (relative Gibbs energies for THF media at 70°C in kcal/mol and referred to the complex equivalent to catalyst 6+CO+N$_2$O, and P = P(tBu$_2$)).
IV. Effective Oxidation State Analysis and Atomic Charges

The effective oxidation state (EOS) analysis allowed us to compute the oxidation state (OS) of the Ru and the ligands. In the EOS method, effective atomic orbitals (eff-AOs), with their respective occupations are computed. To get the OS of each fragment, the electrons are assigned to the eff-AOs used to assign the electrons to the fragments with eff-AOs in order to get the OS. More information about the EOS method can be found in the corresponding references cited in the computational details section of the main manuscript.

According to the calculations, the OS of the Ru is +2, the CO ligands are 0, and the hydride and the pincer are -1 each, in both intermediates (7 and 8), this assignation its clear with a R% larger than 60% (Tables S5 and S6). Even though, some differences between intermediates 7 and 8 can be appreciated if we divide the pincer ligand in different fragments (fragments 5, 6, 7 and 8 in Figure S9). In the case of intermediate 7, the reduced part of the pincer, with an OS of -1, is the side ring while in intermediate 8, the central ring has an OS of -2 and the phosphine (fragment 8) ligand is +1. This is a surprising result taking into account that in complex 8 the lateral ring is coordinated to the metal trough the C, so we expected this fragment to have an OS of -1 in this case. However, it has to be noted that for this Ru-H pincer complexes, especially if we want to separate the PNN into different fragments, the assignation of the electrons is not clear. The difference in occupation number between the last occupied and first unoccupied eff-AOs, $\chi_{LO}$ and $\chi_{FU}$, is small, in the case of system 7, the last electron was assigned to fragment 5, with $\chi_{LO}$ of 0.466 having a small difference of just 0.055 with the $\chi_{FU}$ of the C bridge (fragment 7). This also gives a low reliability index values close to 55% in the cases that the PNN is fragmented. The latter values can be better understood if we look at the shape of the eff-AOs depicted in Figures 10 and 11, we can observe that the last electron pain assigned in intermediate 7 went to an orbital placed in the C-C bond joining the pyridyl rings of the pincer, and the first unoccupied orbital is an s-type like orbital of the P. In the case of intermediate 8,

![Figure S9](image_url)

**Figure S9.** Fragments selected for the EOS and charge calculations, with the corresponding labels.
In the external ring of the PNN ligand X = N, CH or C.

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1 Remember that the larger the R(%) value (it can take values from 0 to 100), the closer the overall assignment of the EOS is to the actual electronic structure of the system. It also has to be noted that values below 50% indicate that the assignment of the electrons has not followed an aufbau principle according to the occupation numbers of the eff-AOs.
Table S5. Alpha electrons, occupation number of last occupied and first unoccupied eff-AOs ($\lambda_{LO}^\alpha$ and $\lambda_{FU}^\alpha$, respectively) and Effective Oxidation State (EOS) for the fragments depicted in Figure S9 in intermediate 7. The reliability index R(%) of the EOS assignment for each calculation are also given. This is a closed-shell singlet, thus, alpha and beta frontier eff-AOs are equivalent (beta results are omitted).

| Fragment | Alpha electrons | $\lambda_{LO}^\alpha$ | $\lambda_{FU}^\alpha$ | Oxidation State | R(%) |
|----------|-----------------|-----------------------|-----------------------|-----------------|------|
| 1        | 7               | 0.610                 | 0.391                 | 2               | 55.6 |
| 2        | 1               | 0.524                 | 0.019                 | -1              | 55.6 |
| 3        | 7               | 0.710                 | 0.181                 | 0               | 55.6 |
| 4        | 7               | 0.751                 | 0.147                 | 0               | 55.6 |
| 5        | 21              | 0.466                 | 0.086                 | -1              | 55.6 |
| 6        | 20              | 0.505                 | 0.409                 | 0               | 55.7 |
| 7        | 3               | 0.546                 | 0.411                 | 0               | 55.3 |
| 8        | 40              | 0.580                 | 0.214                 | 1               | 55.6 |
| 9        | 85              | 0.583                 | 0.089                 | -1              | 63.3 |

Table S6. Alpha electrons, occupation number of last occupied and first unoccupied eff-AOs ($\lambda_{LO}^\alpha$ and $\lambda_{FU}^\alpha$, respectively) and Effective Oxidation State (EOS) for the fragments depicted in Figure S9 in intermediate 8. The reliability index R(%) of the EOS assignment for each calculation are also given. This is a closed-shell singlet, thus, alpha and beta frontier eff-AOs are equivalent (beta results are omitted).

| Fragment | Alpha electrons | $\lambda_{LO}^\alpha$ | $\lambda_{FU}^\alpha$ | Oxidation State | R(%) |
|----------|-----------------|-----------------------|-----------------------|-----------------|------|
| 1        | 7               | 0.612                 | 0.411                 | 2               | 57.7 |
| 2        | 1               | 0.529                 | 0.020                 | -1              | 57.7 |
| 3        | 7               | 0.706                 | 0.184                 | 0               | 57.7 |
| 4        | 7               | 0.743                 | 0.162                 | 0               | 57.7 |
| 5        | 20              | 0.623                 | 0.389                 | 0               | 57.7 |
| 6        | 21              | 0.448                 | 0.087                 | -2              | 51.2 |
| 7        | 3               | 0.443                 | 0.387                 | 0               | 51.5 |
| 8        | 40              | 0.654                 | 0.218                 | 1               | 57.7 |
| 9        | 85              | 0.549                 | 0.099                 | -1              | 61.8 |

Figure S10. Eff-AOs ($\lambda_{LO}^\alpha$ and $\lambda_{FU}^\alpha$) with occupation numbers between 0.200 and 0.700 in intermediate 7. The orbitals were obtained from a calculation considering fragments 1, 2, 3, 4, 5 and a last fragment grouping 6, 7 and 8, having an R% = 55.6.
Figure S11. Eff-AOs ($\lambda_{\text{LO}}$ and $\lambda_{\text{FU}}$) with occupation numbers between 0.200 and 0.700 in intermediate 8. The orbitals were obtained from a calculation considering fragments 1, 2, 3, 4, 5 and a last fragment grouping 6, 7 and 8, having an R% = 57.7.

Table S7. Corresponding 3-D space and Mulliken electron populations and charges for the fragments depicted in Figure S9 in intermediate 7.

| Fragment | 3-D space | Mulliken | 3-D space | Mulliken |
|----------|-----------|----------|-----------|----------|
| 1        | 14.624    | 14.699   | 1.376     | 1.301    |
| 2        | 1.318     | 1.321    | -0.318    | -0.321   |
| 3        | 14.355    | 14.467   | -0.355    | -0.467   |
| 4        | 14.299    | 14.378   | -0.299    | -0.378   |
| 5        | 41.087    | 40.877   | -0.087    | 0.123    |
| 6        | 40.438    | 40.140   | -0.438    | -0.140   |
| 7        | 6.617     | 6.521    | -0.617    | -0.521   |
| 8        | 80.142    | 80.867   | 0.858     | 0.133    |
| 9        | 169.402   | 169.135  | -0.531    | -0.963   |

Table S8. Corresponding 3-D space and Mulliken electron populations and charges for the fragments depicted in Figure S9 in intermediate 8.

| Fragment | 3-D space | Mulliken | 3-D space | Mulliken |
|----------|-----------|----------|-----------|----------|
| 1        | 14.696    | 14.686   | 1.304     | 1.314    |
| 2        | 1.333     | 1.376    | -0.333    | -0.376   |
| 3        | 14.352    | 14.451   | -0.352    | -0.451   |
| 4        | 14.306    | 14.385   | -0.306    | -0.385   |
| 5        | 40.300    | 40.251   | -0.300    | -0.251   |
| 6        | 40.199    | 39.988   | -0.199    | 0.012    |
| 7        | 6.440     | 6.494    | -0.440    | -0.494   |
| 8        | 80.205    | 80.864   | 0.795     | 0.136    |
| 9        | 169.312   | 169.102  | -0.312    | -0.102   |
V. Aromaticity analysis of the pincer ligand.

A part from the HOMA and EDDB aromaticity measures that we presented in the main manuscript we also checked the aromaticity by means of FLU, PDI, MCI and I_{ring} electronic indices. We wanted to characterize the aromaticity of the pincer ligand in their different coordination, through the N (PNN) or the C of the external ring (PNC). For this reason, we analyzed the aromaticity in the two 6-member rings (MR) present in the ligand and the two 5-MR that are formed after the coordination to the metal, all of them shown in Figure S12.

