Supporting Information for

Photo- and Thermal Isomerization of (TP)Fe(CO)Cl₂ [TP = Bis(2-diphenylphosphinophenyl)phenylphosphine]

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2. X-ray, DFT, TD-DFT, and UV-Vis structural data

2.1 Table S1. Details of the X-ray crystal structures

<table>
<thead>
<tr>
<th></th>
<th>A·2CH₂Cl₂</th>
<th>B·CH₂Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>formula</strong></td>
<td>C₃₅H₅₈Cl₆FeOP₃</td>
<td>C₄₄H₃₅Cl₄FeOP₃</td>
</tr>
<tr>
<td><strong>fw</strong></td>
<td>955.20</td>
<td>870.28</td>
</tr>
<tr>
<td><strong>crystal colour</strong></td>
<td>red</td>
<td>orange</td>
</tr>
<tr>
<td><strong>crystal size (mm³)</strong></td>
<td>0.30 × 0.10 × 0.08</td>
<td>0.30 × 0.25 × 0.20</td>
</tr>
<tr>
<td><strong>T (K)</strong></td>
<td>150(2)</td>
<td>150(2)</td>
</tr>
<tr>
<td><strong>crystal system</strong></td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td><strong>space group</strong></td>
<td>P2₁/n (no. 14)</td>
<td>P2₁/c (no.14)</td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>9.9523(6)</td>
<td>10.7927(8)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>23.9480(14)</td>
<td>17.8559(13)</td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>18.0094(10)</td>
<td>21.3432(15)</td>
</tr>
<tr>
<td><strong>α (°)</strong></td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>β (°)</strong></td>
<td>97.046(2)</td>
<td>103.716(2)</td>
</tr>
<tr>
<td><strong>γ (°)</strong></td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>V (Å³)</strong></td>
<td>4259.9(4)</td>
<td>3995.8(5)</td>
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<td><strong>Z</strong></td>
<td>4</td>
<td>4</td>
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<tr>
<td><strong>D_{calc} (g cm⁻³)</strong></td>
<td>1.489</td>
<td>1.447</td>
</tr>
<tr>
<td><strong>μ (mm⁻¹)</strong></td>
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<td>0.800</td>
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<tr>
<td><strong>refl. measured / unique</strong></td>
<td>81121 / 7531</td>
<td>49930 / 7217</td>
</tr>
<tr>
<td><strong>parameters / restraints</strong></td>
<td>525 / 12</td>
<td>478 / 0</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>1952</td>
<td>1784</td>
</tr>
<tr>
<td><strong>R1 / wR2 [I&gt;2σ(I)]</strong></td>
<td>0.0464 / 0.0926</td>
<td>0.0360 / 0.0833</td>
</tr>
<tr>
<td><strong>R1 / wR2 (all refl.)</strong></td>
<td>0.0746 / 0.1022</td>
<td>0.0501 / 0.0921</td>
</tr>
<tr>
<td><strong>GOF</strong></td>
<td>1.060</td>
<td>1.052</td>
</tr>
<tr>
<td><strong>ρ_{min/max} (e Å⁻³)</strong></td>
<td>-0.544 / 0.594</td>
<td>-0.624 / 0.739</td>
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</table>
2.2 Table S2. Optimized geometries for all possible isomers as well as the X-ray established isomer A and B.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>A(X-ray)</th>
<th>B</th>
<th>B (X-ray)</th>
<th>C</th>
<th>D</th>
<th>E</th>
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<tr>
<td>Fe1–P1</td>
<td>2.165</td>
<td>2.1852</td>
<td>2.163</td>
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<td>2.235</td>
<td>2.176</td>
<td>2.266</td>
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<tr>
<td>Fe1–P2</td>
<td>2.253</td>
<td>2.2547</td>
<td>2.223</td>
<td>2.2212</td>
<td>2.251</td>
<td>2.256</td>
<td>2.261</td>
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<td>Fe1–P3</td>
<td>2.251</td>
<td>2.2422</td>
<td>2.333</td>
<td>2.3369</td>
<td>2.216</td>
<td>2.267</td>
<td>2.263</td>
</tr>
<tr>
<td>Fe1–Cl1</td>
<td>2.347</td>
<td>2.3410</td>
<td>2.357</td>
<td>2.3308</td>
<td>2.334</td>
<td>2.343</td>
<td>2.317</td>
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<tr>
<td>Fe1–Cl2</td>
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<td>2.360</td>
<td>2.336</td>
<td>2.356</td>
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<tr>
<td>Fe1–C1</td>
<td>1.731</td>
<td>1.743</td>
<td>1.771</td>
<td>1.790</td>
<td>1.775</td>
<td>1.733</td>
<td>1.767</td>
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2.3 Table S3. Comparison for the IR of ν(CO) from DFT calculation and experimental data.

