Halide Abstraction Competes with Oxidative Addition in the Reactions of Aryl Halides with [Ni(PMe₉,₆Ph₁₋₇₈)₄]

Ignacio Funes-Ardoiz,¹ David J. Nelson,² and Feliu Maseras²[a, c]

c chem_201702331_sm_misinformation.pdf
Contents

COMPUTATIONAL DETAILS ................................................................................................................... S2
BENCHMARK OF FUNCTIONALS ............................................................................................................. S3
PHOSPHINE DISSOCIATION POTENTIAL ENERGY RELAXED SCAN FROM Ni(PMe₃)₄ ................................ S4
ALTERNATIVE MECHANISMS ................................................................................................................. S5
   (A) Outer-sphere electron transfer from [Ni(PMe₃)₄] to ArX ......................................................... S5
   (B) Inner-sphere electron transfer from [Ni(PMe₃)₃] to ArX .......................................................... S6
   (C) Oxidative Addition Pathway from [Ni(PMe₃)₂] ...................................................................... S7
MICROKINETIC MODEL ....................................................................................................................... S8
   (A) Reaction between [Ni(PMe₃)₄] to PhI in toluene ................................................................. S8
   (B) Reaction between [Ni(PMe₃)₄] to PhBr in THF ...................................................................... S10
COORDINATES AND ENERGIES FOR MINIMA AND TRANSITION STATES ........................................ S12
REFERENCES ........................................................................................................................................ S74
COMPUTATIONAL DETAILS

Calculations were performed using Gaussian09 (Rev. D01)\(^1\) at the B3LYP level of theory\(^2,3,4\) with Grimme’s D3 dispersion correction.\(^5\) This correction renders B3LYP appropriate for studying organometallic chemistry.\(^6\) For optimizations and frequency calculations, the 6-31G(d) basis set\(^7,8,9\) was used for H, C, N, O, P, and Cl atoms, and the LANL2DZdp basis set/ECP\(^10\) used for Br and I, and LANL2LTZ(f)\(^11,12,13\) for Ni. The potential energies were refined using the same basis set for Br, I and Ni, and increasing the basis set for H, C, N, O, P and Cl, using 6-311+G(d,p).\(^14\) The solvent is experimentally significant, so all calculations were carried out in solvent (using the SMD method for implicit solvation), unless otherwise stated. Unless otherwise stated all calculations were carried out on THF. Toluene and n-hexane were used in specific cases (see the manuscript text for discussion of solvent effects).

The nature of each stationary point was verified using frequency analyses, and IRC calculations were used to verify that transition states linked the relevant minima. Free energy corrections were computed at 298 K and 1 atm. All energies quoted are Gibbs free energies in solution, in kcal mol\(^{-1}\). Enthalpies are given in the schemes, in brackets, in kcal mol\(^{-1}\).

In the case of open-shell singlet structures, where \(S^2\) is not zero, we corrected the energy by applying the Yamaguchi’s equation,\(^15,16,17,18\) in the form:\(^19\)

\[
E_{\text{singlet}} = \frac{2E_{\text{OSS}} - E_{\text{triplet}} \langle S^2 \rangle_{\text{OSS}}}{2 - \langle S^2 \rangle_{\text{OSS}}}
\]

where \(E_{\text{OSS}}\) is the energy of open-shell singlet calculation, \(E_{\text{triplet}}\) is the energy of the triplet state at the open-shell singlet geometry and \(\langle S^2 \rangle_{\text{OSS}}\) is the \(S^2\) value of the open-shell singlet calculation.

PEt\(_3\) has a number of possible conformations, so the ligands were truncated to PMe\(_3\), which has similar properties (Tolman electronic parameter = 2064.1 cm\(^{-1}\) for PMe\(_3\), 2061.7 cm\(^{-1}\) for PEt\(_3\); cone angle = 118° for PMe\(_3\), 132° for PEt\(_3\)).\(^20\) Tolman determined that both ligands undergo fast ligand exchange at a Ni\(^0\) centre in benzene or toluene solution, although PEt\(_3\) has a slightly greater propensity for dissociation.\(^21\)
BENCHMARK OF FUNCTIONALS

Table S1. Comparison of four different functionals on the key step of Ni(0) oxidation with PhI. Free energies in kcal/mol.

| Method*       | Ni(PMe₃)₄ | Ni(PMe₃)₃ | TSadox | TSabst |
|---------------|----------|----------|--------|--------|
| B3LYP-D3      | 0.0      | 7.8      | 16.2   | 10.0   |
| TPSSh-D3      | 0.0      | 13.4     | 16.2   | 14.8   |
| ωB97X-D       | 0.0      | 10.1     | 21.5   | 11.4   |
| PBE1PBE-D3    | 0.0      | 12.2     | 19.4   | 11.4   |

* Single point energies on B3LYP-D3 geometries using the LANL2DZdp basis set/ECP for I, LANL2LTZ(f) for Ni and 6-311+G(d,p) for the rest of atoms, with free energy corrections from B3LYP-D3 calculations.

The evaluation of different functionals in the key step with PhI and PMe₃ as ligand shows minor differences among all of them. The open-shell single electronic structure for the halogen abstraction transition state was found to be the most stable electronic structure in all the cases (using the wavefunction stability evaluation of g09). We selected B3LYP-D3 as the functional because the dissociation energy of the phosphine was the most consistent with experimental data and the evaluation of the product ratio provides a full agreement with the experimental observations.
PHOSPHINE DISSOCIATION POTENTIAL ENERGY RELAXED SCAN FROM Ni(PMe₃)₄

**Figure S1.** Potential energy relaxed scan for the phosphine dissociation in Ni(PMe₃)₄ complex.

According to the scan, there is no activation barrier for the phosphine dissociation in Ni(PMe₃)₄ complex.
ALTERNATIVE MECHANISMS

(A) Outer-sphere electron transfer from [Ni(PMe3)4] to ArX

Electron transfer from [Ni(PMe3)4] to ArX could in theory occur via an outer sphere mechanism, to form [Ni(PMe3)4]+ and the radical anion of ArX; the latter would then spontaneously dissociate X⁻ to form an aryl radical. This was explored using Marcus-Hush theory, where the barrier to electron transfer can be estimated using equations S1-S3. This assumes that the major energetic barrier is the rearrangement of the products immediately following the electron transfer event. This has been successfully used to describe the reactions of aryl halides with ‘super electron donors’.22

\[ \Delta G^\ddagger \approx \left( \frac{\lambda_i}{4} \cdot \left( 1 + \frac{\Delta G}{\lambda_i} \right) \right)^2 \]  (S1)

\[ \lambda_i = \frac{1}{2} \cdot (\lambda_i^{NiP4^+} + \lambda_i^{ArX}) \]  (S2)

\[ \lambda_i^{(species)} = (E_N(R_C) - E_N(R_0)) + (E_C(R_N) - E_C(R_C)) \]  (S3)

- \( \lambda_i \) is the internal reorganisation energy; \( \lambda_i^{NiP4^+} \) is the internal reorganisation energy of [Ni(PMe3)4]+; and \( \lambda_i^{ArX} \) is the internal reorganisation energy of ArX radical anion
- \( \Delta G \) is the free energy change of the reaction
- \( E_N(R_N) \) and \( E_C(R_C) \) are the energies of the neutral and charged species in their respective geometries; \( E_C(R_N) \) and \( E_N(R_C) \) are the single point energies of the neutral and charged geometries as charged and neutral species, respectively.

While the initial result with [Ni(PMe3)4] and PhI in THF was sensible (\( \Delta G^\ddagger = 15.6 \) kcal mol⁻¹), barriers for PhBr and in toluene and hexane were far too high to account for the NiI products observed, albeit in reduced quantities, in these reactions (see Table S2). The major contributor to these energies was the very large value of \( \Delta G \) for this process in non-polar solvents.

| Solvent | Aryl Halide | \( \Delta G \) (kcal/mol) | \( \lambda_i \) (kcal/mol) | \( \Delta G^\ddagger \) (kcal/mol) |
|---------|-------------|--------------------------|--------------------------|--------------------------|
| THF     | PhI         | 1.2                      | 59.9                     | 15.6                     |
| THF     | PhBr        | 11.8                     | 63.6                     | 22.3                     |
| Toluene | PhI         | 29.8                     | 56.8                     | 33.0                     |
| Hexane  | PhI         | 38.3                     | 61.6                     | 40.5                     |

Table S2. Calculated energies for outer-sphere electron transfer from [Ni(PMe3)4] to ArX.
(B) Inner-sphere electron transfer from $[\text{Ni}(\text{PMe}_3)_3]$ to ArX

Inner-sphere electron transfer from $[\text{Ni}(\text{PMe}_3)_3]$ to ArX could occur via complex $[\text{Ni}(\text{PMe}_3)_3(\text{XAr})]$, with a concomitant change in multiplicity from singlet to triplet. This cannot be described by a simple transition state, and instead requires the geometry at which the singlet and triplet have the same energy to be located, termed the minimum energy crossing point (MECP).

The software tool published by Harvey was used, and the MECP could be located for a number of examples. However, the energies of MECPs for aryl bromides were too high to compete with oxidative addition to $[\text{Ni}(\text{PMe}_3)_2]$ (see Table S3). Energies are quoted as a range, because these structures typically have imaginary frequencies when either or both of the singlet and triplet frequency calculations are performed; there is a small discrepancy in their free energies, because the MECP calculation seeks the geometry at which the potential energy $E$ is the same for both singlet and triplet.

Table S3. Calculated minimum energy crossing points for inner-sphere electron transfer from $[\text{Ni}(\text{PMe}_3)_3]$ to ArX.

| Solvent | Aryl Halide | MECP $G_{\text{rel}}$ (kcal/mol) |
|---------|-------------|---------------------------------|
| THF     | PhI         | 15.0 – 15.2                      |
| THF     | PhBr        | 22.5 – 22.6                      |
| Toluene | PhI         | 16.5 – 16.8                      |
| Toluene | PhBr        | 23.9 – 24.6                      |
| Hexane  | PhI         | 16.7 – 17.1                      |
| Hexane  | PhBr        | 24.7 – 26.0                      |
(C) Oxidative Addition Pathway from [Ni(PMe₃)₂]

Figure S2. Oxidative addition of PhI (purple), PhBr (brown), and PhCl (green) to [Ni(PMe₃)₂]. Energies are in kcal mol⁻¹.

The dissociation energy of the second phosphine is always higher than the oxidative addition transition state from [Ni(PMe₃)₃], so this mechanism is unfavourable in the three cases. We could not find the barrier for PhI oxidative addition, due to the high reactivity of this species with Ni(P)₂, which forms the Ni(II) product 9 directly.
MICROKINETIC MODEL

(A)  Reaction between [Ni(PMe$_3$)$_4$] to PhI in toluene

We used the COPASI program package to run the reactions used in the microkinetic model, with the following equations:

\[
\begin{align*}
\text{(1)} & \quad [\text{Ni}^0(\text{PMe}_3)_4] + \text{PhI} \quad \xrightarrow{k_1} \quad [\text{Ni}^{II}(\text{PMe}_3)_3\text{Ph}]^+\text{I}^- + \text{PMe}_3 \\
\text{(2)} & \quad [\text{Ni}^0(\text{PMe}_3)_4] + \text{PhI} \quad \xrightarrow{k_2} \quad [\text{Ni}^I(\text{PMe}_3)_3\text{I}] + \text{Ph}^- + \text{PMe}_3 \\
\text{(3)} & \quad [\text{Ni}^I(\text{PMe}_3)_3\text{I}] \quad \xrightarrow{k_3} \quad [\text{Ni}^I(\text{PMe}_3)_2\text{I}] + \text{PMe}_3 \\
\text{(4)} & \quad [\text{Ni}^I(\text{PMe}_3)_2\text{I}] + \text{Ph}^- \quad \xrightarrow{k_4} \quad [\text{Ni}^{III}(\text{PMe}_3)_2\text{I}(\text{Ph})] \\
\text{(5)} & \quad \text{Ph}^- + \text{Ph-CH}_3 \quad \xrightarrow{k_5} \quad \text{PhH} + \text{PhCH}_2^-. 
\end{align*}
\]

The activation energies and the associated kinetic constants are in Table 4.

Table S4. Calculated activation free energies and kinetic constants of kinetic model of the reaction between [Ni(PMe$_3$)$_4$] and PhI in toluene.

| Reaction | $\Delta G^\ddagger$ (kcal/mol) | Kinetic constant (M$^{-1}$·s) |
|----------|---------------------|-----------------------|
| 1        | 16.7                | 3.514                  |
| 2        | 9.4                 | 7.932e+5               |
| 3        | 10.0                | 2.784e+5               |
| 3(k$_{3}$)| 3.7                | 1.18e+10               |
| 4$^1$    | 3.7                 | 1.18e+10               |
| 5        | 10.6                | 1.046e+5               |

The reactions 3 and 4 are barrierless. For this reason, we considered them as diffusion-controlled, with the rate constant given by the equation $k_{\text{diff}} = 8k_bT/(3\eta)\cdot1000\cdotN_a$, in M$^{-1}$·s$^{-1}$. The viscosity of toluene at 298 K is 0.560 mPa·s. The diffusion rate constant would correspond to an associated activation free energy of 3.7 kcal/mol, calculated from Eyring equation.

The conditions used to analyze the time course of the reaction were 0.01s in 20 steps, obtaining the results in Table S5. The initial concentrations were taken from the experiments (0.005 M for species
A and B and solvent concentration calculated from the density at 25°C (12.2 M for THF). The numbers represent the concentration of labelled species in mol per litre (Table S5).

Table S5. Concentrations of different species in solution during reaction time in mol/L for the reaction between [Ni(PMe₃)₄] and PhI in toluene.

| Time (s) | A          | B          | C          | D          | E          | F          | G          | H          | I          | J          | K          |
|----------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| 0        | 0.005      | 0.005      | 0          | 0          | 0          | 0          | 0          | 0          | 9.39       | 0.000      | 0          |
| 0.001    | 1.01E-03   | 1.01E-03   | 1.77E-08   | 4.67E-03   | 3.32E-03   | 6.83E-07   | 1.68E-05   | 6.57E-04   | 9.39E+00   | 3.34E-03   | 3.34E-03   |
| 0.005    | 7.20E-04   | 7.20E-04   | 1.90E-08   | 5.00E-03   | 3.56E-03   | 3.49E-07   | 1.68E-05   | 7.05E-04   | 9.39E+00   | 3.58E-03   | 3.58E-03   |
| 0.002    | 5.60E-04   | 5.60E-04   | 1.97E-08   | 5.19E-03   | 3.69E-03   | 2.11E-07   | 1.68E-05   | 7.32E-04   | 9.39E+00   | 3.71E-03   | 3.71E-03   |
| 0.0025   | 4.58E-04   | 4.58E-04   | 2.01E-08   | 5.31E-03   | 3.78E-03   | 1.41E-07   | 1.68E-05   | 7.49E-04   | 9.39E+00   | 3.79E-03   | 3.79E-03   |
| 0.003    | 3.88E-04   | 3.88E-04   | 2.04E-08   | 5.39E-03   | 3.83E-03   | 1.01E-07   | 1.68E-05   | 7.61E-04   | 9.39E+00   | 3.85E-03   | 3.85E-03   |
| 0.0035   | 3.36E-04   | 3.36E-04   | 2.07E-08   | 5.45E-03   | 3.88E-03   | 7.60E-08   | 1.68E-05   | 7.69E-04   | 9.39E+00   | 3.89E-03   | 3.89E-03   |
| 0.004    | 2.96E-04   | 2.96E-04   | 2.08E-08   | 5.50E-03   | 3.91E-03   | 5.91E-08   | 1.68E-05   | 7.76E-04   | 9.39E+00   | 3.93E-03   | 3.93E-03   |
| 0.0045   | 2.65E-04   | 2.65E-04   | 2.10E-08   | 5.53E-03   | 3.94E-03   | 4.74E-08   | 1.68E-05   | 7.81E-04   | 9.39E+00   | 3.95E-03   | 3.95E-03   |
| 0.005    | 2.40E-04   | 2.40E-04   | 2.11E-08   | 5.56E-03   | 3.96E-03   | 3.88E-08   | 1.68E-05   | 7.86E-04   | 9.39E+00   | 3.97E-03   | 3.97E-03   |
| 0.0055   | 2.19E-04   | 2.19E-04   | 2.12E-08   | 5.59E-03   | 3.97E-03   | 3.23E-08   | 1.68E-05   | 7.89E-04   | 9.39E+00   | 3.99E-03   | 3.99E-03   |
| 0.006    | 2.03E-04   | 2.03E-04   | 2.13E-08   | 5.61E-03   | 3.99E-03   | 2.74E-08   | 1.68E-05   | 7.92E-04   | 9.39E+00   | 4.01E-03   | 4.01E-03   |
| 0.0065   | 1.87E-04   | 1.87E-04   | 2.13E-08   | 5.62E-03   | 4.00E-03   | 2.35E-08   | 1.68E-05   | 7.95E-04   | 9.39E+00   | 4.02E-03   | 4.02E-03   |
| 0.007    | 1.74E-04   | 1.74E-04   | 2.14E-08   | 5.64E-03   | 4.01E-03   | 2.03E-08   | 1.68E-05   | 7.97E-04   | 9.39E+00   | 4.03E-03   | 4.03E-03   |
| 0.0075   | 1.63E-04   | 1.63E-04   | 2.14E-08   | 5.65E-03   | 4.02E-03   | 1.78E-08   | 1.68E-05   | 7.99E-04   | 9.39E+00   | 4.04E-03   | 4.04E-03   |
| 0.008    | 1.53E-04   | 1.53E-04   | 2.15E-08   | 5.66E-03   | 4.03E-03   | 1.57E-08   | 1.68E-05   | 8.00E-04   | 9.39E+00   | 4.05E-03   | 4.05E-03   |
| 0.0085   | 1.44E-04   | 1.44E-04   | 2.15E-08   | 5.67E-03   | 4.04E-03   | 1.40E-08   | 1.68E-05   | 8.02E-04   | 9.39E+00   | 4.05E-03   | 4.05E-03   |
| 0.009    | 1.36E-04   | 1.36E-04   | 2.15E-08   | 5.68E-03   | 4.04E-03   | 1.25E-08   | 1.68E-05   | 8.03E-04   | 9.39E+00   | 4.06E-03   | 4.06E-03   |
| 0.0095   | 1.29E-04   | 1.29E-04   | 2.15E-08   | 5.69E-03   | 4.05E-03   | 1.11E-08   | 1.68E-05   | 8.04E-04   | 9.39E+00   | 4.07E-03   | 4.07E-03   |
| 0.01     | 1.23E-04   | 1.23E-04   | 2.16E-08   | 5.70E-03   | 4.05E-03   | 1.02E-08   | 1.68E-05   | 8.05E-04   | 9.39E+00   | 4.07E-03   | 4.07E-03   |