![Figure S12. Schematic representation of the rings selected for measuring the aromaticity.](image)

The results of the different aromaticity indices can be interpreted as following. On the one hand, in the case of indices based on references (HOMA and FLU), the maximum aromaticity is achieved when the system resembles more the references molecules, i.e. benzene for C-C or pyridine for C-N bonds. In the case of HOMA the maximum aromaticity is achieved at a value of 100, while in FLU, the closer the value to zero the more aromatic the compound is. The fact that these indices are based on references suppose a drawback in this case, since we do not have references for Ru-C, Ru-N, and Ru-P bonds, thus we cannot compute the aromaticity of rings III and IV. On the other hand, we have the multicenter indices PDI, I_{ring} and MCI, which measure the delocalization without using references. In the three cases, high positive values (close to those obtained for pyridine in the case of the 6-MR) will be indicative aromatic character, whereas smaller values will correspond to non-aromatic species. It has to be noted that in the case of PDI, just the delocalization between atoms situated in the para positions is taken into account, therefore this index just cab be measured for 6-MRs.

Table S9. HOMA, FLU, PDI, I_{ring} and MCI aromaticity results (in a.u.) of the studied intermediates 7, 13, 14 and 8 systems. Taking into account the 6 and 5-member rings depicted in Figure S12.

| Intermediate | Ring | HOMA | FLU | PDI | I_{ring} | MCI |
|--------------|------|------|-----|-----|---------|-----|
| 7            | I    | 0.93 | 0.02 | 0.085 | 0.034 | 0.049 |
|              | II   | 0.73 | 0.011 | 0.057 | 0.018 | 0.023 |
|              | III  | -    | -    | -    | 0.001 | 0.001 |
|              | IV   | -    | -    | -    | 0.001 | 0.001 |
| 13           | I    | 0.89 | 0.006 | 0.086 | 0.035 | 0.050 |
|              | II   | 0.76 | 0.009 | 0.061 | 0.019 | 0.025 |
|              | III  | -    | -    | -    | 0.001 | 0.001 |
|              | IV   | -    | -    | -    | 0.001 | 0.001 |
| 14           | I    | 0.89 | 0.006 | 0.093 | 0.038 | 0.055 |
|              | II   | 0.75 | 0.008 | 0.063 | 0.019 | 0.024 |
|              | III  | -    | -    | -    | 0.001 | 0.001 |
|              | IV   | -    | -    | -    | 0.001 | 0.001 |
| 8            | I    | 0.86 | 0.006 | 0.087 | 0.035 | 0.049 |
|              | II   | 0.93 | 0.002 | 0.081 | 0.031 | 0.043 |
|              | III  | -    | -    | -    | 0.002 | 0.002 |
|              | IV   | -    | -    | -    | 0.001 | 0.000 |
| pyridine     |      | 0.94 | 0.007 | 0.103 | 0.046 | 0.068 |
Finally, we used the EDDB method which provides both visual and quantitative results. The visual results are the EDDB(r) isosurfaces, which in the case of having delocalized electrons (aromaticity) we will observe a continuous thick surface, like the one observed for pyridine in Figure S13 or for the 6-MRs of the ruthenium complexes in Figure 3b in the main manuscript, while in the case of non-aromatic this surface will have discontinuities. Then we also have the number of delocalized electrons, which together with the Hückel and Baird rules can tell us if the compound is going to be aromatic or not (e.g. for benzene and pyridine we expect 6 delocalized electrons).

![Pyridine](image)

**Figure S13.** EDDB surfaces results corresponding to the electron density of delocalized bonds for pyridine and the pincer ligand in complexes 7, 13, 14 and 8.

**Table S10.** EDDB results of the studied intermediates 7, 13, 14 and 8 systems. Taking into account the 6 and 5-member rings depicted in Figure S12.

| Intermediate | Ring | EDDB(r) | EDDB(r)/atom | Lower limit/Uniformity deloc. Degree | Upper limit/atom |
|--------------|------|---------|---------------|--------------------------------------|------------------|
| 7            | I    | 4.76    | 0.79          | 3.78                                 | 0.63             |
|              | II   | 3.03    | 0.5           | 1.49                                 | 0.25             |
|              | III  | 0.46    | 0.09          | 0.26                                 | 0.05             |
|              | IV   | 0.63    | 0.13          | 0.38                                 | 0.08             |
|              | I    | 4.73    | 0.79          | 3.72                                 | 0.62             |
| 13           | II   | 3.18    | 0.53          | 1.71                                 | 0.28             |
|              | III  | 0.73    | 0.15          | 0.36                                 | 0.07             |
|              | I    | 5.08    | 0.85          | 4.28                                 | 0.71             |
| 14           | II   | 3.15    | 0.52          | 1.75                                 | 0.29             |
|              | III  | 0.35    | 0.07          | 0.25                                 | 0.05             |
|              | IV   | 0.78    | 0.16          | 0.38                                 | 0.08             |
|              | I    | 4.78    | 0.8           | 3.85                                 | 0.64             |
| 8            | II   | 4.63    | 0.77          | 3.57                                 | 0.6              |
|              | III  | 0.43    | 0.09          | 0.32                                 | 0.06             |
|              | IV   | 0.24    | 0.05          | 0.11                                 | 0.02             |
| pyridine     | -    | 5.52    | 0.92          | 5.02                                 | 0.84             |
VI. Egas, Ggas, Esolv., Gsolv. and frequencies

Table S11. Egas and Ggas at BP86-D3BJ/SVP~sdd level of theory, Esolvent at M06-L/cc-pVTZ~sdd level of theory and Gsolvent computed as Ggas - Egas + Esolvent all of them in Hartree for the compounds involved in cycle A and the isomerization process from 7 to 8 starting from catalyst 6. Number of negative frequencies found for each optimized structure at BP86-D3BJ/SVP~sdd level of theory, and the corresponding frequency in the cases when there is a negative one (frequencies in cm⁻¹).

| compound          | Egas          | Ggas          | Esolvent      | Gsolvent      | no. of negative frequencies | frequency |
|-------------------|---------------|---------------|---------------|---------------|-----------------------------|-----------|
| Intermediate:6    | -1398.974938  | -1398.627351  | -1399.736495  | -1399.388907  | 0                           | -         |
| Intermediate:7    | -1512.254745  | -1511.900935  | -1513.114768  | -1512.760958  | 0                           | -         |
| TS:7-9            | -1696.785621  | -1696.424685  | -1697.802399  | -1697.441463  | 1                           | -61.5     |
| Intermediate:9    | -1696.815743  | -1696.449884  | -1697.840123  | -1697.474264  | 0                           | -         |
| TS:9-10+H2O      | -1773.188233  | -1772.807141  | -1774.265694  | -1773.884603  | 1                           | -512.0    |
| TS:9-10+THF      | -1929.085406  | -1928.621604  | -1930.299864  | -1929.836062  | 1                           | -165.5    |
| Intermediate:10   | -1696.771485  | -1696.416883  | -1697.781887  | -1697.472284  | 1                           | -1356.5   |
| TS:10-11axial    | -1587.439741  | -1587.081435  | -1588.37203  | -1588.013724  | 0                           | -         |
| TS:10-11axial+H2O| -1663.799042  | -1663.419166  | -1664.802773  | -1664.422897  | 1                           | -227.9    |
| Intermediate:11axial | -1587.438084  | -1587.077926  | -1588.36435  | -1588.004192  | 0                           | -         |
| TS:11axial-11equatorial | -1587.435829  | -1587.072938  | -1588.358288  | -1587.995397  | 1                           | -818.4    |
| Intermediate:11equatorial | -1587.449677  | -1587.087822  | -1588.376254  | -1588.013497  | 0                           | -         |
| TS:11equatorial-6 | -1587.399412  | -1587.045498  | -1588.326039  | -1587.972125  | 1                           | -934.1    |
| TS:11equatorial-6+H2O | -1663.773975  | -1663.398239  | -1664.758704  | -1664.382968  | 1                           | -1068.9   |
| Intermediate:12   | -1700.719936  | -1700.352305  | -1701.745496  | -1701.377865  | 0                           | -         |
| TS:12-7           | -1700.64934  | -1700.290568  | -1701.668891  | -1701.310119  | 1                           | -1443.3   |
| TS:12-7+H2O      | -1777.036146  | -1776.655278  | -1778.119667  | -1777.738799  | 1                           | -1209.4   |
| TS:7-13           | -1512.205486  | -1511.853122  | -1513.07005  | -1512.717686  | 1                           | -83.3     |
| Intermediate:13   | -1512.21665  | -1511.864187  | -1513.07641  | -1512.723947  | 0                           | -         |
| adduct:13+THF     | -1744.528496  | -1744.069891  | -1745.58093  | -1745.12488  | 0                           | -         |
| TS:13-14          | -1512.20653  | -1511.856824  | -1513.05731  | -1512.707604  | 1                           | -723.8    |
| Intermediate:14   | -1512.214593  | -1511.862892  | -1513.071433  | -1512.719731  | 0                           | -         |
| TS:14-8           | -1512.19972  | -1511.849557  | -1513.05421  | -1512.703795  | 1                           | -465.4    |
Table S12. \( E_{\text{gas}} \) and \( G_{\text{gas}} \) at BP86-D3BJ/SVP~sdd level of theory, \( E_{\text{solvent}} \) at M06-L/cc-pVTZ~sdd level of theory and \( G_{\text{solvent}} \) computed as \( G_{\text{gas}} = E_{\text{gas}} + E_{\text{solvent}} \) all of them in Hartree for the compounds involved in cycle B starting from catalyst 8. Number of negative frequencies found for each optimized structure at BP86-D3BJ/SVP~sdd level of theory, and the corresponding frequency in the cases when there is a negative one (frequencies in cm\(^{-1}\)).