<table>
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<tr>
<th>v(cm⁻¹)</th>
<th>A</th>
<th>B</th>
<th>C</th>
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<tbody>
<tr>
<td>Experimental</td>
<td>1972</td>
<td>2008</td>
<td>1988</td>
</tr>
<tr>
<td>Calculated</td>
<td>1955</td>
<td>1991</td>
<td>1974</td>
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</table>
2.4 Table S4. Electronic transitions in the visible range as calculated with TD-DFT.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda_{\text{expt}} ) (nm)</th>
<th>( \lambda_{\text{calc}} ) (nm) {rel. intensity}</th>
<th>main excitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>482</td>
<td>484 {1415}</td>
<td>HOMO → LUMO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>435 {361}</td>
<td>HOMO-1 → LUMO+4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>401 {206}</td>
<td>HOMO-2 → LUMO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>388 {23}</td>
<td>HOMO-1 → LUMO+1</td>
</tr>
<tr>
<td></td>
<td>366</td>
<td>386 {342}</td>
<td>HOMO → LUMO+4</td>
</tr>
<tr>
<td>B</td>
<td>566</td>
<td>572 {712}</td>
<td>HOMO → LUMO+1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>450 {424}</td>
<td>HOMO-1 → LUMO+1</td>
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<td></td>
<td>362</td>
<td>426 {827}</td>
<td>HOMO-1 → LUMO+1</td>
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<tr>
<td>C</td>
<td>604</td>
<td>604 {108}</td>
<td>HOMO → LUMO+1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>447 {109}</td>
<td>HOMO-1 → LUMO</td>
</tr>
<tr>
<td></td>
<td>364</td>
<td>430 {243}</td>
<td>HOMO-3 → LUMO+1</td>
</tr>
</tbody>
</table>

S6
2.5 Figure S2. TD-DFT Calculated UV-Vis spectrum of species A

2.6 Figure S3. TD-DFT Calculated UV-Vis spectrum of species B

2.7 Figure S4. TD-DFT Calculated UV-Vis spectrum of species C
2.8 Figure S5. UV-Vis spectrum of species A in CD$_2$Cl$_2$

![UV-Vis spectrum of species A in CD$_2$Cl$_2$]

2.9 Figure S6. UV-Vis spectrum of species B in CD$_2$Cl$_2$

![UV-Vis spectrum of species B in CD$_2$Cl$_2$]

2.10 Figure S7. UV-Vis spectrum of species C in CD$_2$Cl$_2$

![UV-Vis spectrum of species C in CD$_2$Cl$_2$]

The steep baseline is caused by condensation of mist on the windows of the UV-Vis cuvette.
2.11 Chart S1. Frontier orbitals of A

Orbital 200 (HOMO-2)

Orbital 201 (HOMO-1)

Orbital 202 (HOMO)

Orbital 203 (LUMO)

Orbital 204 (LUMO+1)

Orbital 205 (LUMO+2)

Orbital 207 (LUMO+4)

Orbital 212 (LUMO+9)
2.12 Chart S2. Frontier orbitals of B

Orbital 199 (HOMO-3)

Orbital 200 (HOMO-2)

Orbital 201 (HOMO-1)

Orbital 202 (HOMO)

Orbital 203 (LUMO)

Orbital 204 (LUMO+1)

Orbital 205 (LUMO+2)

Orbital 206 (LUMO+3)
Chart S3. Frontier orbitals of C

Orbital 199 (HOMO-3)

Orbital 200 (HOMO-2)

Orbital 201 (HOMO-1)

Orbital 202 (HOMO)

Orbital 203 (LUMO)

Orbital 204 (LUMO+1)

Orbital 205 (LUMO+2)

Orbital 206 (LUMO+3)
3. Kinetic Studies for the Isomerization of B to A

3.1 Scheme S1. Reaction model and equations for kinetic fittings

\[
[B] = [B]_0 e^{-kt} \quad \text{Equation (S1)}^9 \\
[A] = 100 - [B]_0 e^{-kt} \quad \text{Equation (S2)}^9
\]

3.2 Table S4. Summary of reaction rate constants obtained by global fit at different temperatures

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>288</th>
<th>293</th>
<th>298</th>
<th>303</th>
<th>308</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k \times 10^{3} \text{ S}^{-1} )</td>
<td>1.21 ± 0.01</td>
<td>1.79 ± 0.01</td>
<td>2.91 ± 0.02</td>
<td>4.73 ± 0.03</td>
<td>8.14 ± 0.05</td>
</tr>
</tbody>
</table>
3.3 Figure S8. Kinetic curves for the thermal isomerization of B to A in CD$_2$Cl$_2$ at 288 K. $k = 1.21 \pm 0.01 \times 10^{-5}$ s$^{-1}$.