The ratio of Ni(I) vs Ni(II) (83:17 in this case) was obtained using the following formula:

\[
\frac{[Ni(I)]}{[Ni(II)]} = \frac{[PhH]}{[[Ni(II)(PMe_3)_3Ph]^+I^-] + [Ni(II)(PMe_3)_2(Ph)I]} 
\]
We ran the same microkinetic model for the reaction between Ni complex and PhBr in THF. The reactions were:

\[
\begin{align*}
[Ni^0(\text{PMe}_3)_4] + \text{PhBr} & \xrightarrow{k_1} [Ni^{\text{III}}(\text{PMe}_3)_3\text{Ph}]^+\text{Br}^- + \text{PMe}_3 & (1) \\
[Ni^0(\text{PMe}_3)_4] + \text{PhBr} & \xrightarrow{k_2} [Ni^{\text{III}}(\text{PMe}_3)_3\text{Br}] + \text{Ph}^- + \text{PMe}_3 & (2) \\
[Ni^{\text{III}}(\text{PMe}_3)_3\text{Br}] & \xrightarrow{k_3} [Ni^{\text{III}}(\text{PMe}_3)_2\text{Br}] + \text{PMe}_3 & (3) \\
[Ni^{\text{III}}(\text{PMe}_3)_2\text{Br}] + \text{Ph}^- & \xrightarrow{k_4} [Ni^{\text{III}}(\text{PMe}_3)_2\text{I}(\text{Ph})] & (4) \\
\text{Ph}^- + \text{Ph-CH}_3 & \xrightarrow{k_5} \text{PhH} + \text{PhCH}_2^- & (5)
\end{align*}
\]

The activation energies and the associated kinetic constants are in Table S6:

**Table S6.** Calculated activation free energies and kinetic constants of kinetic model of the reaction between [Ni(\text{PMe}_3)_4] and PhBr in THF.

| Reaction | $\Delta G^\ddagger$ (kcal/mol) | Kinetic constant (M$^{-1}$·s$^{-1}$) |
|----------|-------------------------------|-------------------------------------|
| 1        | 15.0                          | 62.015                              |
| 2        | 16.3                          | 6.904                               |
| 3        | 6.0                           | 2.471e+8                            |
| 3(k_3)   | 3.6                           | 1.45e+10                            |
| 4$^\ddagger$ | 3.6                       | 1.45e+10                            |
| 5        | 9.5                           | 6.700e+5                            |

The reactions 3 and 4 are also barrierless. We applied the same methodology that above, using the experimental value of 0.456 mPa·s for the viscosity of THF.$^{25}$ The associated activation free energy was calculated from Eyring equation and is 3.6 kcal/mol.
Table S7. Concentrations of different species in solution along reaction time in mol/L for the reaction between [Ni(PMe3)4] and PhBr in THF.

| Time (s) | A      | B      | C      | D      | E      | F      | G      | H      | I      | J      | K      |
|----------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 0        | 1.22E-03 | 1.22E-03 | 3.40E-03 | 4.10E-03 | 5.94E-05 | 8.72E-13 | 2.47E-04 | 7.23E-05 | 1.22E+01 | 3.06E-04 | 3.06E-04 |
| 9        | 4.85E-04 | 4.85E-04 | 4.06E-03 | 4.89E-03 | 7.95E-05 | 1.33E-13 | 2.77E-04 | 9.56E-05 | 1.22E+01 | 3.57E-04 | 3.57E-04 |
| 18       | 3.73E-04 | 3.73E-04 | 4.16E-03 | 5.01E-03 | 8.37E-05 | 7.83E-14 | 2.81E-04 | 9.33E-05 | 1.22E+01 | 3.64E-04 | 3.64E-04 |
| 27       | 3.03E-04 | 3.03E-04 | 4.23E-03 | 5.08E-03 | 8.47E-05 | 5.15E-14 | 2.84E-04 | 1.02E-04 | 1.22E+01 | 3.69E-04 | 3.69E-04 |
| 36       | 2.55E-04 | 2.55E-04 | 4.27E-03 | 5.13E-03 | 8.61E-05 | 3.64E-14 | 2.86E-04 | 1.03E-04 | 1.22E+01 | 3.72E-04 | 3.72E-04 |
| 45       | 2.20E-04 | 2.20E-04 | 4.30E-03 | 5.17E-03 | 8.72E-05 | 2.71E-14 | 2.87E-04 | 1.04E-04 | 1.22E+01 | 3.74E-04 | 3.74E-04 |
| 54       | 1.94E-04 | 1.94E-04 | 4.32E-03 | 5.20E-03 | 8.79E-05 | 2.10E-14 | 2.88E-04 | 1.05E-04 | 1.22E+01 | 3.76E-04 | 3.76E-04 |
| 63       | 1.73E-04 | 1.73E-04 | 4.34E-03 | 5.22E-03 | 8.85E-05 | 1.67E-14 | 2.89E-04 | 1.06E-04 | 1.22E+01 | 3.78E-04 | 3.78E-04 |
| 72       | 1.56E-04 | 1.56E-04 | 4.36E-03 | 5.24E-03 | 8.90E-05 | 1.36E-14 | 2.90E-04 | 1.07E-04 | 1.22E+01 | 3.79E-04 | 3.79E-04 |
| 81       | 1.42E-04 | 1.42E-04 | 4.37E-03 | 5.25E-03 | 8.94E-05 | 1.13E-14 | 2.91E-04 | 1.07E-04 | 1.22E+01 | 3.80E-04 | 3.80E-04 |
| 90       | 1.31E-04 | 1.31E-04 | 4.38E-03 | 5.27E-03 | 8.98E-05 | 9.53E-15 | 2.91E-04 | 1.07E-04 | 1.22E+01 | 3.80E-04 | 3.80E-04 |
| 99       | 1.21E-04 | 1.21E-04 | 4.39E-03 | 5.28E-03 | 9.01E-05 | 8.15E-15 | 2.91E-04 | 1.08E-04 | 1.22E+01 | 3.81E-04 | 3.81E-04 |
| 108      | 1.13E-04 | 1.13E-04 | 4.40E-03 | 5.29E-03 | 9.03E-05 | 7.05E-15 | 2.91E-04 | 1.08E-04 | 1.22E+01 | 3.81E-04 | 3.81E-04 |
| 117      | 1.05E-04 | 1.05E-04 | 4.40E-03 | 5.29E-03 | 9.05E-05 | 6.16E-15 | 2.91E-04 | 1.08E-04 | 1.22E+01 | 3.82E-04 | 3.82E-04 |
| 126      | 9.88E-05 | 9.88E-05 | 4.41E-03 | 5.30E-03 | 9.07E-05 | 5.43E-15 | 2.92E-04 | 1.09E-04 | 1.22E+01 | 3.82E-04 | 3.82E-04 |
| 135      | 9.31E-05 | 9.31E-05 | 4.42E-03 | 5.31E-03 | 9.09E-05 | 4.82E-15 | 2.92E-04 | 1.09E-04 | 1.22E+01 | 3.83E-04 | 3.83E-04 |
| 144      | 8.80E-05 | 8.80E-05 | 4.42E-03 | 5.31E-03 | 9.11E-05 | 4.30E-15 | 2.92E-04 | 1.09E-04 | 1.22E+01 | 3.83E-04 | 3.83E-04 |
| 153      | 8.34E-05 | 8.34E-05 | 4.42E-03 | 5.32E-03 | 9.12E-05 | 3.87E-15 | 2.92E-04 | 1.09E-04 | 1.22E+01 | 3.83E-04 | 3.83E-04 |
| 162      | 7.93E-05 | 7.93E-05 | 4.43E-03 | 5.32E-03 | 9.13E-05 | 3.50E-15 | 2.92E-04 | 1.09E-04 | 1.22E+01 | 3.84E-04 | 3.84E-04 |

The conditions that are used to analyze the time course of the reaction were 180 s in 20 steps, obtaining the Table S7. The initial concentrations were taken from the experiments (0.005 M for species A and B and solvent concentration calculated from the density at 25ºC (12.2 M for THF). The numbers represent the concentration of labelled species in mol per litre.

The ratio of Ni(I) vs Ni(II) (8:92 in this case) was obtained using the following formula:

\[
\frac{[Ni(I)]}{[Ni(II)]} = \frac{[PhH]}{[[Ni(II)(PMe_3)_3Ph]^+Br^-] + [Ni(II)(PMe_3)_2(Ph)Br]} \]
COORDINATES AND ENERGIES FOR MINIMA AND TRANSITION STATES

Energies are given in Hartrees and correspond to the potential energy with the large basis set (first line) and to the free energy correction (second line). The energies used to compute all the profiles were calculated by the sum of \( E + G_{\text{corr}} \). In the case of open-shell singlet structures, the values of the potential energy at triplet electronic structure and the \( S^2 \) of the open-shell singlet are also provided.

Coordinates are Cartesian coordinates in \( \text{Å} \).

**In Tetrahydrofuran**

|          | \( E \) | \( G_{\text{corr}} \) |
|----------|---------|-------------------|
| \( \text{Ni(PMe}_3\text{)}_4 \) |          |                   |
| Ni       | 2.97381100 | 7.49675000 11.85409900 |
| P        | 1.37271500 | 8.84467500 11.13266300 |
| P        | 2.20232100 | 6.27155600 13.51844500 |
| C        | 0.89366400 | 8.16982600 10.75440800 |
| C        | 1.64237000 | 9.81235900 9.56509700  |
| C        | 2.55471800 | 6.82320300 15.26175000 |
| C        | 0.36359500 | 6.01879000 13.68224400 |
| C        | 2.73487100 | 4.49313900 13.67924800 |
| C        | 0.06919600 | 10.85075300 11.84660400 |
| C        | 1.76215600 | 10.90192100 12.40329800 |
| H        | -0.99638400 | 8.94063300 10.36095200 |
| H        | -0.76101600 | 7.74569400 11.66173000 |
| Ni       | 1.69654200 | 9.12553800 8.71509500  |
| P        | 2.95943000 | 10.35007200 9.62310200 |
| P        | 2.17994800 | 7.84212700 15.40599100 |
| C        | 3.63677800 | 6.83117300 15.43347000 |
| C        | -0.12463500 | 6.98511600 13.85086800 |
| C        | 0.11165200 | 5.34883700 14.51507000 |
| H        | 2.35690800 | 3.92165300 12.82559900 |
| H        | 2.36069900 | 4.03111600 14.60259900 |
| P        | 4.57490600 | 8.84467500 12.57536000 |
| P        | 3.74530100 | 6.27155500 10.18975400 |
| C        | 5.05958000 | 10.25113000 11.45389700 |
| C        | 6.26790600 | 8.16982500 12.95379100 |
| C        | 4.30525000 | 9.81235900 14.14310200 |
| C        | 3.39290300 | 6.82320300 8.44644900  |
| C        | 5.58042600 | 6.01879000 10.02559500 |
| C        | 3.21275000 | 4.49313900 10.02895100 |
| C        | 5.87842600 | 10.85075200 11.86159500 |
| C        | 4.18546600 | 10.90192100 11.30480100 |
| C        | 6.94400500 | 8.94063200 13.34724800 |
| C        | 6.70863700 | 7.74569400 12.04646900 |

|          | \( E \) | \( G_{\text{corr}} \) |
|----------|---------|-------------------|
| \( \text{Ni(PMe}_3\text{)}_3 \) |          |                   |
| Ni       | 2.96964300 | 7.43814400 11.73948900 |
| P        | 1.78588200 | 9.17165100 11.21717900 |
| P        | 2.68132400 | 6.67241600 13.74450700 |
| C        | 1.79598400 | 10.58439200 12.42689000 |
| C        | -0.04185000 | 8.88681400 11.07773000 |
| C        | 2.06963900 | 10.11393500 9.63767100  |
| C        | 3.57495300 | 7.68797300 15.01798000 |
| C        | 0.97020400 | 6.63470300 14.49173100 |
| C        | 3.25422900 | 4.69617000 14.22969100 |
| H        | 1.15551600 | 11.41351500 12.09851300 |
| H        | 2.82005700 | 10.95508000 12.54912700 |
| H        | -0.59829000 | 9.79329300 10.87757200 |
| H        | -0.40559000 | 8.42471400 12.01072500 |
| H        | 1.96570000 | 9.43010700 8.78771700  |
| H        | 3.09258400 | 10.50757700 9.63084000  |
Ni(PMe₃)₂

\[
\text{E} = -1091.70993065
\]
\[
\text{G}_{\text{corr}} = 0.185935
\]

PMe₃

\[
\text{E} = -461.173291179
\]
\[
\text{G}_{\text{corr}} = 0.084310
\]
| Atom   | X        | Y        | Z        |
|--------|----------|----------|----------|
| Ni     | -0.49706400 | 0.85226400 | -0.02368300 |
| P      | 0.01251600  | 0.52395400  | -2.15370000 |
| P      | -1.49145900 | -0.97581000 | 0.70533100 |
| P      | 1.42367600  | 1.04561800  | 1.05462400 |
| P      | -1.80334900 | 2.60489900  | 0.24991400 |
| C      | 1.44599200  | 1.50065700  | -2.82277500 |
| C      | 1.58777700  | 2.82186900  | -2.36496000 |
| H      | 0.87764400  | 3.26073000  | -1.64199200 |
| C      | 2.63543100  | 3.63129200  | -2.80649600 |
| H      | 2.71366800  | 4.65272600  | -2.44247100 |
| C      | 3.58266900  | 3.12311500  | -3.70047800 |
| H      | 4.40850900  | 3.74499500  | -4.03692100 |
| C      | 4.36370500  | 1.80793000  | -4.15444000 |
| H      | 4.19856600  | 1.40170300  | -4.84581900 |
| C      | 2.40074000  | 1.00476600  | -3.72544200 |
| C      | 2.33039800  | -0.01259800 | -0.09841600 |
| H      | -1.25265400 | 0.87681700  | -3.47387900 |
| H      | -2.14416600 | 0.27210800  | -3.27470100 |
| C      | -0.87875100 | 0.64356400  | -4.47868900 |
| C      | -1.53122900 | 1.93466000  | -3.43637800 |
| C      | 0.45981000  | -1.21197800 | -2.63527000 |
| H      | -0.37075600 | -1.86526600 | -2.34484200 |
| C      | 1.35010000  | -1.52974500 | -2.08220500 |
| C      | 0.63660500  | -1.33981400 | -3.70938400 |
| C      | -2.50142700 | -1.91250700 | -0.54081700 |
| C      | -2.31480100 | -3.26828100 | -0.85570700 |
| H      | -1.57569000 | -3.85922200 | -0.32841100 |
| C      | -3.07014800 | -3.88233000 | -1.86133600 |
| C      | -2.90794000 | -4.93073300 | -2.09493400 |
| C      | -4.03654600 | -3.15737200 | -2.56063700 |
| C      | -4.62264800 | -3.63567300 | -3.34112900 |
| C      | -4.23998400 | -1.80810100 | -2.25135500 |
| C      | -4.98763600 | -1.23121700 | -2.79067800 |
| C      | -3.47235500 | -1.19386600 | -1.26174200 |
| C      | -3.61022300 | -0.13670100 | -1.05729600 |
| C      | -2.75428100 | -0.82552000 | 2.06837600 |
| C      | -3.51818900 | -0.98231000 | 1.77632000 |
| C      | -2.25263000 | -0.45766700 | 2.97021900 |
| C      | -3.23954100 | -1.78240600 | 2.29665000 |
| C      | -0.43652600 | -2.32011200 | 1.43071300 |
| C      | 0.12415400  | -1.89283200 | 2.26718100 |
| C      | 0.28595900  | -2.66588800 | 0.68385200 |
| C      | -1.01630100 | -3.17576000 | 1.79752000 |
| C      | 1.44036000  | 0.45618400  | 2.81741300 |
| C      | 0.30475000  | 0.73953000  | 3.59775500 |
| C      | -0.52847300 | 1.25974500  | 3.13913100 |
| C      | 0.22032500  | 0.32062800  | 4.92731500 |
| C      | -0.66813800 | 0.55082500  | 5.51070500 |
| C      | 1.26816400  | -0.40728100 | 5.50010800 |
| C      | 1.20116200  | -0.74593800 | 6.53083900 |
| C      | 2.39923900  | -0.70153700 | 4.73529000 |
| C      | 3.21762700  | -1.26989600 | 5.17095000 |
| C      | 2.48802200  | -0.26730000 | 3.40832700 |
| C      | 3.38110100  | -0.50650400 | 2.83910300 |