| compound                  | \( E_{\text{gas}} \)     | \( G_{\text{gas}} \)     | \( E_{\text{solvent}} \) | \( G_{\text{solvent}} \) | no. of negative frequencies | frequency |
|---------------------------|--------------------------|--------------------------|--------------------------|--------------------------|-----------------------------|-----------|
| Intermediate: 8           | -1512.260932             | -1511.905465             | -1513.118761             | -1512.763294             | 0                           | -         |
| TS: 8-9'                  | -1696.820253             | -1696.453796             | -1697.806272             | -1697.439815             | 1                           | -180.7    |
| Intermediate: 9'          | -1696.823402             | -1696.457389             | -1697.847956             | -1697.481942             | 0                           | -         |
| TS: 9'-10'+H\(_2\)O       | -1773.192498             | -1772.811766             | -1774.269270             | -1773.888538             | 1                           | -623.1    |
| TS: 9'-10'                | -1696.773570             | -1696.416531             | -1697.783917             | -1697.426878             | 1                           | -1295.8   |
| Intermediate: 10'         | -1587.450852             | -1587.090311             | -1588.382399             | -1588.021858             | 0                           | -         |
| TS: 10'-11'axial          | -1587.416748             | -1587.057659             | -1588.349466             | -1587.990377             | 1                           | -114.2    |
| TS: 10'-11'axial+H\(_2\)O | -1663.800634             | -1663.420898             | -1664.804813             | -1664.425076             | 1                           | -220.9    |
| Intermediate: 11'axial    | -1587.434818             | -1587.074269             | -1587.361285             | -1588.000736             | 0                           | -         |
| TS: 11'axial-11'equatorial| -1587.430113             | -1587.068447             | -1588.353046             | -1587.991380             | 1                           | -31.6     |
| Intermediate: 11'equatorial| -1587.441911             | -1587.080983             | -1588.366310             | -1588.005382             | 0                           | -         |
| TS: 11'equatorial-6'      | -1587.388742             | -1587.035146             | -1588.317748             | -1587.964152             | 1                           | -807.5    |
| Intermediate: 6'          | -1398.966043             | -1398.618889             | -1399.729533             | -1399.382379             | 0                           | -         |
| Intermediate: 12'         | -1700.716008             | -1700.349229             | -1701.746465             | -1701.379686             | 0                           | -         |
| TS: 12'-8                 | -1700.654209             | -1700.295018             | -1701.674394             | -1701.315203             | 1                           | -1305.2   |
Table S13. $E_{\text{gas}}$ and $G_{\text{gas}}$ at BP86-D3BJ/SVP~sdd level of theory, $E_{\text{solvent}}$ at M06-L/cc-pVTZ~sdd level of theory and $G_{\text{solvent}}$ computed as $G_{\text{gas}} - E_{\text{gas}} + E_{\text{solvent}}$ all of them in Hartree for the compounds involved in the main steps of catalyzed reduction of N$_2$O and the isomerization process of the catalyst starting from system $\text{P(iPr)}_2$ (4).

| compound          | $E_{\text{gas}}$ | $G_{\text{gas}}$ | $E_{\text{solvent}}$ | $G_{\text{solvent}}$ | no. of negative frequencies | frequency |
|-------------------|-----------------|-----------------|-----------------------|-----------------------|-----------------------------|-----------|
| Intermediate: 6   | -1320.391047    | -1320.094463    | -1321.095109          | -1320.798525          | 0                           | -         |
| Intermediate: 7   | -1433.681019    | -1433.378703    | -1434.481233          | -1434.178917          | 0                           | -         |
| TS: 7-9           | -1618.215444    | -1617.909663    | -1619.166381          | -1618.860600          | 1                           | -220.2    |
| Intermediate: 9   | -1618.247112    | -1617.935449    | -1619.209341          | -1618.897678          | 0                           | -         |
| TS: 9-10+H$_2$O   | -1694.621389    | -1694.291721    | -1695.638349          | -1695.308681          | 1                           | -515.1    |
| TS: 9-10          | -1618.204514    | -1617.901298    | -1619.155032          | -1618.851816          | 1                           | -1447.0   |
| Intermediate: 10  | -1508.871578    | -1508.565070    | -1509.744963          | -1509.438455          | 0                           | -         |
| Intermediate: 11  | -1508.867915    | -1508.559418    | -1509.736097          | -1509.427600          | 0                           | -         |
| TS: 11-equatorial | -1508.814723    | -1508.512566    | -1509.682014          | -1509.379857          | 1                           | -931.8    |
| Intermediate: 12  | -1622.148693    | -1621.835201    | -1623.114411          | -1622.800919          | 0                           | -         |
| TS: 12-7          | -1622.078700    | -1621.774046    | -1623.038134          | -1622.733479          | 1                           | -1279.2   |
| TS: 7-13          | -1433.630937    | -1433.332221    | -1434.434980          | -1434.136264          | 1                           | -87.0     |
| Intermediate: 13  | -1433.644251    | -1433.345392    | -1434.443170          | -1434.144311          | 0                           | -         |
| TS: 13-14         | -1433.632133    | -1433.335677    | -1434.420538          | -1434.124081          | 1                           | -768.3    |
| Intermediate: 14  | -1433.642053    | -1433.342829    | -1434.438356          | -1434.139132          | 0                           | -         |
| TS: 14-8          | -1433.624963    | -1433.327344    | -1434.418730          | -1434.121111          | 1                           | -410.2    |
| Intermediate: 8   | -1433.680045    | -1433.377655    | -1434.480853          | -1434.178464          | 0                           | -         |
Table S14. \(E_{\text{gas}}\) and \(G_{\text{gas}}\) at BP86-D3BJ/SVP~sdd level of theory, \(E_{\text{solvent}}\) at M06-L/cc-pVTZ~sdd level of theory and \(G_{\text{solvent}}\) computed as \(G_{\text{gas}} = E_{\text{gas}} + E_{\text{solvent}}\) all of them in Hartree for the compounds involved in the main steps of catalyzed reduction of \(\text{N}_2\text{O}\) and the isomerization process of the catalyst starting from system \(\text{P(CH}_3\text{)}_2\).

Number of negative frequencies found for each optimized structure at BP86-D3BJ/SVP~sdd level of theory, and the corresponding frequency in the cases when there is a negative one (frequencies in cm\(^{-1}\)).

| compound          | \(E_{\text{gas}}\) | \(G_{\text{gas}}\) | \(E_{\text{solvent}}\) | \(G_{\text{solvent}}\) | no. of negative frequencies | frequency |
|-------------------|---------------------|---------------------|-------------------------|-------------------------|-----------------------------|-----------|
| Intermediate: 6   | -1163.240245        | -1163.045585        | -1163.820191            | -1163.625531            | 0                           | -         |
| Intermediate: 7   | -1276.530355        | -1276.330878        | -1277.206082            | -1277.006605            | 0                           | -         |
| TS: 7-9           | -1461.064175        | -1460.861517        | -1461.890400            | -1461.687741            | 1                           | -316.1    |
| Intermediate: 9   | -1461.095192        | -1460.885458        | -1461.933974            | -1461.724240            | 0                           | -         |
| TS: 9-10+H\(_2\)O| -1537.468833        | -1537.243121        | -1538.362058            | -1538.136347            | 1                           | -499.1    |
| TS: 9-10          | -1461.052196        | -1460.851728        | -1461.879213            | -1461.678745            | 1                           | -1470.3   |
| Intermediate: 10  | -1351.719190        | -1351.515431        | -1352.469084            | -1352.265326            | 0                           | -         |
| Intermediate: 11equatorial | -1351.716035  | -1351.509125        | -1352.460414            | -1352.253504            | 0                           | -         |
| TS: 11equatorial-6| -1351.663497        | -1351.464519        | -1352.408160            | -1352.209182            | 1                           | -945.3    |
| Intermediate: 12  | -1464.998130        | -1464.786240        | -1465.839659            | -1465.627769            | 0                           | -         |
| TS: 12-7          | -1464.930759        | -1464.728011        | -1465.764757            | -1465.562009            | 1                           | -1300.9   |
| TS: 7-13          | -1276.478295        | -1276.281289        | -1276.161693            | -1276.964687            | 1                           | -88.5     |
| Intermediate: 13  | -1276.492387        | -1276.295261        | -1277.168245            | -1276.971119            | 0                           | -         |
| TS: 13-14         | -1276.479242        | -1276.284647        | -1277.144432            | -1276.949837            | 1                           | -810.0    |
| Intermediate: 14  | -1276.488123        | -1276.291401        | -1277.159320            | -1276.962598            | 0                           | -         |
| TS: 14-8          | -1276.471288        | -1276.276154        | -1277.141138            | -1276.946003            | 1                           | -409.6    |
| Intermediate: 8   | -1276.528863        | -1276.329981        | -1277.205489            | -1277.006608            | 0                           | -         |
Table S15. $E_{\text{gas}}$ and $G_{\text{gas}}$ at BP86-D3BJ/SVP-sdd level of theory, $E_{\text{solvent}}$ at M06-L/cc-pVTZ-sdd level of theory and $G_{\text{solvent}}$ computed as $G_{\text{gas}} - E_{\text{gas}} + E_{\text{solvent}}$ all of them in Hartree for the compounds involved in the main steps of catalyzed reduction of N$_2$O and the isomerization process of the catalyst starting from system P(CF$_3$)$_2$.

