Supporting Information

Pd-Catalyzed Z-Selective Semihydrogenation of Alkynes: Determining the Type of Active Species


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SI1. The x-ray crystal structure of [Pd(Phenantroline)(TMTU)Me]+PF6−

Figure SI1. The structure of the TMTU-poisoned analogue 2 obtained by X-ray crystal structure determination. Displacement ellipsoids are drawn at 50% probability.

X-ray crystal structure determination of 2. C18H23F6N4PPdS, Fw = 578.84, orange cube, 0.1 × 0.1 × 0.1 mm3, triclinic, P ̅1 (no. 2), a = 6.803(2), b = 11.398(1), c = 14.843(1) Å, α = 103.397(3), β = 92.368(5), γ = 102.778(9) °, V = 1086.7(3) Å3, Z = 2, Dc = 1.769 g/cm3, μ = 1.034 mm−1. Data collections were performed at the X-ray diffraction beamline (XRD1) of the Elettra Synchrotron, Trieste (Italy), with a Pilatus 2M image plate detector. Complete datasets were collected at 100 K (nitrogen stream supplied using an Oxford Cryostream 700) with a monochromatic wavelength of 0.700 Å through the rotating crystal method. Crystals of poisoned analogue complex compound 2 were dipped in N-paratone and mounted on the goniometer head with a nylon loop. The diffraction data were indexed, integrated and scaled using XDS. Complete datasets for the triclinic crystal form observed were obtained by merging three different data collections done on different crystals mounted with different orientations. 5998 reflections were unique (Rint = 0.026), of which 5976 were observed [I>2σ(I)], up to a resolution of (sin θ/λ)max = 0.69 Å.[1] The structures were solved by direct methods using SIR2011,[2] Fourier analyzed and refined by the full-matrix least-squares based on F2 implemented in SHELXL-2013.[3] The Coot program was used for modeling.[4] Anisotropic thermal motion modeling was then applied to atoms with full occupancy. No absorption corrections have been applied to the data. Hydrogen atoms were included (except for disordered water molecules) at calculated positions with isotropic Ufactors = 1.2 Ueq or Ufactors = 1.5 Ueq for methyl groups and refined with a riding model. R1/wR2 [I > 2σ(I)]: 0.0326 / 0.0786. R1/wR2 [all refl.]: 0.0328 / 0.0786. S = 1.085. Residual electron density between 3.23 and -1.14 e/Å3; these values are related to a twin domain (accounting for less than 2% in occupancy) giving a spurious electron density peak close to the atom with more electron (Pd). Geometry calculations and checking for higher symmetry was performed with the PLATON program.

The asymmetric unit contains one complex molecule and a PF6− ion that counterbalances its positive charge (Figure SI1). The angle between the TMTU ligand and the plane defined by the inner coordination sphere of Palladium is 61.0°: this value is intermediate between angles reported in other Pd-TMTU structures published (where values are ~54° or ~80°).[5-7]

CCDC-1049599 contains the supplementary crystallographic data for structure 2. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
SI2. NMR studies of TMTU and CO for the copolymerization reaction

Free TMTU: 3.04 ppm

Solvent: CD₂Cl₂
SI3a. X-ray crystal structures of 5, 8 and 9

Figure SI3.1. ORTEP representation of [Pd\textsuperscript{0}(IMes)(MA)\textsubscript{2}] complex 5 and its CS\textsubscript{2} and TMTU poisoned analogues i.e. 8 and 9. The crystal structure of the TMTU-poisoned analogue 9 was refined with a disorder model. 9a shows the major disorder form (86.4% occupancy) and 9b the minor disorder form (13.6% occupancy). Displacement ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity’s sake.

Through these X-ray crystal structures the coordination properties of the complexes and poison ligands could be studied in further depth. All three structures adopt a planar Y-shaped structure around the Pd\textsuperscript{0} atom. We note that the maleic anhydride ligands (MA) of 5 are directed in opposite directions. This corroborates the inequivalence of the MA as was proposed by NMR-studies\textsuperscript{[8]}. The inequivalence is also displayed in the significant difference in lengths of the olefinic bond in the MA as well as in the MA-Pd distances.