3.4 Figure S9. Kinetic curves for the thermal isomerization of B to A in CD$_2$Cl$_2$ at 293 K. $k = 1.79 \pm 0.01 \times 10^{-5}$ s$^{-1}$. 
3.5 Figure S10. Kinetic curves for the thermal isomerization of B to A in CD$_2$Cl$_2$ at 298 K.

\[ k = 2.91 \pm 0.02 \times 10^{-5} \text{ s}^{-1}. \]

3.6 Figure S11. Kinetic curves for the thermal isomerization of B to A in CD$_2$Cl$_2$ at 303 K.

\[ k = 4.73 \pm 0.03 \times 10^{-5} \text{ s}^{-1}. \]
3.7 Figure S12. Kinetic curves for the thermal isomerization of B to A in CD$_2$Cl$_2$ at 308 K.

\[ k = 8.14 \pm 0.05 \times 10^{-5} \text{ s}^{-1}. \]
4. Kinetic Plots for the Isomerization of C to B and A.

4.1 Scheme S2. Reaction model and equations for kinetic fittings

\[
[C] = [C]_0 e^{-(k_1 + k_2)t} \quad \text{Equation (S3)}^9
\]

\[
[B] = [C]_0 \frac{k_2}{k_3 - (k_1 + k_2)} \left[ e^{-(k_1 + k_2)t} - e^{-k_3t} \right] + [B]_0 e^{-k_3t} \quad \text{Equation (S4)}^9
\]

\[
[A] = 100 - [C] - [B] = [C]_0 e^{-(k_1 + k_2)t} - [C]_0 \frac{k_2}{k_3 - (k_1 + k_2)} \left[ e^{-(k_1 + k_2)t} - e^{-k_3t} \right] - [B]_0 e^{-k_3t} \quad \text{Equation (S5)}^9
\]

4.2 Table S5. Summary of the reaction rate constants for the isomerization reactions obtained by curve fitting.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>270</th>
<th>273</th>
<th>276</th>
<th>279</th>
<th>282</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1 \times 10^{-3})</td>
<td>0.32 ± 0.15</td>
<td>0.76 ± 0.44</td>
<td>0.06 ± 0.46</td>
<td>1.67 ± 0.82</td>
<td>0.63 ± 1.11</td>
</tr>
<tr>
<td>(k_2 \times 10^{-3})</td>
<td>6.65 ± 0.14</td>
<td>10.32 ± 0.43</td>
<td>19.23 ± 0.46</td>
<td>32.2 ± 0.99</td>
<td>57.04 ± 1.68</td>
</tr>
<tr>
<td>(k_3 \times 10^{-3})</td>
<td>0.14 ± 0.04</td>
<td>0.40 ± 0.17</td>
<td>0.75 ± 0.08</td>
<td>0.53 ± 0.06</td>
<td>0.76 ± 0.04</td>
</tr>
</tbody>
</table>
4.3 Figure S13. Kinetic curves for the thermal isomerization of C to B and A in CD$_2$Cl$_2$ at 270 K. $k_1 = 0.32 \pm 0.15 \times 10^{-5} \text{ s}^{-1}$, $k_2 = 6.65 \pm 0.14 \times 10^{-5} \text{ s}^{-1}$, $k_3 = 0.14 \pm 0.04 \times 10^{-5} \text{ s}^{-1}$.

4.4 Figure S14. Kinetic curves for the thermal isomerization of B to A in CD$_2$Cl$_2$ at 273K. $k_1 = 0.76 \pm 0.44 \times 10^{-5} \text{ s}^{-1}$, $k_2 = 10.32 \pm 0.43 \times 10^{-5} \text{ s}^{-1}$, $k_3 = 0.40 \pm 0.17 \times 10^{-5} \text{ s}^{-1}$.
4.5 Figure S15. Kinetic curves for the thermal isomerization of C to B and A in CD$_2$Cl$_2$ at 276 K. $k_1 = 0.06 \pm 0.46 \times 10^{-5}$ s$^{-1}$, $k_2 = 19.23 \pm 0.46 \times 10^{-5}$ s$^{-1}$, $k_3 = 0.75 \pm 0.08 \times 10^{-5}$ s$^{-1}$.