Number of negative frequencies found for each optimized structure at BP86-D3BJ/SVP-sdd level of theory, and the corresponding frequency in the cases when there is a negative one (frequencies in cm$^{-1}$).

| compound | $E_{\text{gas}}$ | $G_{\text{gas}}$ | $E_{\text{solvent}}$ | $G_{\text{solvent}}$ | no. of negative frequencies | frequency |
|----------|-----------------|-----------------|---------------------|---------------------|---------------------------|-----------|
| Intermediate: 6 | -1758.234717 | -1758.094012 | -1759.382710 | -1759.242005 | 0 | - |
| Intermediate: 7 | -1871.522594 | -1871.377382 | -1872.763580 | -1872.618368 | 0 | - |
| TS: 7-9 | -2056.052857 | -2055.901677 | -2057.445403 | -2057.294223 | 1 | -142.2 |
| Intermediate: 9 | -2056.080170 | -2055.924396 | -2057.483552 | -2057.327778 | 0 | - |
| TS: 9-10+H$_2$O | -2132.455757 | -2132.282711 | -2133.741540 | -2133.640545 | 1 | -461.7 |
| TS: 9-10 | -2056.040542 | -2055.892943 | -2057.433321 | -2057.285722 | 1 | -1326.9 |
| Intermediate: 10 | -1946.707177 | -1946.556616 | -1948.022878 | -1947.872316 | 0 | - |
| Intermediate: 11equatorial | -1946.705889 | -1946.553577 | -1948.017010 | -1947.864697 | 0 | - |
| TS: 11equatorial-6 | -1946.652494 | -1946.508626 | -1947.960758 | -1947.816890 | 1 | -953.2 |
| Intermediate: 12 | -2059.985262 | -2059.827233 | -2061.392753 | -2061.234723 | 0 | - |
| TS: 12-7 | -2059.917612 | -2059.769246 | -2061.316486 | -2061.168120 | 1 | -1396.7 |
| TS: 7-13 | -1871.466021 | -1871.322469 | -1872.712378 | -1872.568826 | 1 | -89.9 |
| Intermediate: 13 | -1871.482422 | -1871.340016 | -1872.721115 | -1872.578752 | 0 | - |
| TS: 13-14 | -1871.471829 | -1871.331723 | -1872.701007 | -1872.560901 | 1 | -788.0 |
| Intermediate: 14 | -1871.482562 | -1871.339520 | -1872.716133 | -1872.573091 | 0 | - |
| TS: 14-8 | -1871.457309 | -1871.316271 | -1872.687185 | -1872.546146 | 1 | -536.3 |
| Intermediate: 8 | -1871.518131 | -1871.372949 | -1872.754857 | -1872.609675 | 0 | - |
Table S16. $E_{\text{gas}}$ and $G_{\text{gas}}$ at BP86-D3BJ/SVP~sdd level of theory, $E_{\text{solvent}}$ at M06-L/cc-pVTZ~sdd level of theory and $G_{\text{solvent}}$ computed as $G_{\text{gas}} - E_{\text{gas}} + E_{\text{solvent}}$ of all of them in Hartree for the compounds involved in the main steps of catalyzed reduction of $\text{N}_2\text{O}$ and the isomerization process of the catalyst starting from system external o-CF$_3$. Number of negative frequencies found for each optimized structure at BP86-D3BJ/SVP~sdd level of theory, and the corresponding frequency in the cases when there is a negative one (frequencies in cm$^{-1}$).

| compound       | $E_{\text{gas}}$ | $G_{\text{gas}}$ | $E_{\text{solvent}}$ | $G_{\text{solvent}}$ | no. of negative frequencies | frequency |
|----------------|------------------|------------------|----------------------|----------------------|----------------------------|-----------|
| Intermediate: 6 | -1735.767114     | -1735.420744     | -1736.843666         | -1736.497295         | 0                          | -         |
| Intermediate: 7 | -1849.047224     | -1848.694377     | -1850.223940         | -1849.871092         | 0                          | -         |
| TS: 7-9        | -2033.578392     | -2033.217225     | -2034.911736         | -2034.550569         | 1                          | -76.7     |
| Intermediate: 9 | -2033.607480     | -2033.242474     | -2034.947549         | -2034.582543         | 0                          | -         |
| TS: 9-10+H$_2$O| -2109.983101     | -2109.601813     | -2111.376916         | -2110.995629         | 1                          | -500.8    |
| TS: 9-10       | -2033.565969     | -2033.211296     | -2034.892515         | -2034.537842         | 1                          | -1331.4   |
| Intermediate: 10| -1924.232886    | -1923.876390     | -1925.482166         | -1925.125670         | 0                          | -         |
| Intermediate: 11equatorial | -1924.241015 | -1923.881376     | -1925.483647         | -1925.124008         | 0                          | -         |
| TS: 11equatorial-6 | -1924.192626 | -1923.89611      | -1925.434650         | -1925.081634         | 1                          | -986.6    |
| Intermediate: 12| -2037.510664    | -2037.143813     | -2038.852361         | -2038.485510         | 0                          | -         |
| TS: 12-7       | -2037.443782     | -2037.085098     | -2038.787821         | -2038.419737         | 1                          | -1287.2   |
| TS: 7-13       | -1849.006381     | -1848.656506     | -1850.185262         | -1849.835387         | 1                          | -52.7     |
| Intermediate: 13| -1849.014899     | -1848.665468     | -1850.189854         | -1849.840834         | 0                          | -         |
| TS: 13-14      | -1849.005291     | -1848.659262     | -1850.172096         | -1849.826066         | 1                          | -761.2    |
| Intermediate: 14| -1849.014790     | -1848.666551     | -1850.188098         | -1849.839859         | 0                          | -         |
| TS: 14-8       | -1849.005552     | -1848.653572     | -1850.171172         | -1849.824192         | 1                          | -464.2    |
| Intermediate: 8 | -1849.058379     | -1848.707547     | -1850.236505         | -1849.885673         | 0                          | -         |
Table S17. $E_{\text{gas}}$ and $G_{\text{gas}}$ at BP86-D3BJ/SVP~sdd level of theory, $E_{\text{solvent}}$ at M06-L/cc-pVTZ~sdd level of theory and $G_{\text{solvent}}$ computed as $G_{\text{gas}} = E_{\text{gas}} + E_{\text{solvent}}$ all of them in Hartree for the compounds involved in the main steps of catalyzed reduction of N\textsubscript{2}O and the isomerization process of the catalyst starting from system external p-\textsubscript{CF}_{3}. Number of negative frequencies found for each optimized structure at BP86-D3BJ/SVP~sdd level of theory, and the corresponding frequency in the cases when there is a negative one (frequencies in cm\textsuperscript{-1}).