The X-ray crystal structure of the putative TMTU poisoned catalyst 9 is the first example of a palladium(0) TMTU complex. The structure was disordered with two positions of the Pd atom and two orientations of the MA ligand. Two steric interactions give rise to the formation of these two conformers. In the major disorder form (9a) the anhydride carbonylic oxygen has a steric interaction with the methyl of the thiourea, and in the minor disorder form (9b) the MA ligand is rotated and its olefinic bond is directed to the methyl group of the thiourea. These steric interactions are clearly shown in the CPK model of both disorder forms. A comparison of bond geometries between compound 5 and its TMTU poisoned analogue is severely hampered by the disorder in 9. The geometrical parameters of the palladium complexes 5 and 9 are given in Table SI3.1.
Table SI3.1. Selected bond lengths of the X-ray crystal structures of 5 and 9. 9a and 9b are the major and minor disorder forms in the crystal structure of 9.

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>9a</th>
<th>9b</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd–NHC</td>
<td>2.069(5)</td>
<td>1.978(6)</td>
<td>2.1062(14)</td>
</tr>
<tr>
<td>Pd–MA</td>
<td>1.9486(6)a</td>
<td>1.956(3)a</td>
<td>2.0333(2)a</td>
</tr>
<tr>
<td>Pd–MA(2)</td>
<td></td>
<td></td>
<td>2.0117(3)a</td>
</tr>
<tr>
<td>MA (olefin)</td>
<td>1.437(7)b</td>
<td>1.436(12)b</td>
<td>1.393(2)</td>
</tr>
<tr>
<td>MA (2) (olefin)</td>
<td></td>
<td></td>
<td>1.401(2)</td>
</tr>
<tr>
<td>Pd–S</td>
<td>2.3592(12)</td>
<td>2.503(3)</td>
<td></td>
</tr>
</tbody>
</table>

a Distance between metal and least-squares plane of the ring. b Restraints have been used in the refinement of the disorder model.

The dinuclear compound 8 is located on an exact, crystallographic inversion center between the two metal atoms, and the IMes ligand has an approximate, non-crystallographic $C_2$-symmetry. The general formula is \([\text{Pd}^0\text{IMes} – \mu(\kappa-S, \eta^2)-(\text{CS})_2]_2\) (Figure SI3.1). The \(\text{Pd}^0\text{(IMes)}\) moieties are bridged by two \(\text{CS}_2\) molecules. Each bridging \(\text{CS}_2\) ligand binds in a $\pi$-fashion to one of the Pd-centers and in a $\sigma$-fashion to the other. This results in a planar structure around the two \(\text{Pd}^0\)-nuclei. The wing tips of the NHC are directed perpendicularly to this plane to minimize steric interactions.
Table SI3.2. Comparison of 8 to the analogous phosphine Pd₂(P(Bu)₂Ph)₂(CS₂)₂ compound.[9]

<table>
<thead>
<tr>
<th>Atom-Atom</th>
<th>NHC-CS₂ complex</th>
<th>P-CS₂ complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd–Pd[i]</td>
<td>4.1790(8)[i]</td>
<td>4.2238(10)[ii]</td>
</tr>
<tr>
<td>Pd–S(side)</td>
<td>2.3342(7)</td>
<td>2.313(1)</td>
</tr>
<tr>
<td>Pd–S(end)</td>
<td>2.3193(7)</td>
<td>2.316(1)</td>
</tr>
<tr>
<td>Pd–C</td>
<td>1.964(2)</td>
<td>1.980(5)</td>
</tr>
<tr>
<td>C–S(side)</td>
<td>1.664(3)</td>
<td>1.643(5)</td>
</tr>
<tr>
<td>C–S(end)</td>
<td>1.654(2)</td>
<td>1.650(5)</td>
</tr>
<tr>
<td>NHC–Pd</td>
<td>2.092(2)</td>
<td></td>
</tr>
</tbody>
</table>

[a] Symmetry code: i: 2/3-ϕ, 1/3-y, 1/3-z; ii: -x, -y, 1-z.