4.6 Figure S16. Kinetic curves for the thermal isomerization of C to B and A in CD$_2$Cl$_2$ at 279 K. $k_1 = 1.67 \pm 0.82 \times 10^{-5}$ s$^{-1}$, $k_2 = 32.2 \pm 0.99 \times 10^{-5}$ s$^{-1}$, $k_3 = 0.53 \pm 0.06 \times 10^{-5}$ s$^{-1}$.
4.7 Figure S17. Kinetic curves for the thermal isomerization of C to B and A in CD$_2$Cl$_2$ at 282 K. $k_1 = 0.63 \pm 1.11 \times 10^{-5} \text{ s}^{-1}$, $k_2 = 57.04 \pm 1.68 \times 10^{-5} \text{ s}^{-1}$, $k_3 = 0.76 \pm 0.04 \times 10^{-5} \text{ s}^{-1}$.

4.8 Figure S18. Arrhenius plot for the decay of isomer C to B at different temperatures.

If T = 298 K, $k = 4.53 \times 10^{-3} \text{ s}^{-1}$, then life-time of C at 298 K is $\tau_{1/2} = 90$ s; if T = 273 K, $k = 1.62 \times 10^{-5} \text{ s}^{-1}$, life-time of C at 273 K is $\tau_{1/2} = 6263$ s, that is 1.74 hour.
5. **Photo Irradiation of Isomer A**

The photo irradiation experiment was conducted with a solution of isomer A in CD$_2$Cl$_2$ under a 75 W halogen lamp. The sample was kept at 0 °C during the irradiation time. Cold bath at −78 °C was used to minimize the decay of the photo-excited species during the sample transfer to the NMR spectrometer. The $^{31}$P NMR spectra were measured at −10 °C after a certain time of irradiation. The total irradiation time was labeled on the corresponding spectrum in Figure S14.

**Figure S19.** $^{31}$P NMR spectra recorded at 263 K during the photo irradiation of isomer A at 273 K.
6. Kinetic Studies Under 1 atm of CO

Figure S20. Kinetic curves for the thermal isomerization of B to A under Ar vs CO in CD$_2$Cl$_2$ at 298 K. Reaction rate for B to A: $k_{Ar} = 2.91 \pm 0.02 \times 10^{-5}$ S$^{-1}$, $k_{CO} = 1.07 \pm 0.01 \times 10^{-5}$ S$^{-1}$.

Figure S21. Kinetic curves for the thermal isomerization of C to B under Ar vs CO in CD$_2$Cl$_2$ at 273 K. Reaction rate for C to B: $k_{Ar} = 1.03 \pm 0.06 \times 10^{-4}$ S$^{-1}$, $k_{CO} = 1.66 \pm 0.06 \times 10^{-4}$ S$^{-1}$. 
7. Determination of quantum yield of the photochemical transition of A to B

Separate 0.4 mL samples of 2.2 mM solution of A in CD$_2$Cl$_2$ and 0.349 mM solution of trans-4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (trans-DCM) in CDCl$_3$ ($\Phi_{DCM}^{CHCl_3} = 0.28$)$^1$ were transferred to a Young-valve NMR tube and were placed at exactly the same distance from the light source and irradiated with 525 nm light from a LED. Conversion to the respective photoproducts was measured by intergration of $^1$H NMR signals of A and B, and trans-(DCM) and cis-(DCM) respectively. The conversion of A was 11% after 6 seconds irradiation and the conversion of trans-(DCM) was 8.2% after 2 sec of irradiation.

Using the equation:$^2$

$$\Phi = \frac{c \cdot V \cdot 6.023 \cdot 10^{23}}{I_0 \cdot t_{irr}}$$

Where: $\Phi$ = quantum yield; $c$ = concentration of the photoproduct; $V$ = solution volume; $I_0$ = incident light intensity; $t_{irr}$ = irradiation time

Keeping the same volume of samples, we calculate the quantum yield of A at 525 nm:

$$\Phi_A = \frac{c_A \cdot t_{DCM}}{c_{DCM} \cdot t_A}$$
8. Proposed mechanism for photochemical formation of B

8.1 Scheme S3 Proposed mechanism of photochemical formation of B from A

TD-DFT shows that irradiation of A with visible light leads to charge transfer from the Fe-Cl $\pi^*$ orbital of the chloride ligand trans to the central phosphorus donor. Therefore it is likely that the photochemical formation of B proceeds via initial dissociation of the chlorine radical trans to the central phosphine atom (P1). This should lead to the formation of a pentacoordinate species in which the TP ligand is coordinated in a mer- fashion. This species can further isomerise to the pentacoordinate fac- complex which can rebind the chlorine radical to form species B. Alternative attack of the chlorine radical on the pentacoordinate mer- species leading to E would be hindered by the phenyl group which explains the fact that E is not observed experimentally.