| compound | $E_{\text{gas}}$ | $G_{\text{gas}}$ | $E_{\text{solvent}}$ | $G_{\text{solvent}}$ | no. of negative frequencies | frequency |
|----------|------------------|------------------|----------------------|----------------------|-----------------------------|-----------|
| Intermediate: 6 | -1735.772927 | -1735.429311 | -1736.848522 | -1736.504905 | 0 | - |
| Intermediate: 7 | -1849.051734 | -1848.702183 | -1850.226257 | -1849.876705 | 0 | - |
| TS: 7-9 | -2033.582263 | -2033.225060 | -2034.913295 | -2034.556092 | 1 | -66.2 |
| Intermediate: 9 | -2033.611874 | -2033.251390 | -2034.950732 | -2034.590248 | 0 | - |
| TS: 9-10+H\textsubscript{2}O | -2109.985174 | -2109.608164 | -2111.377006 | -2110.999996 | 1 | -493.3 |
| TS: 9-10 | -2033.572072 | -2033.218613 | -2034.897926 | -2034.544467 | 1 | -1506.1 |
| Intermediate: 10 | -1924.236348 | -1923.882353 | -1925.483207 | -1925.129211 | 0 | - |
| Intermediate: 11\textsubscript{equatorial} | -1924.246516 | -1923.889382 | -1925.487882 | -1925.130748 | 0 | - |
| TS: 11\textsubscript{equatorial}-6 | -1924.196266 | -1923.846646 | -1925.437278 | -1925.087658 | 1 | -939.7 |
| Intermediate: 12 | -2037.516305 | -2037.153276 | -2038.856442 | -2038.493413 | 0 | - |
| TS: 12-7 | -2037.445901 | -2037.090663 | -2038.779776 | -2038.424539 | 1 | -1314.6 |
| TS: 7-13 | -1849.004198 | -1848.654927 | -1850.182242 | -1849.832971 | 1 | -69.7 |
| Intermediate: 13 | -1849.018165 | -1848.667532 | -1850.191087 | -1849.840454 | 0 | - |
| TS: 13-14 | -1849.009487 | -1848.661264 | -1850.173228 | -1849.825005 | 1 | -789.2 |
| Intermediate: 14 | -1849.019326 | -1848.668698 | -1850.189831 | -1849.839203 | 0 | - |
| TS: 14-8 | -1849.003667 | -1848.653688 | -1850.171429 | -1849.821450 | 1 | -490.1 |
| Intermediate: 8 | -1849.060327 | -1848.706047 | -1850.237180 | -1849.882900 | 0 | - |
Table S18. $E_{\text{gas}}$ and $G_{\text{gas}}$ at BP86-D3BJ/SVP~sdd level of theory, $E_{\text{solvent}}$ at M06-L/cc-pVTZ~sdd level of theory and $G_{\text{solvent}}$ computed as $G_{\text{gas}} = E_{\text{gas}} + E_{\text{solvent}}$ all of them in Hartree for the compounds involved in the main steps of catalyzed reduction of N$_2$O and the isomerization process of the catalyst starting from system central p-CF$_3$. Number of negative frequencies found for each optimized structure at BP86-D3BJ/SVP~sdd level of theory, and the corresponding frequency in the cases when there is a negative one (frequencies in cm$^{-1}$).

| compound | $E_{\text{gas}}$ | $G_{\text{gas}}$ | $E_{\text{solvent}}$ | $G_{\text{solvent}}$ | no. of negative frequencies | frequency |
|----------|------------------|------------------|----------------------|----------------------|-----------------------------|-----------|
| Intermediate: 6 | -1735.776269 | -1735.432811 | -1736.853390 | -1736.509932 | 0 | - |
| Intermediate: 7 | -1849.055874 | -1848.705769 | -1850.231305 | -1849.881200 | 0 | - |
| TS: 7-9 | -2033.586376 | -2033.286227 | -2034.917132 | -2034.559383 | 1 | -65.8 |
| Intermediate: 9 | -2033.616042 | -2033.254008 | -2034.955546 | -2034.593511 | 0 | - |
| TS: 9-10 | -2109.988984 | -2109.611688 | -2111.381829 | -2111.004532 | 1 | -489.4 |
| TS: 9-10 | -2033.575556 | -2033.222631 | -2034.902649 | -2034.549723 | 1 | -1349.8 |
| Intermediate: 10 | -1924.240282 | -1923.886416 | -1925.488143 | -1925.134276 | 0 | - |
| Intermediate: 11_{equatorial} | -1924.249924 | -1923.892320 | -1925.492466 | -1925.134862 | 0 | - |
| TS: 11_{equatorial}-6 | -1924.199615 | -1923.849926 | -1925.441798 | -1925.092108 | 1 | -934.2 |
| Intermediate: 12 | -2037.519606 | -2037.155506 | -2038.860503 | -2038.496402 | 0 | - |
| TS: 12-7 | -2037.449786 | -2037.094416 | -2038.784775 | -2038.429456 | 1 | -1318.0 |
| TS: 7-13 | -1849.006111 | -1848.657449 | -1850.187067 | -1849.838404 | 1 | -81.3 |
| Intermediate: 13 | -1849.017158 | -1848.668384 | -1850.192590 | -1849.843815 | 0 | - |
| TS: 13-14 | -1849.007086 | -1848.661416 | -1850.173385 | -1849.827716 | 1 | -726.9 |
| Intermediate: 14 | -1849.015313 | -1848.667507 | -1850.188282 | -1849.840475 | 0 | - |
| TS: 14-8 | -1848.999353 | -1848.652532 | -1850.168793 | -1849.821972 | 1 | -474.3 |
| Intermediate: 8 | -1849.054903 | -1848.705130 | -1850.231409 | -1849.881635 | 0 | - |
Table S19. \( E_{\text{gas}} \) and \( G_{\text{gas}} \) at BP86-D3BJ/SVP~sdd level of theory, \( E_{\text{solvent}} \) at M06-L/cc-pVTZ~sdd level of theory and \( G_{\text{solvent}} \) computed as \( G_{\text{gas}} = E_{\text{gas}} + E_{\text{solvent}} \) all of them in Hartree for the compounds involved in the main steps of catalyzed reduction of \( \text{N}_2\text{O} \) and the isomerization process of the catalyst starting from system \( p\text{-CF}_3 \). Number of negative frequencies found for each optimized structure at BP86-D3BJ/SVP~sdd level of theory, and the corresponding frequency in the cases when there is a negative one (frequencies in cm\(^{-1}\)).

| compound                  | \( E_{\text{gas}} \) | \( G_{\text{gas}} \) | \( E_{\text{solvent}} \) | \( G_{\text{solvent}} \) | no. of negative frequencies | frequency |
|---------------------------|-----------------------|-----------------------|---------------------------|---------------------------|-----------------------------|-----------|
| Intermediate: 6           | -2072.573545          | -2072.233986          | -2073.964816              | -2073.625256              | 0                           | -         |
| Intermediate: 7           | -2185.852194          | -2185.506225          | -2187.342158              | -2186.996189              | 0                           | -         |
| TS: 7-9                   | -2370.382324          | -2370.028712          | -2372.028523              | -2371.674911              | 1                           | -69.7     |
| Intermediate: 9           | -2370.411531          | -2370.055025          | -2372.065691              | -2371.709185              | 0                           | -         |
| TS: 9-10+\text{H}_2\text{O}| -2446.785270          | -2446.412124          | -2448.492494              | -2448.119348              | 1                           | -474.0    |
| TS: 9-10                  | -2370.371500          | -2370.022818          | -2372.013295              | -2371.664612              | 1                           | -1302.2   |
| Intermediate: 10          | -2261.036238          | -2260.686420          | -2262.598709              | -2262.248891              | 0                           | -         |
| Intermediate: 11\text{equatorial} | -2261.046123        | -2260.692780          | -2262.603289              | -2262.249946              | 0                           | -         |
| TS: 11\text{equatorial}-6 | -2260.995736          | -2260.651166          | -2262.552489              | -2262.207919              | 1                           | -936.1    |
| Intermediate: 12          | -2374.315380          | -2373.956108          | -2375.970907              | -2375.611635              | 0                           | -         |
| TS: 12-7                  | -2374.245682          | -2373.894648          | -2375.894967              | -2375.543933              | 1                           | -1323.5   |
| TS: 7-13                  | -2185.804422          | -2185.459030          | -2187.298655              | -2186.953263              | 1                           | -68.0     |
| Intermediate: 13          | -2185.818370          | -2185.471556          | -2187.307105              | -2186.960291              | 0                           | -         |
| TS: 13-14                 | -2185.809769          | -2185.465435          | -2187.289048              | -2186.944714              | 1                           | -786.4    |
| Intermediate: 14          | -2185.819797          | -2185.473007          | -2187.306078              | -2186.959288              | 0                           | -         |
| TS: 14-8                  | -2185.802683          | -2185.456419          | -2187.285313              | -2186.939049              | 1                           | -507.0    |
| Intermediate: 8           | -2185.857671          | -2185.508196          | -2187.349183              | -2186.999708              | 0                           | -         |
Table S20. $E_{\text{gas}}$ and $G_{\text{gas}}$ at BP86-D3BJ/SVP~sdd level of theory, $E_{\text{solvent}}$ at M06-L/cc-pVTZ~sdd level of theory and $G_{\text{solvent}}$ computed as $G_{\text{gas}} - E_{\text{gas}} + E_{\text{solvent}}$ all of them in Hartree for the compounds involved in the main steps of catalyzed reduction of N$_2$O and the isomerization process of the catalyst starting from system external o-OMe. Number of negative frequencies found for each optimized structure at BP86-D3BJ/SVP~sdd level of theory, and the corresponding frequency in the cases when there is a negative one (frequencies in cm$^{-1}$).