Complexes of the form of 8 are quite rare in literature: only a single X-ray crystal structure of such a binuclear binding motif with CS₂ was reported by Farrar et al.[9] with a general formula Pd₂(P(Bu)₂Ph)₂(CS₂)₂. Overall, the metrics and shapes of the bimetallic Pd-planes of both molecules are similar (Table SI3.2). However, we observe significant differences in the bond lengths of the π-coordinated part of the CS₂ molecule to the palladium center. This is presumably caused by the stronger σ-donating properties of the NHC with respect to the phosphine. Interestingly, for both compounds there is only a minor difference between the C–S(η²) and C–S(η¹) bond lengths. An elongation of both bonds with respect to CS₂ is expected. However, a more significant difference between the lengths of the two CS bonds would be expected as π-back donation into the η²-CS-bond would affect this bond strongest. A somewhat larger difference is observed between the Pd–S(η¹) and Pd–S(η²) distance, but it is still minimal. Neither the publication by Farrar et al.[9] nor we, are able to give a satisfactory explanation for this phenomenon. Comparing the obtained structure of compound 8 to that of the other two Pd⁰ compounds shows that the Pd–NHC distance is similar to that of the [Pd⁰(NHC)(TMTU)] compound 9b, and the Pd–S(η¹) distance is significantly shorter. This may mainly be caused by steric factors as there is a significant interaction between the MA and TMTU moieties in complex 9a, which is not an issue for the small CS₂ ligand.
SI3b. Experimental details of the X-ray crystal structure determinations of 5, 8 and 9

X-ray crystal structure determination of 5. C_{29}H_{30}N_2O_4Pd, Fw = 606.93, colorless plate, 0.41 × 0.35 × 0.10 mm³, monoclinic, P2_1/c (no. 14), a = 17.5665(6), b = 13.6471(3), c = 11.6294(3) Å, β = 109.070(1)°, V = 2634.94(13) Å³, Z = 4, D_x = 1.530 g/cm³, μ = 0.75 mm⁻¹. 47521 reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin θ/λ)_{max} = 0.65 Å⁻¹. Intensity data were integrated with the Eval15 software. Analytical absorption correction and scaling was performed with SADABS (correction range 0.82-0.94). 6040 Reflections were unique (R_{int} = 0.015), of which 5765 were observed [I>2σ(I)]. The structure was solved with Direct Methods using the program SHELXS-97. Least-squares refinement was performed with SHELXL-2013 against F² of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined with a riding model. 373 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)] = 0.0306 / 0.0765. R1/wR2 [all refl.]: 0.0417 / 0.0832. S = 1.061. Residual electron density between [I>2σ(I)]. The metric of the lattice is approximately orthorhombic-C, but we see no indications for the presence of this higher symmetry.

X-ray crystal structure determination of 8. C_{30}H_{48}N_4Pd_2S_4 2C_4H_6O + disordered solvent, Fw = 1118.11[^1], yellow needle, 0.48 × 0.19 × 0.09 mm³, trigonal, R̅3 (no. 148), a = b = 35.8920(7), c = 11.0473(5) Å, α = β = γ = 120°, V = 12324.9(9) Å³, Z = 9, D_x = 1.356 g/cm³[^1], μ = 0.85 mm⁻¹[^1], 52468 reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin θ/λ)_{max} = 0.65 Å⁻¹. Intensity data were integrated with the Eval15 software. Absorption correction and scaling was performed with SADABS (correction range 0.61-0.75), 6297 reflections were unique (R_{int} = 0.018), of which 5153 were observed [I>2σ(I)]. The structure was solved using the program SHELXT. Least-squares refinement was performed with SHELXL-2013 against F² of all reflections. The crystal structure contains voids (809 Å³ / unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was taken into account using the SQUEEZE routine of the PLATON software (127 electrons / unit cell). Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined with a riding model. 295 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0306 / 0.0765. R1/wR2 [all refl.]: 0.0417 / 0.0832. S = 1.061. Residual electron density between -0.51 and 0.42 e/Å³. Geometry calculations and checking for higher symmetry was performed with the PLATON program. The metric of the lattice is approximately orthorhombic-C, but we see no indications for the presence of this higher symmetry.