\[ G_{corr} = 0.601644 \]

\[ \text{Ni(PMe}_2\text{Ph)}_3 \]

\[ E = -2128.30803416 \]

\[ G_{corr} = 0.493835 \]
Ni(PMe₃Ph)₂

\[
\begin{align*}
\text{E} &= -1475.2954173 \\
G_{\text{corr}} &= 0.28227
\end{align*}
\]

\[
\begin{align*}
\text{Ni} &= 2.92241100 \quad 7.11859900 \quad 5.19863800 \\
P &= 3.47235300 \quad 5.05218800 \quad 5.30225500 \\
P &= 2.40996600 \quad 9.18799300 \quad 5.00638500 \\
C &= 2.11340800 \quad 8.3268800 \quad 5.01141200 \\
C &= 2.32833800 \quad 2.44477700 \quad 5.01571100 \\
H &= 3.24058800 \quad 2.04670600 \quad 5.19499900 \\
\text{Ni(PMe₂Ph)} &
\]

\[
\begin{align*}
\text{PhMe₃P—Ni—PMe₃Ph} \\
\text{E} &= -822.264490723 \\
G_{\text{corr}} &= 0.130288
\end{align*}
\]

\[
\begin{align*}
\text{Ni} &= 3.64952100 \quad 7.12531700 \quad 5.00244100 \\
P &= 3.41747500 \quad 5.11515900 \quad 5.25861700 \\
C &= 2.50041500 \quad 4.21075400 \quad 3.92761400 \\
P &= 2.24237300 \quad 8.23860200 \quad 4.00590600 \\
H &= 2.58070100 \quad 2.26020700 \quad 4.86635100 \\
C &= 1.55079100 \quad 2.18047800 \quad 2.98316600 \\
H &= 1.35592300 \quad 1.11348400 \quad 3.05667000 \\
C &= 1.10918500 \quad 2.89706000 \quad 1.86640400 \\
P &= 0.57117600 \quad 2.38864500 \quad 1.07077800 \\
C &= 0.36195300 \quad 4.2683000 \quad 1.77702400 \\
P &= 0.12235200 \quad 4.8312900 \quad 0.9130500 \\
C &= 0.25074500 \quad 4.9188800 \quad 2.80286100
\end{align*}
\]
\[ G_{corr} = 0.132457 \]
\[ E = -652.964031445 \]
\[ G_{corr} = 0.801946 \]
\[ E = -3548.5036579 \]
\[ G_{corr} = 0.132457 \]
\[ E = -652.964031445 \]
\[ G_{corr} = 0.801946 \]
\[ E = -3548.5036579 \]
Ni(PMePh$_2$)$_3$  

\[ E = -1858.88033969 \]
\[ G_{corr} = 0.588582 \]
\[ Ni = 8.95691010 \text{ 10.55166600 3.71532900} \]
\[ \text{Ni(PPh}_3\text{)}_4 \]

\[ \begin{align*}
E & = -4315.67341777 \\
G_{\text{corr}} & = 1.003185
\end{align*} \]

Ni \(\text{PPh}_3\) \(\text{Ni(PPh}_3\text{)}_4\)

\begin{align*}
\text{P} & : -1.19882300 \quad -0.44166600 \quad 0.01868500 \\
\text{C} & : -0.58479000 \quad 0.57761700 \quad -1.40342600 \\
\text{C} & : -1.47037300 \quad 0.88000500 \quad -2.44556800 \\
\text{C} & : 0.74092500 \quad 1.03645900 \quad -3.49812500 \\
\text{C} & : -1.04780700 \quad 1.61866600 \quad -3.55411100 \\
\text{H} & : -2.50452300 \quad 0.53393200 \quad -2.39059700 \\
\text{C} & : 1.16584100 \quad 1.77564100 \quad -2.59375900 \\
\text{C} & : 1.43952500 \quad 0.82193600 \quad -0.68572200 \\
\text{C} & : 0.27155500 \quad 2.06731000 \quad -3.62953000 \\
\text{C} & : -1.74831300 \quad 1.84574300 \quad -4.35376400 \\
\text{C} & : 2.19379100 \quad 2.12549900 \quad -2.64718800 \\
\text{C} & : 0.60313200 \quad 2.64495300 \quad -4.48856200 \\
\text{C} & : -0.11094700 \quad -1.94065500 \quad -0.16172500 \\
\text{C} & : 0.95659900 \quad -1.69504300 \quad -0.15159400 \\
\text{C} & : -0.32582500 \quad -2.65911500 \quad 0.63622400 \\
\text{C} & : -0.35467700 \quad -2.41836200 \quad -1.11669300 \\
\text{C} & : -0.41203600 \quad 0.43923800 \quad 1.44440300 \\
\text{C} & : -0.68192000 \quad 1.80931500 \quad 1.61881300 \\
\text{C} & : 0.37817000 \quad -0.21224400 \quad 2.40447600 \\
\text{C} & : -0.16435100 \quad 2.50833900 \quad -2.70825600 \\
\text{C} & : -1.29061100 \quad 2.33641400 \quad 0.88747400 \\
\text{C} & : 0.89057200 \quad 0.48787900 \quad 3.50132300 \\
\text{C} & : 0.60612700 \quad -1.26938100 \quad 2.30535400 \\
\text{C} & : 0.62491100 \quad 1.84896900 \quad 3.65600200 \\
\text{H} & : -0.37694700 \quad 3.56885400 \quad 2.81787500 \\
\text{H} & : 1.50352000 \quad -0.03450100 \quad 4.23175200 \\
\text{H} & : 1.02759600 \quad 2.39243100 \quad 4.50672700 \\
\end{align*}
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| P    | 9.10187700 | 8.45462600 | 4.94328600 |
| C    | 9.97374500 | 7.02050600 | 4.13351700 |
| H    | 10.29676000 | 6.69494900 | 4.48063700 |
| H    | 8.47836300 | 7.22239400 | 5.28677400 |
| C    | 11.99370800 | 6.69473800 | 3.80103500 |
| H    | 13.01338320 | 5.46341200 | 4.09634500 |
| C    | 11.38744000 | 5.00530500 | 2.74726100 |
| H    | 10.01341110 | 4.23191500 | 2.11136000 |
| C    | 10.07393500 | 5.31864000 | 2.39262600 |
| H    | 9.58698700 | 4.79020600 | 1.57700700 |
| C    | 9.16206000 | 6.31123100 | 3.08132200 |
| H    | 8.35460600 | 6.53522500 | 2.78507200 |
| C    | 7.35442200 | 7.82605500 | 4.79261100 |
| C    | 6.65904600 | 8.59817000 | 3.76640200 |
| H    | 6.97809400 | 9.14526300 | 3.14622000 |
| C    | 5.26332200 | 7.91190500 | 3.55412700 |
| H    | 4.76316800 | 8.34039300 | 2.74676800 |
| C    | 4.71535900 | 6.93488700 | 4.38907000 |
| H    | 3.69590800 | 6.59157500 | 4.23789500 |
| C    | 5.49225400 | 6.40381100 | 5.42733500 |
| H    | 5.06929500 | 5.64623500 | 6.08514700 |
| C    | 6.80075000 | 6.83822300 | 5.62322400 |
| H    | 7.38609000 | 6.40840700 | 6.42979600 |
| P    | 11.56165600 | 11.11721200 | 5.21215000 |
| C    | 11.52704000 | 11.88361800 | 6.91666400 |
| C    | 10.32341100 | 12.37090000 | 7.48292500 |
| H    | 9.42536400 | 12.28750000 | 6.83934000 |
| C    | 10.25259300 | 12.95785500 | 6.95889000 |
| H    | 9.92959600 | 13.31534500 | 9.06655500 |
| C    | 11.40401800 | 13.06460100 | 9.47616200 |
| H    | 11.35749600 | 13.51271700 | 10.46539100 |
| C    | 12.62186100 | 12.58935700 | 9.87565200 |
| H    | 13.52615800 | 12.67256100 | 9.57048040 |
| C    | 12.68301500 | 12.00708700 | 7.71052800 |
| H    | 13.63676100 | 11.64395900 | 7.33847100 |
| C    | 13.66811500 | 12.35812200 | 4.34003800 |
| C    | 13.06095000 | 13.58249100 | 4.91042000 |
| C    | 12.78088300 | 13.82963500 | 5.92754100 |
| C    | 13.79818100 | 14.51607000 | 4.17588100 |
| H    | 14.07985100 | 15.45699100 | 4.64231800 |
| C    | 14.17153800 | 14.24704500 | 2.85766100 |
| C    | 14.74458300 | 14.97470400 | 2.28901000 |
| C    | 13.79044500 | 13.03563700 | 2.27702600 |
| H    | 14.05691600 | 12.80788800 | 1.24815700 |
| C    | 13.03894800 | 12.11417200 | 3.00653800 |
| C    | 12.71691100 | 11.20727900 | 2.51521500 |
| C    | 12.77404000 | 9.73859800 | 5.57844900 |
| C    | 12.67234200 | 9.02908000 | 6.79089700 |
| C    | 13.75503100 | 9.32878900 | 4.66145700 |
| C    | 13.51946400 | 7.95640400 | 7.03764600 |
| H    | 11.93121800 | 9.31088900 | 7.52856400 |
| C    | 14.59671400 | 8.24846800 | 4.93965300 |
| C    | 13.88064100 | 9.84720100 | 3.72003100 |
| C    | 14.48520700 | 7.55621000 | 6.14672900 |
| H    | 13.41195800 | 7.43014800 | 8.01849700 |

\[ E = -3279.08460787 \]

\[ \text{G}_{\text{corr}} = 0.735357 \]

Ni(PPh₃)₃
| Name | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | 7.45234400 | 8.65417300 | 0.84096400 |
| H    | 7.63155300 | 8.23393300 | 1.82776900 |
| C    | 10.95421900 | 9.57189200 | 1.28440000 |
| C    | 11.96813000 | 9.63308600 | 2.25591000 |
| H    | 11.78627900 | 10.18138300 | 3.17769100 |
| C    | 13.18068300 | 8.97959050 | 2.06177000 |
| H    | 13.95157700 | 9.02601700 | 2.82594400 |
| C    | 13.39218700 | 8.22808700 | 0.89866800 |
| H    | 14.33155600 | 7.70108800 | 0.75289100 |
| H    | 12.38707800 | 8.14981500 | -0.06788800 |
| C    | 12.54499200 | 7.56717600 | -0.97222400 |
| C    | 11.17572000 | 8.82829900 | 0.12013500 |
| H    | 10.40512200 | 8.76466200 | -0.64345800 |
| P    | 7.12552800 | 10.21040300 | 6.38278400 |
| C    | 5.92922200 | 11.09785400 | 5.74359900 |
| H    | 6.42341700 | 10.72140900 | 7.00670600 |
| H    | 7.46196900 | 10.90828500 | 7.25740000 |
| C    | 5.59485000 | 10.10256100 | 7.94085900 |
| H    | 6.00016100 | 8.91771800 | 8.90843700 |
| H    | 4.25667800 | 9.83970900 | 7.63068500 |
| H    | 3.61359600 | 9.34584800 | 8.35586500 |
| C    | 3.75417000 | 10.21040300 | 6.38278400 |
| C    | 2.71435800 | 10.01452000 | 6.13238900 |
| C    | 4.58234200 | 10.83829400 | 5.44688300 |
| C    | 4.17427200 | 11.11504100 | 4.47938700 |
| C    | 7.96901000 | 13.10545600 | 5.30704800 |
| C    | 7.40642800 | 13.83818300 | 6.63627500 |
| C    | 6.41021900 | 13.59240600 | 6.72331500 |
| C    | 8.11980000 | 14.87532100 | 9.66686500 |
| C    | 7.67233100 | 15.43154600 | 7.78651200 |
| C    | 9.40510800 | 15.19616600 | 6.52089800 |
| C    | 9.96046200 | 16.00159200 | 6.99448000 |
| C    | 9.97584500 | 14.47485200 | 5.46778700 |
| C    | 10.97593000 | 14.71580100 | 5.11840900 |
| C    | 9.26321100 | 13.43463000 | 4.86899100 |
| C    | 9.70959000 | 12.85636100 | 4.06374600 |
| P    | 9.05279500 | 8.60018700 | 4.91027800 |
| C    | 10.45809000 | 7.46459600 | 4.49516900 |
| C    | 11.59952800 | 7.30476100 | 5.29227400 |
| C    | 11.68002600 | 7.83072000 | 6.23912600 |
| C    | 12.64119300 | 6.46592700 | 4.87947700 |
| C    | 13.52183900 | 6.35874000 | 5.50739300 |
| C    | 12.54896400 | 5.77083900 | 3.67293200 |
| C    | 13.35884500 | 5.12047500 | 3.35278900 |
| C    | 11.41154300 | 5.92359600 | 2.87129700 |
| C    | 11.33722000 | 5.39708400 | 1.92355700 |
| C    | 10.38242200 | 6.77021100 | 2.37498400 |
| C    | 9.51507000 | 6.90500300 | 2.63327800 |
| C    | 7.70169400 | 7.36439500 | 5.18441600 |
| C    | 6.39155900 | 7.74437900 | 4.85597900 |
| C    | 6.21598300 | 8.73364900 | 4.44808400 |
| C    | 5.32335040 | 6.86586200 | 5.05064400 |
| C    | 4.31457400 | 7.18151800 | 4.79853400 |
| C    | 5.55511700 | 5.58925000 | 5.56819600 |
| C    | 4.72645000 | 4.90202300 | 5.71872600 |

**Ni(PPh₃)₂**

\[
\text{Ni(PPh₃)₂} = \text{Ph}_3\text{P} - \text{Ni} - \text{PPh₃}
\]

\[
\begin{align*}
\text{E} &= -2242.46752288 \\
\text{G}_{\text{corr}} &= 0.47734
\end{align*}
\]

| Name | X      | Y      | Z      |
|------|--------|--------|--------|
| Ni   | -1.29396100 | 1.93989600 | -0.01465100 |
| P    | -2.05630200 | 3.89533300 | -0.39166100 |
| C    | -2.90685900 | 4.68036000 | 1.04850900 |
| C    | -2.92276700 | 6.06035900 | 1.30058700 |
| H    | -2.40181000 | 6.74269100 | 0.63516600 |
| C    | -3.60553500 | 6.56620100 | 2.41076000 |
| C    | -3.60949100 | 7.63690600 | 2.59738300 |
| C    | -4.27870200 | 5.70093400 | 3.27677500 |
| H    | -4.80640700 | 6.09736800 | 4.14033600 |
| C    | -4.26366600 | 4.32376000 | 3.03557600 |
| H    | -4.77618000 | 3.64491300 | 3.71121400 |

S21
\[
\begin{align*}
E &= -1205.8504571 \\
G_{\text{corr}} &= 0.227205 \\
E &= -1036.54805321 \\
G_{\text{corr}} &= 0.227205
\end{align*}
\]
S23

PhBr

\[
E = -244.896841005
\]

\[G_{\text{corr}} = 0.059764\]

PhCl

\[
E = -691.950425949
\]

\[G_{\text{corr}} = 0.061491\]

PhI

\[
E = -243.107736972
\]

\[G_{\text{corr}} = 0.058614\]

PhH

\[
E = -232.324141291
\]

\[G_{\text{corr}} = 0.073358\]
H Abstraction TS: Ph• + THF

\[
\begin{align*}
E &= -464.165098393 \\
G_{\text{corr}} &= 0.161901 \\
v &= -902.54 \text{ cm}^{-1}
\end{align*}
\]