| compound       | $E_{\text{gas}}$ | $G_{\text{gas}}$ | $E_{\text{solvent}}$ | $G_{\text{solvent}}$ | no. of negative frequencies | frequency |
|----------------|------------------|------------------|----------------------|----------------------|-----------------------------|-----------|
| Intermediate: 6 | -1513.427803     | -1513.052999     | -1514.290988         | -1513.916184         | 0                           | -         |
| Intermediate: 7 | -1626.709254     | -1626.328163     | -1627.670869         | -1627.289778         | 0                           | -         |
| TS: 7-9        | -1811.242000     | -1810.853892     | -1812.358988         | -1811.970880         | 1                           | -42.4     |
| Intermediate: 9 | -1811.274090     | -1810.880902     | -1812.398919         | -1812.005731         | 0                           | -         |
| TS: 9-10+H$_2$O| -1887.646511     | -1887.237244     | -1888.822974         | -1888.413707         | 1                           | -624.8    |
| TS: 9-10       | -1811.230917     | -1810.846135     | -1812.343624         | -1811.958842         | 1                           | -1447.4   |
| Intermediate: 10 | -1701.895166   | -1701.509414     | -1702.928555         | -1702.542804         | 0                           | -         |
| Intermediate: 11 _equatorial_ | -1701.904217 | -1701.515311 | -1702.931173 | -1702.542266 | 0 | - |
| TS: 11 _equatorial_+6 | -1701.854727 | -1701.473207 | -1702.881798 | -1702.500278 | 1 | -961.0 |
| Intermediate: 12 | -1815.175344 | -1814.780458 | -1816.301295 | -1815.906409 | 0 | - |
| TS: 12-7       | -1815.106045     | -1814.719341     | -1816.226041         | -1815.839337         | 1                           | -1276.5   |
| TS: 7-13       | -1626.660676     | -1626.280627     | -1627.625605         | -1627.245556         | 1                           | -68.0     |
| Intermediate: 13 | -1626.672478 | -1626.292770 | -1627.634669 | -1627.254962 | 0 | - |
| TS: 13-14      | -1626.660704     | -1626.283837     | -1627.613758         | -1627.236891         | 1                           | -687.4    |
| Intermediate: 14 | -1626.667168 | -1626.288521 | -1627.625908 | -1627.247260 | 0 | - |
| TS: 14-8       | -1626.652311     | -1626.274805     | -1627.608332         | -1627.230825         | 1                           | -458.9    |
| Intermediate: 8 | -1626.708918     | -1626.327230     | -1627.672615         | -1627.290927         | 0                           | -         |
Table S21. $E_{\text{gas}}$ and $G_{\text{gas}}$ at BP86-D3BJ/SVP~sdd level of theory, $E_{\text{solvent}}$ at M06-L/cc-pVTZ~sdd level of theory and $G_{\text{solvent}}$ computed as $G_{\text{gas}} - E_{\text{gas}} + E_{\text{solvent}}$ all of them in Hartree for the compounds involved in the main steps of catalyzed reduction of N\textsubscript{2}O and the isomerization process of the catalyst starting from system external p-OMe. Number of negative frequencies found for each optimized structure at BP86-D3BJ/SVP~sdd level of theory, and the corresponding frequency in the cases when there is a negative one (frequencies in cm$^{-1}$).

| compound   | $E_{\text{gas}}$ | $E_{\text{solvent}}$ | $G_{\text{gas}}$ | $G_{\text{solvent}}$ | no. of negative frequencies | frequency |
|------------|------------------|---------------------|------------------|---------------------|----------------------------|-----------|
| Intermediate: 6     | -1513.425005     | -1514.288395       | -1513.050530     | -1513.913920        | 0                          | -         |
| Intermediate: 7     | -1626.705324     | -1627.666965       | -1812.354932     | -1811.966547        | 0                          | -         |
| TS: 7-9             | -1811.236797     | -1810.848412       | -1812.392956     | -1812.000275        | 0                          | -         |
| Intermediate: 9     | -1811.267400     | -1810.874718       | -1812.392956     | -1812.000275        | 0                          | -         |
| TS: 9-10+H$_2$O     | -1887.639644     | -1888.818221       | -1888.409971     | -1888.409971        | 1                          | -527.5    |
| TS: 9-10            | -1811.226283     | -1810.841623       | -1812.393286     | -1811.954626        | 1                          | -1425.4   |
| Intermediate: 10    | -1701.890916     | -1701.505374       | -1702.924457     | -1702.538915        | 0                          | -         |
| Intermediate: 11$_{\text{equatorial}}$ | -1701.900780    | -1701.512024       | -1702.928949     | -1702.540194        | 0                          | -         |
| TS: 11$_{\text{equatorial}}$-6 | -1701.851008    | -1702.878726       | -1702.497747     | -1702.497747        | 1                          | -943.4    |
| Intermediate: 12    | -1815.171279     | -1814.776592       | -1816.298044     | -1815.903356        | 0                          | -         |
| TS: 12-7            | -1815.100509     | -1814.713934       | -1816.221659     | -1815.835084        | 1                          | -1304.3   |
| TS: 7-13            | -1626.656397     | -1626.276526       | -1627.621758     | -1627.241887        | 1                          | -76.5     |
| Intermediate: 13    | -1626.670881     | -1626.291158       | -1627.630531     | -1627.250809        | 0                          | -         |
| TS: 13-14           | -1626.661215     | -1626.284453       | -1627.612540     | -1627.235778        | 1                          | -766.8    |
| Intermediate: 14    | -1626.668854     | -1626.289826       | -1627.625970     | -1627.246942        | 0                          | -         |
| TS: 14-8            | -1626.654216     | -1627.608632       | -1627.230748     | -1627.230748        | 1                          | -465.0    |
| Intermediate: 8     | -1627.710706     | -1627.672836       | -1627.290596     | -1627.290596        | 0                          | -         |
Table S22. $E_{\text{gas}}$ and $G_{\text{gas}}$ at BP86-D3BJ/SVP~sdd level of theory, $E_{\text{solvent}}$ at M06-L/cc-pVTZ~sdd level of theory and $G_{\text{solvent}}$ computed as $G_{\text{gas}} = E_{\text{gas}} + E_{\text{solvent}}$ all of them in Hartree for the compounds involved in the main steps of catalyzed reduction of N$_2$O and the isomerization process of the catalyst starting from system central p-OMe. Number of negative frequencies found for each optimized structure at BP86-D3BJ/SVP~sdd level of theory, and the corresponding frequency in the cases when there is a negative one (frequencies in cm$^{-1}$).

| compound       | $E_{\text{gas}}$  | $G_{\text{gas}}$  | $E_{\text{solvent}}$ | $G_{\text{solvent}}$ | no. of negative frequencies | frequency |
|----------------|-------------------|-------------------|----------------------|----------------------|-----------------------------|-----------|
| Intermediate: 6 | -1513.421799      | -1513.047547      | -1514.285123         | -1513.910871         | 0                           | -         |
| Intermediate: 7 | -1626.701474      | -1626.32109       | -1627.663349         | -1627.282965         | 0                           | -         |
| TS: 7-9        | -1811.232596      | -1810.844834      | -1812.351195         | -1811.963433         | 1                           | -57.2     |
| Intermediate: 9 | -1811.262887      | -1810.870507      | -1812.388972         | -1811.996592         | 0                           | -         |
| TS: 9-10+H$_2$O| -1887.6354        | -1887.227548      | -1888.814527         | -1888.406675         | 1                           | -527.8    |
| TS: 9-10       | -1811.218509      | -1810.836541      | -1812.330741         | -1811.948772         | 1                           | -1362.4   |
| Intermediate: 10| -1701.886699      | -1701.502349      | -1702.921031         | -1702.53668          | 0                           | -         |
| Intermediate: 11equatorial| -1701.896732 | -1701.508515      | -1702.925032         | -1702.536814         | 0                           | -         |
| TS: 11equatorial-6 | -1701.846781 | -1701.466419      | -1702.875116         | -1702.494754         | 1                           | -938.8    |
| Intermediate: 12| -1815.168005      | -1814.773629      | -1816.29507          | -1815.900694         | 0                           | -         |
| TS: 12-7       | -1815.096683      | -1814.710545      | -1816.217972         | -1815.831834         | 1                           | -1308.9   |
| TS: 7-13       | -1626.653881      | -1626.274464      | -1627.620701         | -1627.241284         | 1                           | -78.9     |
| Intermediate: 13| -1626.665382      | -1626.286042      | -1627.626247         | -1627.246908         | 0                           | -         |
| TS: 13-14      | -1626.655571      | -1626.279198      | -1627.607237         | -1627.230865         | 1                           | -733.2    |
| Intermediate: 14| -1626.664132      | -1626.285521      | -1627.621956         | -1627.243346         | 0                           | -         |
| TS: 14-8       | -1626.650651      | -1626.273048      | -1627.605496         | -1627.227892         | 1                           | -463.7    |
| Intermediate: 8 | -1626.709541      | -1626.327749      | -1627.671928         | -1627.290136         | 0                           | -         |
Table S23. $E_{\text{gas}}$ and $G_{\text{gas}}$ at BP86-D3BJ/SVP~sdd level of theory, $E_{\text{solv}}$ at M06-L/cc-pVTZ~sdd level of theory and $G_{\text{solv}}$ computed as $G_{\text{gas}} = E_{\text{gas}} + E_{\text{solv}}$ all of them in Hartree for the compounds involved in the main steps of catalyzed reduction of N2O and the isomerization process of the catalyst starting from system p-OMe. Number of negative frequencies found for each optimized structure at BP86-D3BJ/SVP~sdd level of theory, and the corresponding frequency in the cases when there is a negative one (frequencies in cm$^{-1}$).