1-I-PMe₃

\[
\begin{align*}
E &= -1796.04683539 \\
G_{\text{corr}} &= 0.375599 \\
\end{align*}
\]
\[
1\text{-I-PPh}_3
\]

\[
E = -3522.20848963
\]

\[
G_{\text{corr}} = 0.817953
\]
\[
\begin{align*}
\text{Ni} & \quad -1.26659300 \quad -0.71246100 \quad 0.36778700 \\
\text{H} & \quad 7.02266300 \quad 7.14542200 \quad 3.50342300 \\
\text{C} & \quad 5.59266000 \quad 7.58129400 \quad 5.06088200 \\
\text{C} & \quad 5.42067000 \quad 7.86371500 \quad 6.41805900 \\
\text{H} & \quad 8.98485000 \quad 7.28841400 \quad 4.98188000 \\
\text{C} & \quad 9.76264200 \quad 12.16537100 \quad 0.66706100 \\
\text{P} & \quad -3.52146500 \quad -0.88934500 \quad -0.01169600 \\
\end{align*}
\]

**1-Br-PMe₃**

\[
\begin{align*}
E & = -1797.838352 \\
G_{\text{corr}} & = 0.37561
\end{align*}
\]

**1-Cl-PMe₃**

\[
\begin{align*}
E & = -2244.89074075 \\
G_{\text{corr}} & = 0.378569
\end{align*}
\]
TS-1-2-1-PMe₂Ph

\[ E = -2371.42764175 \]

\[ \Delta G_{corr}^\circ = 0.528074 \]

Ni  
-1.74979600  3.37904100  0.08652900
P   
-1.25700300  3.37594500  -2.08759300
P   
 0.19711900  3.46751600  1.17526800
P   
-3.18227900  5.04013700  0.40522900
C   
 0.22383400  4.42093300  -2.47387000
C   
 0.12572000  5.82191800  -2.40823400
H   
-0.82953400  6.29058400  -2.20045000
C   
 1.24784300  6.63044500  -2.58942200
H   
 1.14155100  7.71072300  -2.53162200
C   
 2.49978000  6.05661500  -2.83037300
H   
 3.37608500  6.68546600  -2.96456000
C   
 2.61364800  4.66594500  -2.89681600
H   
 3.58044300  4.20562000  -3.08533700
C   
 1.48655800  3.85685500  -2.72331500
H   
 1.60475900  2.77882900  -2.77762700
C   
-2.50073400  4.10732400  -3.26200000
H   
-3.41017400  3.49793500  -3.21666000
C   
-2.13243100  4.12789600  -4.29483200
H   
-2.75568300  5.12511400  -2.95682300
C   
-0.85705500  1.84842200  -3.07423800
C   
-1.77636400  1.27709000  -3.19962100
H   
-0.13015900  1.22072200  -2.55110100
C   
-0.46549500  2.10619300  -4.06485600
C   
 0.24234300  3.44704000  3.02459400
C   
-0.25474700  4.56762800  3.71409200
C   
-0.58457500  5.43953200  3.15489500
C   
-0.35315500  4.57278000  5.10413200
C   
-0.79991700  5.45112500  5.61537700
C   
 0.03834500  3.44773700  5.83979900
C   
-0.04235400  3.44663000  6.92364800
C   
 0.54217000  2.33120900  5.16396900
C   
 0.85635400  1.45479100  5.73313800
C   
 0.64694100  2.33235800  3.77487500
C   
 1.03395000  1.44757700  3.27831600
C   
 1.40661600  2.12432200  2.74324000
C   
 0.97113900  1.13194300  0.89424700
C   
 2.34332000  2.19999100  1.30804000
C   
 1.63028600  2.23060700  -0.32450000
C   
 1.31282600  4.92262400  0.86607800
C   
 0.80123700  5.85834500  1.09729000
C   
 1.58856400  4.94103400  -0.19003300
C   
 2.22334900  4.85146400  1.47217100
C   
-2.56082600  6.69432400  -0.15126100
C   
-3.03570300  7.34926300  -1.29970700
C   
-3.84846000  6.92494800  -1.87985000
C   
-2.46872700  8.55522400  -1.72606700
C   
-2.84810000  9.03793300  -2.62337800

TS-1-2-1-PMethylPh

\[ E = -2946.81030933 \]

\[ \Delta G_{corr}^\circ = 0.678608 \]

Ni  
-2.39362100  0.71517600  -0.00066400
P   
-1.97553200  1.34589900  -0.75826200
C   
-3.46716100  2.39100200  -1.13934200
C   
-4.19916500  2.13501700  -2.31230600
C   
-3.84503600  1.39603300  -3.02235300
C   
-5.39338900  2.80742800  -2.57788300
C   
-5.94095600  2.58930000  -3.49155000
C   
-5.88432000  3.75371700  -1.67335300
C   
-6.81693100  4.27385500  -1.87550400
C   
-5.16004400  4.02879000  -0.51384000
C   
-5.52448300  4.76930200  0.19637300
C   
-3.96231900  3.35842100  -0.24950500
C   
-3.41730600  3.59028800  0.65937100
C   
-1.01087200  2.48029200  0.34458700
C   
-1.30303300  2.44361900  1.71661400
C   
-2.05411100  1.75321800  2.07901600
C   
-0.63199200  3.26980800  2.61987900
C   
-0.88676900  3.22520400  3.67557900
C   
 0.37083600  4.12941500  2.16666000
C   
 0.90613800  4.76518000  2.86725400
C   
 0.68640600  4.16278300  0.80512500
C   
 1.46993700  4.82456000  0.44414500
C   
-0.00365800  3.35224300  -0.10054800
\[ E = -3522.177200 \]
\[ G_{corr} = 0.828053 \]
H -4.89409300 1.81887100 3.63959100
C -3.32743100 2.03418400 2.18696600
C -3.72657300 1.21328400 1.60786600
C -0.14550600 3.75277600 0.08685700
C -0.68849600 5.02422800 -0.17521800
H -1.75778000 5.13611900 -0.32850000
C 0.13159800 6.19458400 -0.24035100
C -0.30591900 7.12229900 -0.45031000
C 1.51070700 6.02973500 -0.03336000
H 2.14898400 6.90788700 -0.08764700
C 2.05849900 4.77755500 0.24592100
H 3.12668500 4.66324600 0.40810300
C 1.22987100 3.65408600 0.30690100
H 1.66128200 2.68773600 0.51707000
P 1.91455700 0.00775700 1.11206000
C 2.10253300 0.87485000 2.74901000
C 1.11595200 1.77135200 3.16628100
H 0.23684700 1.90409400 2.55245900
C 1.23361000 2.46765000 4.37189900
H 0.44377500 3.15028200 4.67307700
C 2.35069500 2.26852100 5.18361500
C 2.44666700 2.80393000 6.12478600
C 3.34775400 1.37177800 4.78144400
H 4.22171100 1.21020600 5.40738900
C 3.22503200 0.68165800 3.57566000
C 4.00886200 -0.07228000 3.27524200
C 3.35591900 0.75866200 0.18159900
C 4.11824100 1.83226000 0.67477900
C 3.91588800 2.24632600 1.65545200
C 5.13803800 2.40250100 -0.09252200
H 5.70580300 3.23620300 0.31061000
C 5.42938100 1.90852200 -1.36536100
H 6.22306900 2.35386600 -1.95958300
C 4.68356800 0.84044300 -1.86771000
C 4.88362800 0.44448500 -2.85995800
C 3.65563000 0.28430800 -1.10630000
C 3.07145100 -0.51784000 -1.53370600
C 2.62631600 -1.64948900 1.60742700
C 2.18826600 -2.23311400 2.81107900
C 3.54570100 -2.36516000 0.82771200
C 2.64057900 -3.49037100 3.21157500
C 1.84853100 -1.07089900 3.46622900
C 3.99934300 -3.62675800 1.22717000
C 3.92810900 -1.95029300 -0.09507000
C 3.54712000 -4.19804200 2.41705400
C 2.28403800 -3.91369100 4.14735000
C 4.71432700 -4.15665500 0.60271100
C 3.90200800 -5.17742600 2.72713000
C -2.43095300 2.58603300 -1.13414000
C -1.98067800 3.18808000 -2.32545400
C -3.77716800 2.18803700 -1.07432900
C -2.84684000 3.40652800 -3.39781600
C -0.94582900 3.49022200 -2.42692100
C -4.64549300 2.40936600 -2.14656200
H -4.17342400 1.70313200 -0.19336700
C -4.18714600 3.02279200 -3.31397200
H -2.46351000 3.87146900 -4.30209700
H -5.68318300 2.09622400 -2.06431800
H -4.86262700 3.19338700 -4.14789900
C 0.51711600 1.09461300 -3.21514500
C 1.32662600 2.06259500 -2.60656000
C 1.73281000 3.20460900 -3.29756300
H 1.61601400 1.92625200 -1.57483100
C 0.51923300 2.43980200 -5.24162800
H -0.50346300 0.56139200 -5.04780000
C 1.32292300 3.39993900 -6.41885600
H 2.34881000 3.94403000 -2.79313300
H 0.19710700 2.58314000 -6.27004400
H 1.62296100 4.29394800 -5.15947600
I -1.39476300 -0.76157800 3.45212600
C -1.23931100 -1.42543000 1.36322200
C -2.26925500 -1.02800000 0.47308600
C -0.68116500 -2.72605600 1.21632900
C -2.74949000 -1.93421300 -0.49622800
H -2.84801600 -0.13755200 0.66863300
C -1.13780900 -3.57989000 0.22529200
H 0.08294100 -3.63574000 1.90395000
C -2.19751900 -3.19742700 -0.62064800
H -3.57157900 -1.62848800 -1.13512800
H -0.68692500 -4.56416500 0.12519200
H -2.58038600 -3.88931600 -1.36414900

\[
\begin{align*}
E &= -1797.83515434 \\
G_{\text{corr}} &= 0.376299
\end{align*}
\]

TS-1-2-Br-PMe₃
|atom  | x   | y   | z    |
|------|-----|-----|------|
| H    | -4.46708700 | 0.73853400 | 1.48450400 |
| H    | -4.30153500 | 1.38579700 | -0.14299600 |
| C    | -0.08395800 | -1.23399800 | -1.78089400 |
| H    | -3.81880200 | -0.37676400 | -2.40858900 |
| H    | -3.57686000 | -2.11892700 | -2.17546500 |
| C    | -5.16776000 | -1.39176900 | -1.84440100 |
| H    | -5.40727400 | -0.73219900 | -2.99808900 |
| C    | -0.13842600 | -0.12391200 | -3.86578700 |
| H    | 0.28324600  | -1.56581700 | -2.91077000 |
| C    | -1.42325600 | -1.14036500 | -3.16057000 |
| C    | 1.37056400  | 1.75957500  | 1.98863000  |
| H    | 2.37675900  | 1.44853000  | 2.28417200  |
| H    | -1.46190000 | 2.44249600  | -1.13415900 |
| C    | -0.88621900 | 2.26352600  | -2.82404700 |
| C    | 1.31888500  | 0.93415400  | 1.45576800  |
| H    | 2.00849700  | 0.17445100  | -1.08407200 |
| H    | 1.61313000  | 1.23419700  | -2.26728000 |
| C    | 1.73766800  | 1.81015100  | -0.82090400 |
| C    | 1.23997400  | -3.11262000 | -0.28563700 |
| C    | 1.79681000  | -2.61872100 | 0.51870100  |
| C    | 0.51660000  | 2.61872100  | -0.51870100 |
| C    | 1.51709000  | -4.17262000 | -0.31834800 |
| C    | 1.52306200  | -2.64208000 | 0.82358900  |
| C    | 1.31818000  | -3.91937900 | -1.33165900 |
| C    | -1.15531400 | -3.45720700 | -2.29154500 |
| H    | -0.88670800 | -4.92763900 | -1.32211200 |
| C    | -2.39715500 | -4.00121900 | -1.14572100 |
| C    | -0.81645000 | -3.98245800 | 1.48861000  |
| C    | -0.23750000 | -3.59375900 | 2.33090400  |
| C    | -1.87340000 | -3.97990900 | 1.77336600  |
| C    | -0.50121400 | -5.01054500 | 1.27372600  |

**TS-1-2-Cl-PMe3**

\[
E = -2244.88655801 \\
G_{corr} = 0.375799
\]

| atom  | x   | y   | z    |
|------|-----|-----|------|
| Ni   | -1.23252900 | -0.77061800 | 0.35454000 |
| P    | -0.39112000 | 0.25867200  | -1.43565400 |
| P    | -0.57644300 | -2.90774000 | -0.00475400 |
| P    | -3.53626200 | -0.93447600 | -0.04528100 |
| C    | -0.81171000 | 0.42225500  | 1.71381400  |
| C    | -1.47089600 | -0.49380800 | 2.58062200  |
| C    | 0.55292000  | 0.73837300  | 1.94636900  |
| C    | -0.72318600 | -1.14949700 | 3.59698500  |
| H    | -2.55301100 | -0.53049500 | 2.63065500  |
| C    | 1.26169900  | 0.06361700  | 2.92740900  |
| H    | 1.03966300  | 1.49203100  | 1.33877400  |
| C    | 0.62776900  | -0.89436600 | 3.75409000  |
| H    | -1.23891800 | -1.82418500 | 4.27664800  |
| C    | 2.32177200  | 0.27205600  | 3.05724500  |
| H    | 1.19668800  | -1.39906200 | 4.53075000  |
| C    | -4.40836400 | -2.31869500 | 0.82307900  |
| H    | -4.25148300 | -2.25210400 | 1.90338200  |
| H    | -5.48661400 | -2.31816000 | 0.62057300  |
| H    | -3.98935900 | -3.27825100 | 0.50106900  |

**2-I-PMe3**

\[
E = -1796.11261245 \\
G_{corr} = 0.377983
\]

| atom  | x   | y   | z    |
|------|-----|-----|------|
| Ni   | -1.34730500 | -1.28806300 | -0.05416300 |
| P    | 0.13800300  | -0.01722600 | -1.18121900 |
| P    | -0.74326100 | -3.31385500 | -0.98594800 |
| P    | -3.38744800 | -1.83419900 | 0.77960900  |
| C    | -1.40212600 | 0.17175600  | 1.21355600  |
| C    | -0.58311700 | 0.07766000  | 2.33223500  |
| C    | -2.13038100 | 1.37032500  | 1.19689000  |
| C    | -0.50799000 | 0.82572200  | 3.39705100  |
| C    | 0.00752700  | -0.99297300 | 2.37673000  |
| C    | -2.06431700 | 2.27712000  | 2.26152500  |
| C    | -2.74733200 | 1.61728900  | 0.33740200  |
| C    | -1.25519200 | 2.00708100  | 3.36738700  |

**S33**
$G_{corr} = 0.674795$

$E = -2946.88279278$

$G_{corr} = 0.674795$

2-I-PMe$_2$H

\[
\text{PhMeP}^+\text{PMe$_2$H}^-
\]

$E = -2946.88279278$

2-I-PMe$_2$H

$E = -2946.88279278$
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | 13.77761500| 9.93459500| 3.40376000|
| H       | 12.25141600| 8.84491600| 3.26391700|
| C       | 14.07015100| 10.96697000| 5.20071200|
| H       | 13.22820400| 12.52188700| 6.44893500|
| H       | 14.58013300| 9.32734800| 3.89121300|
| H       | 15.09932400| 11.17278100| 5.48485100|
| I       | 9.81287400| 13.92470900| 8.17378800|
| Ni      | 9.35558800| 10.48196500| 4.19095400|
| P       | 9.33807600| 10.20429700| 1.79316600|
| C       | 7.96021900| 9.265613800| 1.03570300|
| C       | 6.75993000| 9.90573200| 0.68930600|
| H       | 6.67119500| 10.98238100| 0.76271200|
| C       | 5.66216000| 9.16066700| 0.25446200|
| H       | 4.74295500| 9.67396200| 0.01817000|
| C       | 5.74405200| 7.68233000| 1.70101000|
| C       | 4.98745200| 7.18989500| 0.16507500|
| H       | 6.92974900| 7.12287300| 0.52949300|
| C       | 7.00074900| 6.03973600| 0.48038800|
| C       | 8.02848900| 7.86321200| 0.96507600|
| H       | 8.93483300| 7.34402000| 0.12544700|
| C       | 10.89202000| 9.46296200| 1.13876800|
| C       | 12.03632000| 9.81321300| 1.78020900|
| H       | 12.06879900| 10.40696400| 2.68702200|
| C       | 13.32459400| 9.41092100| 1.26398900|
| C       | 14.23669090| 9.67395500| 1.79703000|
| C       | 13.37259200| 8.63978400| 0.10081400|
| H       | 14.32958700| 8.31063000| 0.29740700|
| C       | 12.18677800| 8.29392000| 0.55149900|
| H       | 12.21676800| 7.70324600| 1.46330800|
| C       | 10.95417000| 8.71282800| 0.04561200|
| H       | 10.04719400| 8.45724500| 0.58271600|
| P       | 8.04590200| 12.38190700| 0.44131000|
| C       | 7.09975100| 12.24380700| 6.02106800|
| H       | 6.86620500| 13.33692000| 6.86596200|
| C       | 7.25012000| 14.31984900| 6.61631100|
| H       | 6.14643600| 13.16785300| 8.05203200|
| C       | 5.97861200| 14.02306300| 8.70103400|
| H       | 5.64975200| 11.91579000| 8.40592500|
| C       | 5.09282800| 11.78504400| 9.33023400|
| C       | 5.88304400| 10.81568500| 7.57066000|
| C       | 5.51540200| 9.82962500| 7.84167200|
| C       | 6.61042300| 10.98171700| 6.39299400|
| H       | 6.82715900| 11.01181700| 5.77501000|
| C       | 8.83714300| 14.03860000| 4.51089100|
| C       | 8.10731100| 15.22552000| 4.32243300|

$$G_{corr} = 0.824754$$

$$E = -3522.2418558$$

S36
2-Br-PMe₃

\[
\begin{align*}
E & = -1797.88492862 \\
G_{\text{corr}} & = 0.379868
\end{align*}
\]

2-Cl-PMe₃

\[
\begin{align*}
E & = -2244.9507208 \\
G_{\text{corr}} & = 0.382069
\end{align*}
\]
| Atom | X  | Y  | Z  |
|------|----|----|----|
| H    | -2.73170800 | -2.62414100 | 2.81906200 |
| H    | -4.46187700 | -2.88325400 | 2.46841600 |
| C    | -3.21061300 | -3.69231500 | 1.48634200 |
| C    | -4.02328500 | 0.03787400  | 1.92121400 |
| H    | -5.01781500 | -2.23547000 | 2.29968000 |
| H    | -3.35095300 | 0.22245000  | 2.76053200 |
| H    | -4.09465100 | 0.94976900  | 1.32131000 |
| C    | -4.87351300 | -1.58555400 | -0.22447900 |
| H    | -4.73343600 | -0.99053900 | -1.13103100|
| H    | -5.00384100 | -2.63608000 | -0.48378900 |
| C    | -5.77379400 | -1.24765700 | 0.29980000  |
| C    | 2.06114500  | -1.88818400 | -1.24685900 |
| H    | 2.98984900  | -1.36955500 | -1.51021800 |
| H    | 2.29221800  | -2.65228400 | -0.49744600 |
| C    | 1.67552200  | -2.37963600 | -2.14168400 |
| C    | 0.87231700  | 0.69348700  | -1.77115100 |
| C    | 0.30067900  | 0.39382400  | -2.65204000 |
| C    | 0.37927200  | 1.56670500  | -3.36413100 |
| C    | 1.89819800  | 0.95519400  | -2.05504200 |
| C    | 1.95775600  | 0.01810400  | 0.79742400  |
| H    | 2.05401000  | 0.07045580  | 1.61293100  |
| C    | 2.94988400  | 0.22045700  | 0.37853800  |
| C    | 1.53955600  | 0.94248000  | 1.19943000  |
| C    | -1.00237500 | -2.30761200 | -3.31676700 |
| C    | 0.00484600  | -1.88636300 | -3.34100700 |
| C    | -1.05097000 | -3.15705300 | -4.00781800 |
| C    | -1.70066300 | -1.52537500 | -3.62951300 |
| C    | -3.09176800 | -3.66586200 | -2.02131300|
| H    | -3.80594600 | -2.95359600 | -2.43956900 |
| H    | -2.90017800 | -4.44996100 | -2.76296100|
| H    | -3.51814100 | -1.12966900 | -1.12752200|
| C    | -0.47920200 | -4.31413200 | -1.23834000|
| H    | 0.55240700  | -0.05168500 | -1.00078700 |
| H    | -0.90888700 | -4.81629200 | -0.36176000 |
| H    | -0.48608800 | -5.01724100 | -2.07927600 |
| Cl   | -2.83582000 | 0.67862500  | -2.23140800 |

**3-I-PMe2Ph**

![Image]

\[
E = -1718.51055427
\]

\[
G_{corr} = 0.367239
\]

**3-I-PMe3**

\[
E = -1334.92584591
\]

\[
G_{corr} = 0.268058
\]

**Ni**

-0.88779600 1.2886800 0.17164000

P

-1.92336000 0.82913900 -1.78754000

P

0.26010600 1.35214600 2.12148600

C

-0.67528100 0.97875500 3.12273600

C

0.17869600 2.09458200 -0.08611000

C

0.07412500 2.82157300 -2.28383300

C

1.16445900 2.26212000 -0.45888300

H

1.81846800 3.12936100 -0.42016900

C

1.31626700 1.30022000 -5.07201300

C

2.08863800 1.43527000 -5.82615300

C

0.47624200 0.19482700 -5.10936500

C

0.59386700 -0.55021000 -5.89191200

C

-0.51654700 0.02775000 -4.13975100

H

-1.15658700 -0.84925400 -4.17888600

C

-3.30824500 1.89347500 -2.38107900

H

-4.11875700 1.87470800 -1.64533200

H

-3.67037000 1.52215900 -3.34353200

S38
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -2.96523600 | 2.92386300 | -2.49482700 |
| H    | -2.66097000 | -0.84540100 | -1.96651600 |
| C    | -3.37488400 | -0.99081900 | -1.14915000 |
| H    | -1.89174700 | -1.61607000 | -1.89342700 |
| H    | -3.19204100 | -0.93927300 | -2.91917200 |
| C    | -0.74057700 | 0.45272400  | 3.36398800  |
| C    | -2.11951100 | 0.72377300  | 3.40708900  |
| H    | -0.40055900 | 0.27958400  | 4.33633200  |
| C    | -2.40512000 | -0.89380100 | 5.18704500  |
| H    | -3.04869500 | -1.41293900 | 5.88961000  |
| C    | -1.03729900 | -1.16952100 | 5.14929900  |
| H    | -0.61333600 | -1.90598800 | 5.82194200  |
| C    | -2.06447700 | -0.50179600 | 2.45021200  |
| H    | 0.85305700  | -0.73471600 | 4.22634800  |
| C    | 1.92462100  | 0.57195500  | 2.14644100  |
| H    | 1.86061600  | -0.48950200 | 1.90995000  |
| C    | 2.40016800  | 0.69913700  | 3.12145800  |
| H    | 2.54105900  | 1.06613500  | 3.38800000  |
| C    | 0.61216400  | 2.96358700  | 2.94520800  |
| H    | -0.32225000 | 3.48455000  | 3.16372400  |
| H    | 1.21182800  | 3.58905000  | 2.92701100  |
| C    | 1.62423600  | 2.79221700  | 3.87704000  |
| C    | -0.19395500 | -0.48161600 | 0.02175500  |
| H    | 0.93378300  | -0.74482900 | -0.77601900 |
| H    | -0.78247000 | -1.56246300 | 0.70173200  |
| C    | 1.45418100  | -0.20333900 | -0.89251800 |
| H    | 1.40930000  | 0.06749900  | -1.31981000 |
| C    | -0.26443000 | -2.85765800 | 0.59114200  |
| H    | -1.65219600 | -1.39181000 | 1.33091600  |
| C    | 0.85695000  | -3.10153000 | -0.20804800 |
| C    | 2.32713000  | -2.41529200 | -1.51788300 |
| C    | -0.73844700 | -3.67316300 | 1.12924400  |
| H    | 1.26023700  | -4.10739200 | -0.29617100 |
| I    | -1.80826200 | 3.77488400  | 0.35355800  |

**3-I-PMePh₂**

\[
\begin{align*}
\text{E} &= -2102.09126305 \\
G_{corr} &= 0.464839
\end{align*}
\]

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| Ni   | 1.40454700 | 0.74332100 | -1.73438000 |
| P    | 0.50619900 | 0.95557600 | -3.32110600 |
| C    | 0.04501500 | 2.24782700 | -3.62684300 |
| H    | 0.27767600 | 3.08052200 | -2.96833400 |
| C    | -0.72810000 | 2.47045300 | -4.76675600 |
| H    | -1.07753100 | 3.47454800 | -4.99252800 |
| C    | -1.05479900 | 1.40449000 | -5.61045700 |
| H    | -1.65854100 | 1.57655400 | -6.49748300 |
| C    | -0.60522000 | 0.11715900 | -5.30748700 |
### 3-I-PPh₃

**Energy (E):** -2485.66788399  
**Gcorr:** 0.564945

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| H    | -0.45721800 | 3.62292700 | 2.61751200 |
| H    | -1.93080700 | 3.06926300 | 3.47524500 |
| PhP  |             |            | Ni         |
| C    | -0.18342600 | -1.11965200 | 0.00127000 |
| C    | -1.15088600 | -0.43098300 | -0.41739300|
| H    | -1.58399100 | 0.84721600  | 0.48721600 |
| C    | -1.56026900 | -0.91475700 | -5.28042000|
| H    | -2.30787400 | -0.36970500 | -5.82798200|
| C    | -1.01632400 | -2.10096700 | -5.76221500|
| H    | -1.33917600 | -2.48173800 | -6.72752700|
| C    | -0.05459500 | -2.78936600 | -5.02213000|
| H    | 0.37922600  | -3.70747700 | -5.40962900 |
| C    | 0.36583600  | -2.30055100 | -3.78079900 |
| H    | 1.12644300  | -2.84267500 | -3.23008000 |
| C    | 1.68749500  | -1.40972400 | -1.02902300 |
| H    | 2.96838700  | -0.92242800 | -0.74061500 |
| C    | 3.23212200  | 0.10220000  | -0.97736600 |
| H    | 3.90584900  | -1.74433000 | -0.11055400 |
| C    | 4.89354600  | -1.35246200 | 0.11663100  |
| H    | 3.57548400  | -3.05638100 | 0.23437100  |
| C    | 4.30765500  | -3.69239000 | 0.72461500  |
| H    | 2.29514000  | -3.54527800 | -0.04199100 |
| C    | 2.02589400  | -4.56150400 | 0.23363400  |
| H    | 1.35175500  | -2.72375100 | -0.65761200 |
| C    | 0.34893100  | -3.10124000 | -0.84149100 |
| H    | -2.42605900 | 0.95622900  | 1.66722300  |
| C    | -2.96952800 | -0.28390200 | 2.90345200  |
| H    | -2.74442700 | -1.64295200 | 2.63930300  |
| H    | -2.26819300 | -1.93495400 | 1.70968200  |
| C    | -3.13215100 | -2.61556300 | 3.56324600  |
| H    | -2.95211300 | -3.66493600 | 3.34639100  |
| C    | -3.74524900 | -2.23870600 | 4.76016100  |
| H    | -4.04849900 | -2.99538600 | 5.47878000  |
| C    | -3.96093300 | -0.88527500 | 5.03756000  |
| H    | -4.42855200 | -0.58685600 | 5.97189700  |
| C    | -3.56938500 | 0.08906100  | 4.11899700  |
| H    | -3.71916800 | 1.13826300  | 4.35521900  |
| C    | -1.64899100 | 2.27388100  | 2.69854600  |
| C    | -1.73667600 | 3.62429300  | 2.32978200  |
| H    | -2.34210600 | 3.92371300  | 1.48006200  |
| C    | -1.04944700 | 4.60123900  | 3.05469500  |
| C    | -1.12951400 | 5.64382500  | 2.75819100  |
| C    | -0.27075400 | 4.24213800  | 4.15644500  |
| H    | 0.26367700  | 5.00304200  | 4.71898300  |
| C    | -0.18233800 | 2.89866000  | 4.53187000  |
| H    | 0.42558300  | 2.60746700  | 5.38411200  |
| C    | -0.86349900 | 1.92082300  | 3.80836400  |
| H    | -0.76625400 | 0.88042200  | 4.09876900  |
3-Br-PMe₃

\[
\begin{align*}
E &= -1336.71315151 \\
G_{\text{corr}} &= 0.270212
\end{align*}
\]

3-Cl-PMe₃

\[
\begin{align*}
E &= -1783.76597845 \\
G_{\text{corr}} &= 0.270514
\end{align*}
\]

S41
4-I-PMe₃

\[ E = -1796.05427209 \]

\[ G_{corr} = 0.373122 \]

4-I-PMe₂Ph

\[ E = -2371.44101625 \]

\[ G_{corr} = 0.520621 \]
4-Br-PMe₃

\[ E = -1797.83621232 \]

\[ G_{\text{corr}} = 0.373538 \]
|     |  H        |  H        |  H        |  H        |  H        |  H        |  H        |  H        |  H        |
|-----|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
|     | 0.39063600 | 10.67328000 | 12.38705700 |          |          |          |          |          |          |
|     | -0.07021500 | 8.05016400 | 9.24130100 |          |          |          |          |          |          |
|     | 1.76915800 | 10.77816700 | 8.69836200 |          |          |          |          |          |          |
|     | 3.52067800 | 5.25109200 | 8.27049300 |          |          |          |          |          |          |
|     | 4.86066600 | 8.48527900 | 11.92885700 |          |          |          |          |          |          |
|     | 1.01547500 | 4.80380500 | 10.45015900 |          |          |          |          |          |          |
|     | 4.20618100 | 10.16954000 | 15.10315200 |          |          |          |          |          |          |
|     | 5.59316500 | 9.73434600 | 11.40472600 |          |          |          |          |          |          |
|     | 5.10300000 | 7.09690700 | 14.55306600 |          |          |          |          |          |          |
| Br  | 0.78679500 | 6.93691200 | 13.42165500 |          |          |          |          |          |          |
| C   | 1.54549600 | 5.54112800 | 14.54133900 |          |          |          |          |          |          |
| C   | 2.88301100 | 5.21043900 | 14.34091400 |          |          |          |          |          |          |
| C   | 0.76483800 | 4.90026100 | 15.50304200 |          |          |          |          |          |          |
| C   | 3.45709900 | 4.20873000 | 15.12831300 |          |          |          |          |          |          |
| H   | 3.14419900 | 2.77438900 | 16.70997000 |          |          |          |          |          |          |
|     | 1.17139000 | 1.29443500 | 1.96033000 |          |          |          |          |          |          |
|     | 3.94746900 | 2.93379800 | 3.69217000 |          |          |          |          |          |          |
|     | 5.71772900 | 3.40626400 | 1.07181000 |          |          |          |          |          |          |
|     | 5.19280700 | 0.04063300 | 2.54094000 |          |          |          |          |          |          |
|     | 0.27772800 | 0.11414900 | 2.65444300 |          |          |          |          |          |          |
|     | 1.12778100 | 0.45978700 | 1.71067700 |          |          |          |          |          |          |
|     | 0.49229800 | -0.02861200 | 4.02533200 |          |          |          |          |          |          |
|     | 0.00000000 | 0.00000000 | 0.00000000 |          |          |          |          |          |          |
|     | 2.22525300 | -1.20031700 | 2.16197600 |          |          |          |          |          |          |
|     | 0.04328500 | -0.33277500 | 0.66495200 |          |          |          |          |          |          |
|     | 1.59497800 | 0.77038200 | 4.45747900 |          |          |          |          |          |          |
|     | 0.00000000 | 0.00000000 | 0.00000000 |          |          |          |          |          |          |
|     | 0.00000000 | 0.00000000 | 0.00000000 |          |          |          |          |          |          |
|     | 0.00000000 | 0.00000000 | 0.00000000 |          |          |          |          |          |          |
|     | 0.00000000 | 0.00000000 | 0.00000000 |          |          |          |          |          |          |
|     | 0.00000000 | 0.00000000 | 0.00000000 |          |          |          |          |          |          |
|     | 0.00000000 | 0.00000000 | 0.00000000 |          |          |          |          |          |          |
|     | 0.00000000 | 0.00000000 | 0.00000000 |          |          |          |          |          |          |
|     | 0.00000000 | 0.00000000 | 0.00000000 |          |          |          |          |          |          |
|     | 0.00000000 | 0.00000000 | 0.00000000 |          |          |          |          |          |          |
|     | 0.00000000 | 0.00000000 | 0.00000000 |          |          |          |          |          |          |
|     | 0.00000000 | 0.00000000 | 0.00000000 |          |          |          |          |          |          |
|     | 0.00000000 | 0.00000000 | 0.00000000 |          |          |          |          |          |          |
|     | 0.00000000 | 0.00000000 | 0.00000000 |          |          |          |          |          |          |
| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| C    | -2.77862900 | -0.79961800 | -3.11662200 |
| C    | -0.66522600 | -1.85110300 | -1.03576200 |
| C    | -3.45658000 | -2.43370100 | -1.09571500 |
| H    | 0.62494300  | 3.47568900  | 1.02696100  |
| H    | -0.66179500 | 3.78404000  | -0.16544300 |
| H    | 0.69126600  | 1.54968000  | 2.76036000  |
| C    | 0.53632100  | 0.20553300  | 1.59624300  |
| H    | -2.52675700 | 2.40545000  | 3.23548600  |
| C    | -2.56546400 | 3.73232300  | 2.06560700  |
| C    | -1.48434700 | -0.10029100 | -3.39835900 |
| C    | -2.32581800 | -0.38839200 | -3.45149000 |
| H    | 0.14566800  | -1.13013300 | -1.18887300 |
| H    | -0.53393600 | -2.68680600 | -1.73293900 |
| C    | -3.46471100 | -2.76340900 | -0.05171200 |
| C    | -3.17153000 | -3.27582400 | -1.73866400 |
| C    | -1.60024500 | 0.21723700  | -2.53585600 |
| H    | -1.22299400 | 3.50235500  | 3.09668800  |
| C    | 0.46634000  | 2.46755200  | -0.41807000 |
| H    | -0.55110400 | 0.29366600  | -0.57137000 |
| C    | -4.66198400 | 0.10816400  | 1.61614300  |
| C    | -1.92010500 | -1.75569100 | -3.62601200 |
| C    | -2.37030700 | -2.41823600 | 3.84460600  |
| C    | -1.60563700 | -2.95235600 | 3.14808300  |
| C    | -1.84267400 | -1.32403000 | 1.72179800  |
| C    | -3.56458500 | -3.44244100 | 4.49029300  |
| C    | -5.30708100 | -2.21152000 | 4.11400400  |
| C    | -2.23529900 | -3.70814600 | 4.14309300  |
| C    | -0.57091400 | -3.15713700 | 2.87905200  |
| C    | -4.52029700 | -4.03127400 | 5.26479300  |
| C    | -1.69165900 | -4.50262000 | 4.64814100  |