| compound   | $E_{\text{gas}}$  | $G_{\text{gas}}$  | $E_{\text{solv}}$ | $G_{\text{solv}}$ | no. of negative frequencies | frequency |
|------------|-------------------|-------------------|-------------------|-------------------|-----------------------------|-----------|
| Intermediate: 6 | -1627.871935 | -1627.470794 | -1628.837039 | -1628.435898 | 0 | - |
| Intermediate: 7 | -1741.152155 | -1740.744712 | -1742.215520 | -1741.808078 | 0 | - |
| TS: 7-9 | -1925.683854 | -1925.269189 | -1926.903881 | -1926.489216 | 1 | -52.0 |
| Intermediate: 9 | -1925.714678 | -1925.295230 | -1926.941996 | -1926.522548 | 0 | - |
| TS: 9-10+H2O | -2002.086937 | -2001.651973 | -2003.367118 | -2002.932154 | 1 | -544.8 |
| TS: 9-10 | -1925.673560 | -1925.262351 | -1926.888406 | -1926.477197 | 1 | -1435.5 |
| Intermediate: 10 | -1816.337991 | -1815.926184 | -1817.473522 | -1817.06115 | 0 | - |
| Intermediate: 11equatorial | -1816.347931 | -1815.932622 | -1817.477681 | -1817.062373 | 0 | - |
| TS: 11equatorial+6 | -1816.298482 | -1815.890874 | -1817.427927 | -1817.02319 | 1 | -944.0 |
| Intermediate: 12 | -1929.619435 | -1929.197996 | -1930.847614 | -1930.426175 | 0 | - |
| TS: 12-7 | -1929.547924 | -1929.134630 | -1930.770731 | -1930.357437 | 1 | -1304.6 |
| TS: 7-13 | -1741.104758 | -1740.698014 | -1742.172513 | -1741.765770 | 1 | -72.7 |
| Intermediate: 13 | -1741.119529 | -1740.712936 | -1742.180169 | -1741.773575 | 0 | - |
| TS: 13-14 | -1741.110222 | -1740.706718 | -1742.162504 | -1741.759000 | 1 | -800.2 |
| Intermediate: 14 | -1741.118365 | -1740.712413 | -1742.176261 | -1741.770309 | 0 | - |
| TS: 14-8 | -1741.104839 | -1740.699780 | -1742.159893 | -1741.754835 | 1 | -465.2 |
| Intermediate: 8 | -1741.162936 | -1740.753540 | -1742.225589 | -1741.816193 | 0 | - |

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Table S24. $E_{\text{gas}}$ and $G_{\text{gas}}$ at BP86-D3BJ/SVP~sdd level of theory, $E_{\text{solvent}}$ at M06-L/cc-pVTZ~sdd level of theory and $G_{\text{solvent}}$ computed as $G_{\text{gas}} - E_{\text{gas}} + E_{\text{solvent}}$ all of them in Hartree for the compounds involved in the main steps of catalyzed reduction of N$_2$O starting from system 2. Number of negative frequencies found for each optimized structure at BP86-D3BJ/SVP~sdd level of theory, and the corresponding frequency in the cases when there is a negative one (frequencies in cm$^{-1}$).

| compound          | $E_{\text{gas}}$   | $G_{\text{gas}}$   | $E_{\text{solvent}}$ | $G_{\text{solvent}}$ | no. of negative frequencies | frequency |
|-------------------|-------------------|-------------------|----------------------|----------------------|-----------------------------|-----------|
| Intermediate: 6   | -1403.784557      | -1403.351233      | -1404.552751         | -1404.119427         | 0                           | -         |
| Intermediate: 7   | -1517.063654      | -1516.625480      | -1517.935305         | -1517.497131         | 0                           | -         |
| TS: 7-9           | -1701.603882      | -1701.154141      | -1702.624409         | -1702.174668         | 1                           | -35.8     |
| Intermediate: 9   | -1701.630552      | -1701.180117      | -1702.659091         | -1702.208656         | 0                           | -         |
| TS: 9-10+H$_2$O   | -1778.003634      | -1777.535771      | -1779.088305         | -1778.620441         | 1                           | -503.5    |
| TS: 9-10          | -1701.590277      | -1701.148791      | -1702.610517         | -1702.169032         | 1                           | -1261.7   |
| Intermediate: 10  | -1592.257936      | -1591.814440      | -1593.198157         | -1592.754661         | 0                           | -         |
| Intermediate: 11equatorial | -1592.262700 | -1591.817358      | -1593.194595         | -1592.749254         | 0                           | -         |
| Intermediate: 12  | -1705.525251      | -1705.073553      | -1706.560331         | -1706.108634         | 0                           | -         |
| TS: 12-7          | -1705.462772      | -1705.018871      | -1706.486447         | -1706.042546         | 1                           | -1223.0   |

Table S25. $E_{\text{gas}}$ and $G_{\text{gas}}$ at BP86-D3BJ/SVP~sdd level of theory, $E_{\text{solvent}}$ at M06-L/cc-pVTZ~sdd level of theory and $G_{\text{solvent}}$ computed as $G_{\text{gas}} - E_{\text{gas}} + E_{\text{solvent}}$ all of them in Hartree for the compounds involved in the main steps of catalyzed reduction of N$_2$O starting from system 3. Number of negative frequencies found for each optimized structure at BP86-D3BJ/SVP~sdd level of theory, and the corresponding frequency in the cases when there is a negative one (frequencies in cm$^{-1}$).

| compound          | $E_{\text{gas}}$   | $G_{\text{gas}}$   | $E_{\text{solvent}}$ | $G_{\text{solvent}}$ | no. of negative frequencies | frequency |
|-------------------|-------------------|-------------------|----------------------|----------------------|-----------------------------|-----------|
| Intermediate: 6   | -1415.003945      | -1414.667540      | -1415.781756         | -1415.445350         | 0                           | -         |
| Intermediate: 7   | -1528.282991      | -1527.940455      | -1529.159148         | -1528.816611         | 0                           | -         |
| TS: 7-9           | -1712.813426      | -1712.463701      | -1713.845953         | -1713.496228         | 1                           | -66.9     |
| Intermediate: 9   | -1712.843479      | -1712.489384      | -1713.883491         | -1713.529396         | 0                           | -         |
| TS: 9-10+H$_2$O   | -1789.216534      | -1788.846839      | -1790.309389         | -1789.939694         | 1                           | -510.7    |
| TS: 9-10          | -1712.799334      | -1712.455207      | -1713.825487         | -1713.481360         | 1                           | -1347.3   |
| Intermediate: 10  | -1603.466639      | -1603.120397      | -1604.415700         | -1604.069458         | 0                           | -         |
| Intermediate: 11equatorial | -1603.478135       | -1603.128088     | -1604.420482         | -1604.070436         | 0                           | -         |
| TS: 11equatorial+6 | -1603.423323       | -1603.080558     | -1604.365792         | -1604.023026         | 1                           | -862.6    |
| Intermediate: 12  | -1716.743068      | -1716.387315      | -1717.784553         | -1717.428800         | 0                           | -         |
| TS: 12-7          | -1716.677052      | -1716.329786      | -1717.712154         | -1717.364888         | 1                           | -1315.6   |
Table S26. \(E_{\text{gas}}\) and \(G_{\text{gas}}\) at BP86-D3BJ/SVP~sdd level of theory, \(E_{\text{solvent}}\) at M06-L/cc-pVTZ~sdd level of theory and \(G_{\text{solvent}}\) computed as \(G_{\text{gas}} - E_{\text{gas}} + E_{\text{solvent}}\) all of them in Hartree for the compounds involved in the main steps of catalyzed reduction of Na\(_2\)O starting from system 15. Number of negative frequencies found for each optimized structure at BP86-D3BJ/SVP~sdd level of theory, and the corresponding frequency in the cases when there is a negative one (frequencies in cm\(^{-1}\)).