**TS-4-5-I-PMe2Ph**

\[
\begin{align*}
E (OSS) &= -2371.43028050 \\
E (T) &= -2371.41605770 \\
S^2(OSS) &= 0.5479 \\
G_{corr} &= 0.519749 \\
\nu &= -276.90 \text{ cm}^{-1}
\end{align*}
\]

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| Ni   | -0.34083600 | 0.44923300 | 0.01234500 |
| P    | 0.04180000  | -0.14834500 | -0.20972030 |
| C    | -1.65254700 | -1.15548400 | 0.87201600 |
| P    | 1.49086700  | 0.73557400  | 1.28600800 |
| C    | 1.63446600  | 0.56804900  | -2.68730000 |
| C    | 1.71899800  | 1.96512500  | -2.85211000 |
| H    | 0.83959500  | 2.57708400  | -2.63917300 |
| C    | 2.92418800  | 2.57764300  | -3.16521600 |
| H    | 2.96855600  | 3.65870500  | -3.27125600 |

---

**TS-4-5-I-PMe2Ph**

\[
\begin{align*}
E (OSS) &= -2371.43028050 \\
E (T) &= -2371.41605770 \\
S^2(OSS) &= 0.5479 \\
G_{corr} &= 0.519749 \\
\nu &= -276.90 \text{ cm}^{-1}
\end{align*}
\]
\begin{table}
\centering
\begin{tabular}{cccc}
\hline
 & C & H & P \\
\hline
\text{C} & -4.47000300 & 2.58088400 & 1.29879100 \\
\text{C} & -3.67916900 & 2.57981000 & 3.98680900 \\
\text{H} & -1.69349800 & 3.00022500 & 3.24416500 \\
\text{C} & -5.40920000 & 2.32666900 & 2.30906200 \\
\text{H} & -4.77373500 & 2.56384700 & 0.25395200 \\
\text{C} & -5.01291900 & 2.32344900 & 3.65047000 \\
\text{H} & -3.36740300 & 2.57338800 & 5.02938900 \\
\text{H} & -6.44596700 & 2.12573300 & 2.04633000 \\
\text{H} & -5.74104200 & 2.11813200 & 4.43117300 \\
\hline
\text{E (OSS)} & -2946.81831720 \\
\text{E (T)} & -2946.80534049 \\
\text{S^2(OSS)} & 0.5464 \\
\text{G_{corr}} & 0.670258 \\
\hline
\end{tabular}
\caption{TS-4-5-I-PMePh$_2$}
\end{table}
\[ S_2(OSS) = 0.5443 \]
\[ G_{corr} = 0.372202 \]
\[ v = -285.62 \text{ cm}^{-1} \]
\[ \text{Ni} \quad 0.99546000 \quad -0.07223400 \quad 0.07217300 \]
\[ \text{TS}-4-5-Br-PMe}_3 \]
\[ E(\text{OSS}) = -1797.8223389 \]
\[ E(T) = -1797.8047425 \]
\[ S^2(\text{OSS}) = 0.5443 \]
\[ G_{corr} = 0.372202 \]
\[ v = -285.62 \text{ cm}^{-1} \]
\[ \text{Ni} \quad 0.95826500 \quad -4.18057000 \quad -1.63092700 \]
\[ \text{P} \quad 1.23643400 \quad 5.16741900 \quad -2.66310100 \]
\[ \text{C} \quad -0.65690300 \quad 3.32729500 \quad -6.06907200 \]
\[ \text{H} \quad 0.35656700 \quad 5.32846100 \quad -4.99445700 \]
\[ -1.49822600 \quad -1.37237200 \quad 1.16386300 \]
\[ -1.04456900 \quad -3.05897400 \quad -1.70845700 \]
\[ 0.29115200 \quad -5.66035400 \quad 0.13497200 \]
\[ -1.23532000 \quad -2.28589800 \quad 1.83060500 \]
\[ -0.07818000 \quad -5.79632800 \quad -1.19324700 \]
\[ 0.94715900 \quad -6.25861200 \quad 0.65098000 \]
\[ 0.54864300 \quad -3.67050100 \quad 0.03306100 \]
\[ 3.52163700 \quad -3.8749900 \quad -1.55618400 \]
\[ 0.58464300 \quad -3.67050100 \quad 0.03306100 \]
\[ TS-4-5-Cl-PMe}_3 \]
\[ E(\text{OSS}) = -1797.8223389 \]
\[ E(T) = -1797.8047425 \]
\[ S^2(\text{OSS}) = 0.5443 \]
\[ G_{corr} = 0.372202 \]
\[ v = -285.62 \text{ cm}^{-1} \]
\[ \text{Ni} \quad 0.95826500 \quad -4.18057000 \quad -1.63092700 \]
\[ \text{P} \quad 1.23643400 \quad 5.16741900 \quad -2.66310100 \]
\[ \text{C} \quad -0.65690300 \quad 3.32729500 \quad -6.06907200 \]
\[ \text{H} \quad 0.35656700 \quad 5.32846100 \quad -4.99445700 \]
\[ -1.49822600 \quad -1.37237200 \quad 1.16386300 \]
\[ -1.04456900 \quad -3.05897400 \quad -1.70845700 \]
\[ 0.29115200 \quad -5.66035400 \quad 0.13497200 \]
\[ -1.23532000 \quad -2.28589800 \quad 1.83060500 \]
\[ -0.07818000 \quad -5.79632800 \quad -1.19324700 \]
\[ 0.94715900 \quad -6.25861200 \quad 0.65098000 \]
\[ 0.54864300 \quad -3.67050100 \quad 0.03306100 \]
\[ TS-4-5-Br-PMe}_3 \]
\[ E(\text{OSS}) = -1797.8223389 \]
\[ E(T) = -1797.8047425 \]
\[ S^2(\text{OSS}) = 0.5443 \]
\[ G_{corr} = 0.372202 \]
\[ v = -285.62 \text{ cm}^{-1} \]
\[ \text{Ni} \quad 0.95826500 \quad -4.18057000 \quad -1.63092700 \]
\[ \text{P} \quad 1.23643400 \quad 5.16741900 \quad -2.66310100 \]
\[ \text{C} \quad -0.65690300 \quad 3.32729500 \quad -6.06907200 \]
\[ \text{H} \quad 0.35656700 \quad 5.32846100 \quad -4.99445700 \]
\[ -1.49822600 \quad -1.37237200 \quad 1.16386300 \]
\[ -1.04456900 \quad -3.05897400 \quad -1.70845700 \]
\[ 0.29115200 \quad -5.66035400 \quad 0.13497200 \]
\[ -1.23532000 \quad -2.28589800 \quad 1.83060500 \]
\[ -0.07818000 \quad -5.79632800 \quad -1.19324700 \]
\[ 0.94715900 \quad -6.25861200 \quad 0.65098000 \]
\[ 0.54864300 \quad -3.67050100 \quad 0.03306100 \]

S50
S2(OSS) = 1.0067
E (T) = -1796.05665155
E (OSS) = -1796.05732288

Ni                -0.62583000    0.66902000    0.02368500
Cl                 0.60732300    0.62395700    1.48038700
H                  3.03027300   -3.68048400    4.85448100
H                  0.63961800   -3.12686500    5.23401400
H                  4.34166500   -2.45919400    3.12703300
C                  2.55569100   -2.90133700    4.26349700
C                  1.20799400   -2.58950500    4.47732100
C                  3.29384600   -2.14662200    3.91961200
C                  0.58388500   -1.58523100    3.71963300
C                  2.67623400   -1.21251400    2.53262400
C                  3.03027300   -3.68048400    4.85448100
Cl                 0.60732300    0.62395700    1.48038700

|    |    |    |
|----|----|----|
|    |    |    |

Gcorr  = 0.366149

\[
P\end{align*}

5-I-PMe\textsubscript{3}

E (OSS) = -1796.05732288
E (T) = -1796.05665155
S^2(OSS) = 1.0067
Gcorr  = 0.366149

Ni   -0.62583000    0.66902000    0.02368500
P    -1.21459500    2.27719400   -1.52055600
C    -1.59541400    3.90919700   -0.75042900
C    -2.77287800    1.91895600   -2.43877600
C    -0.58524000    2.75157000   -2.88104000
H    -1.97539300    4.62646200   -1.48736700
H    -0.69109300    4.31914200   -0.28898500
C    -3.05842200    2.75133400   -3.09273100
C    -3.57373000    1.73183400   -1.71626900
H    0.12216000    1.88801300   -3.52897800
H    0.90012900    3.06789400   -2.45640200
P    0.92071400    1.77038500    1.30936900
P    -0.26235200   -1.26585900   -1.16032400
C    2.12032600    2.82469800    0.37654700
C    2.06860700    0.74664000    2.33593400

5-I-PMe\textsubscript{2}Ph

\[
P\end{align*}

E (OSS) = -2371.44147589
E (T) = -2371.44128873
S^2(OSS) = 1.0117
Gcorr  = 0.516916

Ni   -0.47346700    0.63783000   -0.19883400
P    0.06944800   -0.28957200   -2.22969100
P    -1.77334800   -1.00075600    0.75351400
P    1.27933300    1.02946800    2.12852300
C    1.72530300    0.37709700   -2.67487600
C    1.82546400    1.73960900   -3.01012100
\[
\begin{align*}
\text{E (OSS)} &= -2946.82852389 \\
\text{E (T)} &= -2946.82830820 \\
\text{S^2 (OSS)} &= 1.0113 \\
\text{G_{corr}} &= 0.66871
\end{align*}
\]
| Atoms | Coordinates |
|-------|-------------|
| C     | -3.71351700 1.88107100 4.22070900 |
| H     | -4.14516200 1.01513300 4.71570400 |
| C     | -3.15992400 1.73884000 2.94692700 |
| H     | -3.14961600 0.76149100 2.47733500 |
| C     | -1.04349600 4.22527500 0.31405700 |
| C     | -1.71789100 5.32598900 -0.23653500 |
| C     | -2.75410000 5.23439900 -0.54573200 |
| C     | -1.06068800 6.54842900 -0.39345700 |
| H     | -0.50726000 7.39054600 -0.83060400 |
| C     | 0.26881700 6.69113200 0.01339900 |
| H     | 0.77784500 7.64321700 -0.11173900 |
| C     | 0.94079800 5.60526000 0.58125500 |
| H     | 1.97606000 5.70068600 0.89507100 |
| C     | 0.28696800 4.38172800 0.72606900 |
| C     | 0.81672400 5.33460000 1.14420000 |
| C     | 1.76003800 0.63596600 1.45006800 |
| C     | 1.61419700 1.02358300 3.24760000 |
| C     | 0.35435700 1.34367800 3.76936000 |
| C     | -0.51350900 1.34541700 3.12114900 |
| C     | 0.19870900 1.64040000 5.12618600 |
| C     | -0.78820000 1.88499300 5.50943500 |
| C     | 1.30694900 1.61415300 5.97448200 |
| C     | 1.19124300 1.84382800 7.03050000 |
| C     | 2.56816500 2.18966000 5.46567000 |
| C     | 3.43088700 1.25169800 6.12605700 |
| C     | 2.72159100 0.98310000 4.11197300 |
| C     | 3.70154100 0.71780700 3.74230100 |
| C     | 2.96175900 1.88167000 0.80786600 |
| C     | 3.37696000 3.00442200 1.53911300 |
| C     | 3.03939100 3.14825800 2.56014100 |
| C     | 4.22087000 3.95533900 0.95903900 |
| C     | 4.53233300 4.81966700 1.54058500 |
| C     | 4.66680600 3.79757800 -0.35527400 |
| C     | 5.32176700 4.53972500 -0.80373600 |
| C     | 4.26613000 2.67692500 -1.08858500 |
| H     | 4.60398700 2.54002000 -2.11239200 |
| C     | 3.41880200 1.73020000 -0.51395700 |
| C     | 3.11466300 0.86734000 -1.09668000 |
| C     | 2.77799900 -0.91180800 1.52095900 |
| C     | 2.13290200 -2.09221900 1.92725200 |
| C     | 4.14777000 -0.95829400 1.22367600 |
| C     | 2.84134000 -3.28958300 2.02740700 |
| C     | 1.07152700 -2.80873300 2.15251900 |
| C     | 4.85285700 -2.16161200 1.31555100 |
| C     | 4.67512500 -0.06306000 0.91320800 |
| C     | 4.20394300 -3.30532000 1.71684200 |
| C     | 2.32474000 -4.19150300 2.34358300 |
| C     | 5.91285600 -2.17963000 1.07508700 |
| C     | 4.75397400 -4.26522200 1.78874500 |

5-Br-PMe₃

E(OSS) = \(-1797.8345227\)
E(T) = \(-1797.8341439\)
S²(OSS) = \(1.0115\)

Gcorr = 0.368688
\[
E(T) = -2.244.88718919 \\
S^\text{OSS} = 1.0118 \\
G_{\text{corr}} = 0.370729
\]
| Atoms | \( x \) | \( y \) | \( z \) |
|-------|-------|-------|-------|
| Ni    | 3.19335000 | 7.61491500 | 11.71328600 |
| P     | 1.42114100  | 8.89806000 | 11.02938100 |
| C     | 0.92926700  | 10.20501400 | 12.23542700 |
| C     | -0.14454400 | 7.94826000 | 10.80984700 |
| C     | 1.53713400  | 9.85467100 | 9.45469000 |
| H     | 0.00722700  | 10.71403700 | 11.93061000 |
| H     | 1.73419900  | 10.94368500 | 12.31335900 |
| H     | -0.99097200 | 8.60345000 | 10.57235500 |
| H     | -0.35757600 | 7.39969300 | 11.73337800 |
| H     | 1.66951500  | 9.16654200 | 8.61384500 |
| H     | 2.41126400  | 10.51382600 | 9.49478900 |
| P     | 4.67452100  | 9.10374900 | 12.61927200 |
| P     | 3.72089000  | 6.19142300 | 10.00155600 |
| C     | 5.17192800  | 10.56633900 | 11.60707600 |
| C     | 6.29539000  | 8.30412600 | 12.99476300 |
| C     | 4.24443100  | 9.87646900 | 14.23909700 |
| C     | 3.47263200  | 6.77897500 | 8.26781500 |
| C     | 5.51298200  | 5.74015200 | 9.99938200 |
| C     | 2.91216400  | 4.53276300 | 9.96311700 |
| H     | 5.94598000  | 11.16362400 | 12.10392800 |
| H     | 4.29733600  | 11.20496000 | 11.42812700 |
| H     | 6.99713300  | 9.00042000 | 13.46914000 |
| H     | 6.73882700  | 7.92256500 | 12.06883300 |
| H     | 4.00335100  | 9.08339400 | 14.95427800 |
| H     | 3.35683100  | 10.50649200 | 14.12017600 |
| H     | 3.98225500  | 7.73355400 | 8.13028300 |
| H     | 2.40375800  | 6.92744900 | 8.08120600 |
| H     | 6.11448200  | 6.64307500 | 9.84946500 |
| H     | 5.74919300  | 5.01732500 | 9.20899900 |
| H     | 3.14119400  | 4.00121000 | 10.89240200 |
| H     | 3.25166400  | 3.93747700 | 9.10942800 |
| H     | 0.78299700  | 9.74915000 | 13.21948000 |
| H     | -0.01831900 | 7.21718900 | 10.00393800 |
| H     | 0.63923400  | 10.46021600 | 9.28337800 |
| H     | 3.86141000  | 6.05808400 | 7.53849000 |
| H     | 5.77644700  | 5.30789500 | 10.97047500 |
| H     | 1.82558000  | 4.65920500 | 9.90808200 |
| H     | 5.06726700  | 10.48533600 | 14.63304300 |
| H     | 5.55019000  | 10.22549200 | 10.63980000 |
| H     | 6.12182700  | 7.45502400 | 13.66458500 |
| I     | 2.49872700  | 6.02825200 | 13.83966400 |

6-I-PMe₃

\[
E = -1564.41378215 \\
G_{corr} = 0.285068
\]
\[
6\text{-I-PMe}_2\text{Ph}
\]

\[
\begin{align*}
E &= -2139.7985927 \\
G_{\text{corr}} &= 0.434689
\end{align*}
\]

\[
\begin{array}{cccc}
\text{C} & 0.97962900 & 0.91500400 & 5.48958500 \\
\text{H} & 2.22347900 & 0.06583000 & 3.95828900 \\
\text{C} & 1.42179900 & 0.76664800 & 4.17039000 \\
\text{C} & 0.83291800 & 1.51040900 & 3.13717500 \\
\text{H} & 2.22347900 & 0.06583000 & 3.95828900 \\
\end{array}
\]

\[
\begin{align*}
6\text{-I-PMePh}_2
\end{align*}
\]

\[
\begin{align*}
E &= -2715.18416817 \\
G_{\text{corr}} &= 0.58561
\end{align*}
\]

\[
\begin{array}{cccc}
\text{C} & -0.04558100 & 1.81404600 & 5.79150300 \\
\text{H} & -0.38593700 & 1.92848000 & 6.81729900 \\
\text{C} & -0.63738600 & 2.56121500 & 4.76757500 \\
\text{H} & -1.44175400 & 3.25563100 & 4.99298900 \\
\text{C} & -0.20922250 & 2.40174900 & 3.44913600 \\
\text{H} & -0.69712220 & 2.95188800 & 2.64769400 \\
\text{C} & 2.48677900 & -0.04467300 & 1.29934200 \\
\text{H} & 1.97514100 & -0.97590500 & 1.56313200 \\
\text{H} & 3.35185000 & 0.93665500 & 1.95762500 \\
\text{P} & 2.84201300 & -0.12808800 & 0.26660300 \\
\text{C} & 2.42417600 & 2.81434900 & 1.12461400 \\
\text{H} & 1.83768800 & 3.73674200 & 1.18151500 \\
\text{H} & 2.87084900 & 2.75110500 & 0.12724700 \\
\text{C} & 3.21752200 & 2.83703700 & 1.87984100 \\
\text{I} & -1.56805600 & 3.63130000 & -0.51879800 \\
\end{array}
\]

\[
\begin{align*}
\text{Ni} & 0.77183100 & 0.79556700 & 0.03949200 \\
\text{P} & 0.80753700 & 0.85591400 & -2.25606400 \\
\text{C} & -0.73225800 & 0.13153800 & -2.96427300 \\
\text{C} & -1.86958400 & 0.92691100 & -3.17833600 \\
\text{H} & -1.81996300 & 2.00293400 & -3.04201500 \\
\text{C} & -3.07996900 & 0.34641000 & -3.56649900 \\
\text{H} & -3.95010200 & 0.97711200 & -3.72994600 \\
\text{C} & -3.17188300 & -1.03620100 & -3.74701900 \\
\text{H} & -4.11407400 & -1.48696800 & -4.06479000 \\
\text{C} & -2.04229000 & -1.83481700 & -3.54444600 \\
\text{C} & -2.10170100 & -2.91071900 & -3.68719500 \\
\text{C} & -0.83281000 & -1.25731500 & -3.15659200 \\
\text{C} & 0.03346700 & -1.89137700 & -2.99336500 \\
\text{C} & 2.12623800 & -0.15772600 & -3.03843200 \\
\text{C} & 2.82698600 & -1.06694800 & -2.23297800 \\
\text{C} & 2.60346100 & -1.12769900 & -1.17319300 \\
\text{C} & 3.80774000 & -1.89444400 & -2.78586900 \\
\text{C} & 4.33557800 & -2.59776300 & -2.14857500 \\
\text{C} & 4.10164700 & -1.81389300 & -4.14826700 \\
\text{C} & 4.86726000 & -2.45303900 & -4.58002800 \\
\text{C} & 3.40761800 & -0.90906000 & -4.95924000 \\
\text{C} & 3.63246800 & -0.84615600 & -6.02089300 \\
\text{C} & 2.42187100 & -0.08853600 & -4.40998500 \\
\text{C} & 1.88017800 & 0.59721400 & -5.05552200 \\
\text{C} & 0.94198700 & 2.49319800 & -3.10153700 \\
\text{C} & 0.78656700 & 2.42615600 & -4.18725000 \\
\text{C} & 1.93998700 & 2.89549600 & -2.90102600 \\
\text{C} & 0.20800000 & 3.18391100 & -2.67726600 \\
\text{C} & -0.80083700 & 2.33419500 & 0.77010800 \\
\text{C} & -1.11560400 & 2.07758000 & 2.56197400 \\
\text{C} & -0.12738300 & 2.45055500 & 3.48903300
\end{align*}
\]
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| H    | -0.28338900 | 2.15943400 | 5.55024200 |
| C    | -1.41985700 | 1.47653700 | 5.29084700 |
| H    | -1.53697000 | 1.24391000 | 6.34598200 |
| C    | 2.40106700 | 1.09200800 | 4.37444000 |
| H    | -3.28419000 | 0.55462300 | 4.71063500 |
| C    | -2.25246000 | 1.39024800 | 3.01699800 |
| H    | -3.02015200 | 1.07053000 | 2.31977800 |
| C    | -0.21380800 | 4.07512300 | 0.67898400 |
| H    | -0.93476600 | 5.13050100 | 1.26172900 |
| C    | -1.84861800 | 4.96215000 | 1.81372000 |
| H    | -0.47645500 | 6.44279100 | 1.14607800 |
| C    | -1.03776000 | 7.25394500 | 1.60258900 |
| H    | 0.70524000 | 6.14470000 | 0.46431600 |
| C    | 1.06064500 | 7.73780600 | 0.35901800 |
| C    | 1.42880400 | 5.66993400 | 0.13206400 |
| H    | 2.35084000 | 5.87389900 | -0.67008700 |
| C    | 0.97243900 | 4.35398900 | -0.01306300 |
| C    | 1.54197800 | 3.53571200 | -0.44170200 |
| H    | -2.49890700 | 2.48286000 | 0.05334800 |
| H    | -3.12140300 | 3.16284400 | 0.64422000 |
| C    | -2.98224300 | 1.50498600 | 0.00039000 |
| H    | -2.40790100 | 2.87820700 | -0.96193300 |
| P    | 0.19163300 | -1.07276100 | 1.26852400 |
| C    | 1.02094300 | -2.56613000 | 0.58144500 |
| C    | 2.34977100 | -2.84887800 | 0.94144000 |
| H    | 2.85660400 | -2.24075300 | 1.68467500 |
| C    | 3.03911800 | -3.89854000 | 0.33203200 |
| H    | 4.06602400 | -4.10688800 | 0.62192100 |
| C    | 2.41603100 | -4.67713500 | -0.64809600 |
| H    | 2.95553300 | -5.49111700 | -1.12417100 |
| C    | 1.09574700 | -4.40028900 | -1.01287600 |
| H    | -0.60261000 | 0.00019500 | -1.77325200 |
| C    | 0.40268500 | -3.35217800 | -0.40422500 |
| H    | -0.62092400 | -3.14537600 | -0.70148900 |
| C    | -1.59326500 | -1.50545800 | 1.26658500 |
| C    | -2.35936000 | -1.10658800 | 0.16031500 |
| H    | -1.88049100 | -0.57110900 | -0.65330400 |
| C    | -3.72869200 | -1.37774300 | 0.10706200 |
| H    | -4.30371000 | -1.06628900 | -0.76078100 |
| C    | -4.35057300 | -2.03580900 | 1.17119000 |
| H    | -5.41800700 | -2.23791000 | 1.13912300 |
| C    | -3.59556800 | -2.43426900 | 2.27894700 |
| H    | -4.07553100 | -2.94713100 | 3.10864600 |
| C    | -2.22364700 | -2.17842800 | 2.32475400 |
| H    | -1.65253800 | -2.49579800 | 3.19181500 |
| C    | 0.67114600 | -1.10269600 | 3.04895800 |
| H    | 0.63805300 | -2.10899900 | 3.47753600 |
| C    | 0.00065900 | -0.44258800 | 3.60485300 |
| C    | 1.68550300 | -0.70314100 | 3.13386400 |
| I    | 3.28360800 | 1.28260500 | 0.98221000 |

6-I-PPh₃

\[
E = -3290.56151807
\]

\[
G_{corr} = 0.735468
\]
**6-Br-PMe₃**

\[
E = -1566.19226774
\]

\[
G_{corr} = 0.287107
\]
\[ E = -1552.04429788 \]

\[ G_{\text{corr}} = 0.182396 \]

8-Br-PMe₃

\[ \text{Ni} \quad -2.51527500 \quad 1.80092000 \quad -0.03276900 \]
\[ \text{P} \quad -4.38851900 \quad 1.48763400 \quad -1.18364500 \]
\[ \text{C} \quad -5.42814700 \quad 0.19073800 \quad -0.37829600 \]
\[ \text{Br} \quad -4.40243900 \quad 0.95404800 \quad -2.95305400 \]
\[ \text{C} \quad -5.53034900 \quad 2.93934200 \quad -1.21686000 \]
\[ \text{E} \quad -6.41317600 \quad 0.10190500 \quad -0.85156400 \]
\[ \text{P} \quad -5.55218000 \quad 0.44620700 \quad 0.68028500 \]
\[ \text{C} \quad -5.44884200 \quad 0.86884900 \quad -3.32584000 \]
\[ \text{H} \quad -3.92640700 \quad -0.01728000 \quad -3.05528200 \]
\[ \text{H} \quad -5.04366800 \quad 3.77575200 \quad -1.73080100 \]
\[ \text{P} \quad -5.74682800 \quad 3.24839400 \quad -0.18913800 \]
\[ \text{C} \quad 0.84711000 \quad 1.01423100 \quad -1.07728500 \]
\[ \text{C} \quad 0.50677000 \quad 0.16478500 \quad -0.01508200 \]
\[ \text{C} \quad -0.97523200 \quad -0.22175500 \quad -2.43164100 \]
\[ \text{H} \quad 0.59936000 \quad 3.04152600 \quad -1.17650700 \]
\[ \text{H} \quad -0.32606200 \quad 2.81174100 \quad -2.67435900 \]
\[ \text{H} \quad 0.84549000 \quad 0.85786600 \quad 0.76098000 \]
\[ \text{H} \quad 1.37125500 \quad -0.16925600 \quad -0.60104700 \]
\[ \text{H} \quad -1.55022300 \quad 0.23092300 \quad -3.24509000 \]
\[ \text{C} \quad -1.53561000 \quad -1.08148600 \quad -2.04845000 \]
\[ \text{C} \quad -4.91174100 \quad -0.77349200 \quad -0.43968200 \]
\[ \text{C} \quad 0.88047200 \quad 1.36260200 \quad -3.56781700 \]
\[ \text{C} \quad -6.47074300 \quad 2.70394900 \quad -1.72917700 \]
\[ \text{H} \quad 1.16291800 \quad 1.86504700 \quad -2.20074200 \]
\[ \text{H} \quad 0.04842400 \quad -0.70315200 \quad 0.47080400 \]
\[ \text{H} \quad -0.01359900 \quad -0.57019400 \quad -2.82716000 \]
\[ \text{C} \quad -1.89536400 \quad 2.30945900 \quad 1.70066000 \]
\[ \text{C} \quad -3.20549600 \quad 2.91896000 \quad 1.56358300 \]
\[ \text{C} \quad -4.27886400 \quad 2.46159500 \quad 2.39853800 \]
\[ \text{C} \quad -4.11752400 \quad 1.38229200 \quad 3.23048300 \]
\[ \text{C} \quad -2.84792000 \quad 0.73501200 \quad 3.31437900 \]
\[ \text{C} \quad -1.76043100 \quad 1.20268900 \quad 2.61272000 \]
\[ \text{C} \quad -3.29064200 \quad 3.91571200 \quad 1.13276200 \]
\[ \text{C} \quad -5.22225000 \quad 3.00345500 \quad 2.37495700 \]
\[ \text{C} \quad -4.93930000 \quad 1.03241300 \quad 3.85335300 \]
\[ \text{C} \quad -2.72962000 \quad -0.13928000 \quad 3.96092500 \]
\[ \text{Br} \quad -0.78725900 \quad 0.73586900 \quad 2.72885000 \]

7-Cl-PMe₃

\[ E = -1552.04429788 \]

\[ G_{\text{corr}} = 0.182396 \]

\begin{align*}
\text{Ni} & \quad 3.06690600 \quad 7.31937300 \quad 11.59599400 \\
\text{Br} & \quad 4.53599100 \quad 6.21555900 \quad 10.09988000 \\
\text{H} & \quad 0.34253200 \quad 6.17763100 \quad 13.76685600 \\
\text{H} & \quad 4.69483900 \quad 7.72734000 \quad 14.78979100 \\
\text{P} & \quad 0.40746900 \quad 8.08955500 \quad 10.21980800 \\
\text{P} & \quad 4.28453600 \quad 4.89796700 \quad 13.99716200 \\
\text{H} & \quad 2.65338700 \quad 4.31490100 \quad 13.62245200 \\
\text{H} & \quad 1.40658800 \quad 10.96868500 \quad 9.63695700 \\
\text{P} & \quad 3.40688500 \quad 4.83554700 \quad 15.28569700 \\
\text{P} & \quad 1.40338200 \quad 9.98270000 \quad 13.51978600 \\
\text{H} & \quad -0.19563400 \quad 8.08955500 \quad 10.21980800 \\
\text{P} & \quad 4.28453600 \quad 4.89796700 \quad 13.99716200 \\
\text{H} & \quad 2.65338700 \quad 4.31490100 \quad 13.62245200 \\
\text{H} & \quad 1.40658800 \quad 10.96868500 \quad 9.63695700 \\
\end{align*}
\[ G_{\text{corr}} = 0.268325 \]
\[ E = -1783.69729748 \]

\[ G_{\text{corr}} = 0.268563 \]
\[ E = -1783.69729748 \]

\[ \nu_{\text{Ni}} = -2.60106300 \quad 1.65679100 \quad 0.00721300 \]

\[ \text{TS-8-9-Br-PMe}_{3} \]

\[ G_{\text{corr}} = 0.268325 \]
\[ v = -85.30 \text{ cm}^{-1} \]

\[ \nu_{\text{Ni}} = -2.60106300 \quad 1.65679100 \quad 0.00721300 \]

\[ \text{TS-8-9-Cl-PMe}_{3} \]

\[ G_{\text{corr}} = 0.269087 \]
\[ v = -104.13 \text{ cm}^{-1} \]

\[ \nu_{\text{Ni}} = -0.80924900 \quad 0.56031400 \quad -0.1255070 \]

\[ \text{Cl} \]

\[ -2.60106300 \quad 1.65679100 \quad 0.00721300 \]
\[
G_{\text{corr}} = 0.268779 \\
E = -1334.70742817 \\
G_{\text{corr}} = 0.268779
\]

9-Br-PMe₃

\[
E = -1336.69800763 \\
G_{\text{corr}} = 0.271175
\]

9-I-PMe₃
Gcorr  = 0.270617
E  = -1783.75121852
9-Cl-PMe₃

Cl
Me₃P
Ni

E  =  -1783.75121852
Gcorr  =  0.270617

Ni -1.66158000 0.51749800 -0.01575800
P -0.21648400 -0.68257500 1.45203100
C -2.86027200 1.38547500 1.88710500
C -2.42448100 2.38335800 2.77399600
C -1.99047800 2.06959500 4.06051500
C -1.98751600 0.74050000 4.50530300
C -2.42208600 -0.26661800 3.63999300
C -2.84608400 0.05664800 2.34736700
C -2.43524700 3.42245900 2.45338300
H -1.65832100 0.49487100 5.50991700
H -1.65832100 2.86267500 4.73269400
H -2.43524700 3.42245900 2.45338300

Cl  -3.47625700 1.53010200 0.95223600

TS-9-3-I-PMe₃

E  =  -1334.89533628

Gcorr  =  0.265005
v  =  -88.03 cm⁻¹
### TS-9-3-Br-PMe3

| Element | x          | y          | z          |
|---------|------------|------------|------------|
| Ni      | 0.71481000 | 1.22553000 | -0.03001400|
| P       | -0.48274500| 3.04627000 | -0.97831300|
| C       | -1.43605900| 3.86803000 | 0.37238000 |
| C       | -1.79203400| 2.73018900 | -2.23942500|
| C       | 0.43314200 | 4.47372200 | -1.71463700|
| H       | -1.99258300| 4.73828700 | 0.00432300 |
| H       | -0.74611400| 4.18705700 | 1.16113300 |
| P       | 2.55352300 | 0.68320500 | -0.99142800|
| C       | 2.07813800 | 0.17636500 | -2.69552300|
| C       | 3.85228400 | 1.95522600 | -1.24535800|
| C       | 3.46790400 | -0.76434000| -0.33441400|
| H       | 1.63524700 | 1.02841400 | -2.20817000|
| C       | 1.33202600 | -0.62227400| -2.63956000|
| C       | 3.41084000 | 2.83675000 | -1.72116700|
| H       | 4.65372200 | 1.56320600 | -1.88157800|
| H       | 3.86903200 | -0.52168200| 0.65353600 |
| C       | 4.28885400 | -1.04096500| -1.00519500|
| H       | -2.13681500| 3.14760800 | -1.97049200|
| H       | -1.33229300| 2.35883500 | -3.16211700|
| H       | -0.24207700| 5.29949800 | -1.97049200|
| C       | 2.95280900 | -0.17970200| -3.25290600|
| H       | 4.26977000 | 2.25072600 | -0.27888100|
| H       | 2.77825400 | -1.60817000| -0.23434800|
| C       | 1.78582400 | 1.56724300 | 1.44928400 |
| C       | 1.89417200 | 0.62190200 | 2.48136600 |
| C       | 2.41474600 | 0.99310400 | 3.72550100 |
| C       | 2.85479000 | 2.30303000 | 3.94479800 |
| C       | 2.77585200 | 3.24220600 | 2.91253000 |
| C       | 2.25860000 | 2.87139400 | 1.66522300|
| H       | 1.54544100 | -0.39262500| 2.31388300 |
| H       | 2.47598300 | 0.25731700 | 4.52466200 |
| H       | 3.26216600 | 2.58759100 | 4.91169100 |
| H       | 3.12375300 | 4.26058900 | 3.07196300 |
| H       | 2.21411400 | 3.60036800 | 0.85929000|
| Br      | -1.02463200| -0.51900700| 0.31646300|