| compound | \(E_{\text{gas}}\) | \(G_{\text{gas}}\) | \(E_{\text{solvent}}\) | \(G_{\text{solvent}}\) | no. of negative frequencies | frequency |
|----------|---------------------|---------------------|------------------------|------------------------|-----------------------------|-----------|
| Intermediate: 6 | -1847.540434 | -1847.016684 | -1848.452888 | -1847.929138 | 0 | - |
| Intermediate: 7 | -1960.821592 | -1960.288940 | -1961.835201 | -1961.302549 | 0 | - |
| TS: 7-9 | -2145.333173 | -2144.791756 | -2146.505512 | -2145.964095 | 1 | -113.1 |
| Intermediate: 9 | -2145.356679 | -2144.814381 | -2146.533037 | -2145.990739 | 0 | - |
| TS: 9-10\(+\)H\(_2\)O | -2221.738201 | -2221.176597 | -2222.971077 | -2222.409474 | 1 | -560.8 |
| TS: 9-10 | -2145.325235 | -2144.786904 | -2146.492076 | -2145.953745 | 1 | -1287.9 |
| Intermediate: 10 | -2035.999941 | -2035.462757 | -2037.085699 | -2036.548515 | 0 | - |
| Intermediate: 11\(_{\text{equatorial}}\) | -2036.017350 | -2035.478420 | -2037.093367 | -2036.554437 | 0 | - |
| TS: 11\(_{\text{equatorial}}\)-6 | -2035.959167 | -2035.426508 | -2037.035944 | -2036.503284 | 1 | -201.3 |
| Intermediate: 12 | -2149.275691 | -2148.728357 | -2150.449849 | -2149.902515 | 0 | - |
| TS: 12-7 | -2149.199580 | -2148.659345 | -2150.371624 | -2149.831389 | 1 | -24.5 |

Table S27. \(E_{\text{gas}}\) and \(G_{\text{gas}}\) at BP86-D3BJ/SVP~sdd level of theory, \(E_{\text{solvent}}\) at M06-L/cc-pVTZ~sdd level of theory and \(G_{\text{solvent}}\) computed as \(G_{\text{gas}} - E_{\text{gas}} + E_{\text{solvent}}\) all of them in Hartree for the compounds involved in the main steps of catalyzed reduction of Na\(_2\)O starting from system 16. Number of negative frequencies found for each optimized structure at BP86-D3BJ/SVP~sdd level of theory, and the corresponding frequency in the cases when there is a negative one (frequencies in cm\(^{-1}\)).

| compound | \(E_{\text{gas}}\) | \(G_{\text{gas}}\) | \(E_{\text{solvent}}\) | \(G_{\text{solvent}}\) | no. of negative frequencies | frequency |
|----------|---------------------|---------------------|------------------------|------------------------|-----------------------------|-----------|
| Intermediate: 6 | -1475.173595 | -1474.813777 | -1475.989341 | -1475.629524 | 0 | - |
| Intermediate: 7 | -1588.454093 | -1588.087722 | -1589.367202 | -1589.000831 | 0 | - |
| TS: 7-9 | -1772.984568 | -1772.610371 | -1774.054258 | -1773.680061 | 1 | -78.2 |
| Intermediate: 9 | -1773.014577 | -1772.636485 | -1774.092350 | -1773.714259 | 0 | - |
| TS: 9-10\(+\)H\(_2\)O | -1849.387435 | -1848.993646 | -1850.518523 | -1850.124734 | 1 | -470.3 |
| TS: 9-10 | -1772.973779 | -1772.603530 | -1774.038763 | -1773.668515 | 1 | -1381.6 |
| Intermediate: 10 | -1663.637731 | -1663.267730 | -1664.623822 | -1664.253821 | 0 | - |
| Intermediate: 11\(_{\text{equatorial}}\) | -1663.647816 | -1663.273797 | -1664.628571 | -1664.254551 | 0 | - |
| TS: 11\(_{\text{equatorial}}\)-6 | -1663.593356 | -1663.226623 | -1664.574826 | -1664.208093 | 1 | -854.3 |
| Intermediate: 12 | -1776.913386 | -1776.533618 | -1777.993615 | -1777.613847 | 0 | - |
| TS: 12-7 | -1776.847704 | -1776.476649 | -1777.920620 | -1777.549565 | 1 | -1301.7 |
Table S28. $E_{\text{gas}}$ and $G_{\text{gas}}$ at BP86-D3BJ/SVP~sdd level of theory, $E_{\text{solv}}$ at M06-L/cc-pVTZ~sdd level of theory and $G_{\text{solv}}$ computed as $G_{\text{gas}} - E_{\text{gas}} + E_{\text{solv}}$ all of them in Hartree for the intermediates used (5, 6, 7, 8, 10 and 10') in the conformational studies of the complex in section I of the SI. Number of negative frequencies found for each optimized structure at BP86-D3BJ/SVP~sdd level of theory, and the corresponding frequency in the cases when there is a negative one (frequencies in cm$^{-1}$).

| compound     | $E_{\text{gas}}$ | $G_{\text{gas}}$ | $E_{\text{solv}}$ | $G_{\text{solv}}$ | no. of negative frequencies | frequency |
|--------------|------------------|------------------|------------------|------------------|-----------------------------|-----------|
| Intermediate: 5 (E1) | -1859.748214     | -1859.387902     | -1860.633252     | -1860.272940     | 0                           | -         |
| Intermediate: 5 (E2) | -1859.748988     | -1859.387976     | -1860.632596     | -1860.271584     | 0                           | -         |
| Intermediate: 6 (E1) | -1398.974955     | -1398.627428     | -1399.736656     | -1399.389129     | 0                           | -         |
| Intermediate: 6 (E2) | -1398.974938     | -1398.627351     | -1399.736495     | -1399.389070     | 0                           | -         |
| Intermediate: 7 (E1) | -1512.255086     | -1511.900129     | -1513.115818     | -1512.760861     | 0                           | -         |
| Intermediate: 7 (E2) | -1512.254745     | -1511.900935     | -1513.114768     | -1512.760958     | 0                           | -         |
| Intermediate: 8 (E1) | -1512.257192     | -1511.902784     | -1513.119076     | -1512.764668     | 0                           | -         |
| Intermediate: 8 (E2) | -1512.260932     | -1511.905465     | -1513.121869     | -1512.766402     | 0                           | -         |
| Intermediate: 10 (E1) | -1587.441651     | -1587.082488     | -1588.375451     | -1588.016289     | 0                           | -         |
| Intermediate: 10 (E2) | -1587.439741     | -1587.081435     | -1588.37203       | -1588.013724     | 0                           | -         |
| Intermediate: 10' (E1) | -1587.445794     | -1587.086755     | -1588.378268     | -1588.019229     | 0                           | -         |
| Intermediate: 10' (E2) | -1587.450862     | -1587.090191     | -1588.382384     | -1588.021713     | 0                           | -         |

Table S29. $E_{\text{gas}}$ and $G_{\text{gas}}$ at BP86-D3BJ/SVP~sdd level of theory, $E_{\text{solv}}$ at M06-L/cc-pVTZ~sdd level of theory and $G_{\text{solv}}$ computed as $G_{\text{gas}} - E_{\text{gas}} + E_{\text{solv}}$ all of them in Hartree for the reactants, products, salts and solvent molecules involved in the process. Number of negative frequencies found for each optimized structure at BP86-D3BJ/SVP~sdd level of theory, and the corresponding frequency in the cases when there is a negative one (frequencies in cm$^{-1}$).

| compound     | $E_{\text{gas}}$ | $G_{\text{gas}}$ | $E_{\text{solv}}$ | $G_{\text{solv}}$ | no. of negative frequencies | frequency |
|--------------|------------------|------------------|------------------|------------------|-----------------------------|-----------|
| CO$_2$       | -188.454666      | -188.468517      | -188.640260      | -188.654113      | 0                           | -         |
| CO           | -113.224433      | -113.242104      | -113.331271      | -113.348942      | 0                           | -         |
| H$_2$O       | -7.63596770      | -7.63599870      | -7.6461180       | -7.646428        | 0                           | -         |
| HCl          | -460.699986      | -460.714531      | -460.822786      | -460.837330      | 0                           | -         |
| N$_2$O       | -184.547594      | -184.561749      | -184.716390      | -184.730545      | 0                           | -         |
| N$_2$        | -109.443447      | -109.459801      | -109.544207      | -109.560561      | 0                           | -         |
| OH$_2$       | -75.6627480      | -75.6745290      | -75.8701370      | -75.8819170      | 0                           | -         |
| pyridine     | -248.117731      | -248.063408      | -248.329791      | -248.275468      | 0                           | -         |
| tBuOH        | -233.510452      | -233.414099      | -233.722211      | -233.625858      | 0                           | -         |
| THF          | -232.287182      | -232.207883      | -232.492759      | -232.413460      | 0                           | -         |