### TS-9-3-Cl-PMe3

| Element | x          | y          | z          |
|---------|------------|------------|------------|
| Ni      | -0.46345900| 1.07262400 | -0.11445600|
| P       | -1.64277900| 2.96437400 | -0.98048100|
| C       | -2.43743500| 3.79902700 | 0.46244500 |
In Toluene

Ni(PMe₃)₆

\[ \begin{align*}
G_{\text{corr}} &= 0.403970 \\
E &= -2014.13708291
\end{align*} \]

Ni(PMe₃)₃

\[ \begin{align*}
G_{\text{corr}} &= 0.294185 \\
E &= -1552.92426336
\end{align*} \]
### Ni(PMe₃)₂

\[
\begin{align*}
E &= -1091.70878163 \\
G_{corr} &= 0.186059
\end{align*}
\]

| Atom  | X          | Y          | Z          |
|-------|------------|------------|------------|
| Ni    | 2.97653100 | 7.45276000 | 11.84232000|
| P     | 1.82795000 | 9.14246000 | 11.22109500|
| C     | 2.32165900 | 10.94878800| 12.58173000|
| P     | 0.68642000 | 8.83952400 | 11.04859000|
| C     | 1.07201500 | 10.86214700| 11.59584000|
| H     | 0.53716000 | 10.41595600| 12.47698000|
| H     | 3.20431800 | 10.27569000| 12.10376000|
| H     | 3.22795000 | 8.96275000  | 12.03769000|
| H     | 5.16331800 | 8.49120000  | 11.92517000|
| H     | 3.14702800 | 6.96274000  | 12.02537000|
| H     | 6.04531000 | 6.54254000  | 12.04697000|
| H     | 2.67125000 | 4.95123400  | 12.02137000|
| H     | 3.30302800 | 3.64532800  | 12.02537000|
| H     | 4.30432000 | 3.14702800  | 12.04697000|
| H     | 1.53231800 | 2.09623400  | 12.02137000|
| H     | 1.65021500 | 1.05621800  | 12.02537000|
| C     | 4.02451200 | 1.04521800  | 12.04697000|

### PhI

\[
\begin{align*}
E &= -243.107411301 \\
G_{corr} &= 0.058655
\end{align*}
\]

| Atom  | X          | Y          | Z          |
|-------|------------|------------|------------|
| C     | 2.37157500 | -0.21732900| 0.00004300 |
| C     | 3.76822800 | -0.23265400| 0.00051000 |
| C     | 4.45944700 | 0.98171500 | -0.00005600|
| C     | 3.76393600 | 2.19238200 | -0.00103400|
| C     | 2.36761900 | 2.19011800 | -0.00148000|
| C     | 1.66000600 | 0.98489800 | -0.00094800|
| H     | 4.31110600 | -1.17155600| 0.00129100 |
| H     | 5.54623300 | 0.97381700 | 0.00029700 |
| H     | 4.30742100 | 3.13298200 | -0.00147600|
| I     | 1.81887400 | 3.12816300 | -0.00226200|

### Ph•

\[
\begin{align*}
E &= -231.634469524 \\
G_{corr} &= 0.059636
\end{align*}
\]

| Atom  | X          | Y          | Z          |
|-------|------------|------------|------------|
| C     | 1.08903600 | -0.03726000| 0.00006800 |
| C     | 2.48710300 | -0.02944900| 0.00046800 |
| C     | 3.19309100 | 1.17730400 | -0.00006300|
| C     | 2.50138000 | 2.40050800 | -0.00093800|
| C     | 1.12511000 | 2.33023600 | -0.00131100|
| C     | 0.37584200 | 1.17352000 | -0.00088100|
| H     | 0.54732900 | -0.98048800| 0.00048500 |
| H     | 3.03023100 | -0.97063200| 0.00119900 |
| H     | 4.28086300 | 1.17485100 | 0.00024600 |
| H     | 3.03752200 | 3.34612200 | -0.00135700|
| H     | -0.71121200| 1.18196800 | -0.00119500|

### Toluene

\[
\begin{align*}
E &= -271.65526549 \\
G_{corr} &= 0.098610
\end{align*}
\]

| Atom  | X          | Y          | Z          |
|-------|------------|------------|------------|
| C     | 5.36852300 | -0.42567700| 0.02178100 |
| H     | 4.47301500 | -0.85534500| 0.49141000 |
| H     | 5.87686300 | 0.17269100 | 0.78652500 |
| H     | 6.02627100 | -1.25935300| -0.24677800|
Toluene radical

\[ E = -271.002248804 \]
\[ G_{\text{corr}} = 0.085412 \]

TS-1-2-I-PMe₃

\[ E = -1796.04472876 \]
\[ G_{\text{corr}} = 0.377611 \]

H Abstraction TS: Ph⊂ + Toluene

\[ E = -503.285594423 \]
\[ G_{\text{corr}} = 0.170965 \]
4-I-PMe₃

E = -1796.05331975
Gcorr = -0.374202

TS-4-5-I-PMe₃

E (OSS) = -1796.04305854
E (T) = -1796.02642847
S²(OSS) = 0.6013
Gcorr = 0.371398
v = -188.75 cm⁻¹
E (OSS) = -1796.0490861
E (T) = -1796.04880792
S^2(OSS) = 1.0098
G_{corr} = 0.369947

5-I-PMe₃

6-I-PMe₃
C -4.17073000  2.07806700  0.93713600  C  0.98561800  6.78770700  14.52758800
C -5.20502000 -0.18462800  0.93713600  C  3.21612900  5.00879800  14.14315600
C -3.71537500  1.84136500 -1.88501700  H  1.06731200 11.36551300  12.18679200
H -5.13735100  2.54125700  0.70425000  H  2.70003000 10.85700500  12.69592800
H -3.40975300  2.86365600  0.99811800  H -0.66755400  9.73261700  10.80900900
H -6.09094100  0.42899800 -0.69384000  H -0.48658800  8.32496400  11.89205900
H -5.35087600 -0.74269800  0.43972200  H  2.09272000  9.40044900  8.84533200
H -3.55483700  1.18376100 -2.74671500  H  3.16784900 10.45810900  9.76951400
H -2.90261900  2.57640500 -1.86908300  H  3.34566500  8.57878000  15.02748100
P -0.41917700  0.93142700  0.69769200  H  4.72298100  7.67434800  14.76902600
P -0.96025700 -1.86388100 -1.49890000  H  0.59966400  7.81254300  14.50468800
C  0.36832000  2.34285100 -0.38093900  H  0.97072900  6.42970200  15.56371600
C  1.45901800  0.06443300  1.00569400  H  2.61246500  4.32647600  13.53548700
C -0.45114800  1.75441900  2.31875600  H  3.11262400  4.74087500  15.20133100
C  0.06553300 -1.13830000 -2.85632700  H  1.27001500 10.12157700  13.44506400
C  0.10925200 -3.24578600 -0.90411300  H -0.21515500  8.13603900  10.15179000
C -2.26680500 -2.77092200 -2.43936500  H  1.46406800 10.93554000  9.51324400
H  1.20553300  2.91013500  0.04293100  H  4.26021300  4.88926600  13.83718800
H -0.48304700  3.01876100 -0.51857700  H  0.32163600  6.15787600  13.92568000
H  2.21298200  0.72914500  1.44426200  H  3.54516700  7.31616200  16.06226700
H  1.85020500 -0.30440000  0.06586400  I  4.75342400  6.19204700  10.2449700
H -0.70886200  0.98519200  3.05354400  i
H -1.30629200  2.43263400  2.23085400
H  0.97406800 -0.69586400 -2.43361700
H -0.49920900 -0.34275900 -3.35401200
H  0.99547200 -2.83431100 -0.40903800
H  0.42646300 -3.91106000 -1.71673700
H -2.91041000 -3.29548200 -1.72511300
H -1.84768200 -3.49675300 -3.14646500
H -4.23258200  1.58340400  1.91170300
H -5.07727700 -0.91280700 -1.29921900
H -4.66769300  2.37070500 -2.01253700
H  0.35840700 -1.88907400 -3.60093100
H -0.44854300 -3.82098000 -0.15809500
H -2.88293000 -2.05157500 -2.99025600
H  0.42104200  2.31937900  2.66880900
H  0.65791700  1.96145200 -1.36634900
H  1.27401900 -0.77149300  1.68817600
H -2.49903000 -2.01070500  2.17983600

7-I-PMe₃

\[
E = -1103.20076166
\]
\[
G_{corr} = 0.179104
\]

|    |    |    |    |
|----|----|----|----|
| Ni | 3.02107300 | 7.39600400 | 11.66721000 |
| P  | 1.70436400 | 9.17505000 | 11.25412200 |
| P  | 2.68797800 | 6.74398900 | 13.81325500 |
| C  | 1.67778300 | 10.51280700 | 12.50681500 |
| C  | -0.09120800 | 8.81947700 | 10.99845700 |
| C  | 2.13905100 | 10.09063600 | 9.69413400 |
| C  | 3.66405900 | 7.70987000 | 15.04595400 |
In n-Hexane

**PhH**

\[
\begin{align*}
E & = -232.323983605 \\
G_{corr} & = 0.073465 \\
C & \begin{array}{ccc}
3.70589900 & 1.91299500 & 0.09731400 \\
5.02855700 & 2.16828700 & -0.27308500 \\
5.30587000 & 2.86508100 & -1.45295300 \\
4.25182000 & 3.30556600 & -2.26273300 \\
2.92907100 & 3.05022800 & -1.89226100 \\
2.65602400 & 2.35345000 & -0.71257900 \\
3.49371700 & 1.37081000 & 1.01535700 \\
5.84529900 & 1.82523200 & 0.35707100 \\
4.46380500 & 3.84788300 & -3.18074700 \\
2.11242000 & 3.39344200 & -2.52243700 \\
1.62680800 & 2.15474600 & -0.42445400 \\
6.33077500 & 3.06381900 & -1.74109800 \\
\end{array}
\end{align*}
\]

**Hexane**

\[
\begin{align*}
E & = -237.171989133 \\
G_{corr} & = 0.158283 \\
C & \begin{array}{ccc}
4.30635300 & 1.65426000 & -0.70126800 \\
4.96429200 & 2.26450200 & -1.33697500 \\
3.30432200 & 1.72035900 & -1.14707800 \\
4.77290600 & 0.19029800 & -0.75004600 \\
4.10385100 & -0.42259700 & -0.12725000 \\
4.66018800 & -0.18425700 & -1.77768600 \\
6.22335100 & -0.32579000 & -0.30265000 \\
\end{array}
\end{align*}
\]

**H Abstraction TS: Ph• + Hexane**

\[
\begin{align*}
E & = -468.799635792 \\
G_{corr} & = 0.228793 \\
v & = -1304.15 \text{ cm}^{-1} \\
C & \begin{array}{ccc}
0.55681800 & -0.96172200 & 0.0587600 \\
1.92526500 & -0.67751400 & 0.1599400 \\
2.49884800 & 0.16891700 & -0.7778010 \\
1.76974000 & 0.74242900 & -1.80926800 \\
0.40163500 & 0.45395200 & -1.90396200 \\
-0.20007000 & -0.39613100 & -0.97151900 \\
0.08461400 & -1.62301700 & 0.78183600 \\
2.51910700 & -1.11513500 & 0.95975500 \\
\end{array}
\end{align*}
\]
H  2.24418000  1.40278500  -2.53235200  H  9.92103100  -1.49168100  0.26597300
H  -0.19135800  0.89186500  -2.70395800  H  9.90679100  -1.42357600  -1.50253200
H  -1.26129000  -0.61873800  -1.04778100  H  9.97536600  -2.98950200  -0.67811700
C  5.15691000  0.66655100  -0.54524300  C  5.31896300  1.48871800  0.72097900
H  5.39731900  1.24462000  -1.44718000  H  5.00364400  0.91841000  1.60424500
H  3.92261800  0.45474300  -0.67194100  H  6.36411000  1.78915300  0.87951600
C  5.82140000  -0.70265900  -0.55585400  H  4.71734900  2.40425700  0.68133600
H  5.48939900  -1.27445800  0.32354600
H  5.47745400  -1.26359200  -1.43635800
C  7.35937700  -0.65076200  -0.56795900
H  7.71936500  -0.12366500  0.32654300
H  7.69465200  -0.05641300  -1.43097500
C  8.00628800  -2.04019400  -0.62570700
H  7.65072900  -2.56801500  -1.52205000
H  7.66481200  -2.63414000  0.23423000
C  9.53651900  -1.98552100  -0.63559200
REFERENCES

1 Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lippari, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

2 Becke, A. D. J. Chem. Phys. 1993, 98, 5648-5652.

3 C. Lee, W. Yang, R.G. Parr Phys. Rev. B. Condens. Matter 1988, 37, 785-789.

4 P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, J. Phys. Chem. 1994, 98, 11623-11627.

5 S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104-19.

6 N. Fey, B. M. Ridgway, J. Jover, C. L. McMullin, J. N. Harvey, J. N. Dalton Trans. 2011, 40, 11184-11191.

7 M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, J. Chem. Phys. 1982, 77, 3654-3665.

8 P. C. Hariharan, J. A. Pople, Theoret. Chim. Acta 1973, 28, 213-222.

9 W. J. Hehre, R. Ditchfield, J. A. Pople, J. Chem. Phys. 1972, 56, 2257-2261.

10 W. R. Wadt, P. J. Hay, J. Chem. Phys. 1985, 82, 284-298.

11 P. J. Hay, W. R. Wadt, J. Chem. Phys. 1985, 82, 270-284.

12 L. E. Roy, P. J. Hay, R. L. Martin, J. Chem. Theor. Comput. 2008, 4, 1029-1031.

13 A. W. Ehlers, M. Böhmé, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp, G. Frenking, Chem. Phys. Lett. 1993, 208, 111-114.

14 R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople, J. Chem. Phys. 1980, 72, 650-654.

15 K. Yamaguchi, F. Jensen, A. Dorigo, K. N. Houk, Chem. Phys. Lett. 1988, 149, 537-542.

16 S. Yamanaka, T. Kawakami, H. Nagao, K. Yamaguchi, Chem. Phys. Lett. 1994, 231, 25-33.

17 M. H. Lim, S. E. Worthington, F. J. Dulles, C. J. Cramer, in Chemical Applications of Density Functional Theory, Vol. 629 (Eds. B. B. Laird, R. B. Ross, T. Ziegler), American Chemical Society, Washington DC, 1996; p 402.

18 H. Isobe, Y. Takano, Y. Kitagawa, T. Kawakami, S. Yamanaka, K. Yamaguchi, K. N. Houk, Mol. Phys. 2002, 100, 717-727.

19 H. Yu, Y. Fu, Q. Guo, Z. Lin, Organometallics 2009, 28, 4443-4451.

20 C. A. Tolman, Chem. Rev. 1977, 77, 313-348.

21 C. A. Tolman, W. C. Seidel, L. W. Gosser, J. Am. Chem. Soc. 1974, 96, 53-60.

22 J. A. Murphy, S.-Z. Zhou, D. W. Thomson, F. Schoenebeck, M. Mahesh, S. R. Park, T. Tuttle, L. E. A. Berlouis, Angew. Chem. Int. Ed. 2007, 46, 5178-5183.

23 a) L. E. Rush, P. G. Pringle, J. N. Harvey, Angew. Chem. Int. Ed. 2014, 53, 8672-8676. b) C. H. Bamford, C. F. H. Tipper, R. G. Compon, Comprehensive Chemical Kinetics, Vol. 25, Elsevier, B.V., Amsterdam, 1985.

24 Taken from Sigma-Aldrich database: http://www.sigmaaldrich.com/chemistry/solvents/toluene-center.html

25 Taken from Sigma-Aldrich database: http://www.sigmaaldrich.com/chemistry/solvents/tetrahydrofuran-center.html