[^1] Derived values do not contain the contribution of the disordered solvent molecules.

X-ray crystal structure determination of 9. C_{30}H_{30}N_4O_3PdS, Fw = 641.10, yellow needle, 0.44 × 0.23 × 0.10 mm³, monoclinic, P2_1/n (no. 14), a = 13.2975(5), b = 14.2960(6), c = 15.7136(7) Å, β = 90.4304(13)°, V = 2987.1(2) Å³, Z = 4, D_x = 1.426 g/cm³, μ = 0.73 mm⁻¹. 43869 reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin θ/λ)_{max} = 0.65 Å⁻¹. Intensity data were integrated with the Saint software. Absorption correction and scaling was performed with SADABS based on multiple measured reflections (correction range 0.65-0.75). 6878 Reflections were unique (R_{int} = 0.051), of which 6248 were observed [I>2σ(I)]. The structure was solved with Direct Methods using the program SHELXS-97. Least-squares refinement was performed with SHELXL-2013 against F² of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. The palladium atom and the maleic anhydride ligand were refined with a disorder model for positional
disorder (occupancy 0.863(3):0.136(3)). All hydrogen atoms were introduced in calculated positions and refined with a riding model. 400 parameters were refined with 41 restraints (1,2 and 1,3 distances in the disordered groups, flatness of the MA ligand). R1/wR2 [I > 2σ(I)]: 0.0562 / 0.1326. R1/wR2 [all refl.]: 0.0619 / 0.1346. S = 1.253. Residual electron density between -0.76 and 1.15 e/Å³. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[14]

CCDC 1050449 (compound 5), 1050450 (8), and 1050451 (9) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
SI4. Leaching form supported Pd NP catalysts in the semihydrogenation using molecular hydrogen

Figure SI4. Leaching of Pd from Pd on Carbon in the semihydrogenation of 1-phenyl-1-propyne using molecular hydrogen and the influence of the poison ligands thereon.

SI5. Leaching form supported Pd NP catalysts in the semihydrogenation using formic acid

A Maitlis filtration test on the reactions with these supported catalysts was performed, in which no activity of the filtrate was observed for any of the catalyst materials. Additionally ICP-AES measurements showed that the leaching of Pd from the particle (pre)catalysts is minimal (Figure SI5). Based on these observations it seems that for these supported particle-based catalysts the activity originates from Pd on the support.

Figure SI5. Pd leaching from the catalyst materials in the transfer semihydrogenation reaction using formic acid and the influence of the poison ligands thereon (ICP-AES).

SI6. Estimating the percentage of Pd on the outside of the 44 nm particles

Assuming all Pd is present as spherical particles with a diameter of 44 nm with a density of palladium of 12.02 g/cm$^3$ (the density of Pd) and an atomic surface that is simplified to squares with edges that are equal to the atomic diameter of Pd, we estimate that about 3% of the Pd atoms are on the outside of the particle. The percentage of Pd that is active for such NPs is even lower. Not all of the metal on the outside of a particle can be catalytically active, since there are also coordinating “ligands” and other stabilizing species present on the surface of the particle. Additionally, the substrates have what is called a footprint,[18] meaning that a coordinating substrate molecule blocks neighboring surface Pd atoms. When 30% of the metal on the surface of a NP is active, this is a high amount for NPs this size.[19, 20] Assuming that such an amount of the surface Pd atoms is active less than 1% of the Pd of the observed NPs is expected to be active. This is in contrast to the observed and over estimated 12% of active Pd that has been found. The difference is large, which makes the observed NPs unlikely as sole catalytic active species.
SI7. Estimating the percentage of Pd on the outside of the 30 nm particles

Assuming all Pd is present as spherical particles with a diameter of 30 nm with a density of palladium of 12.02 g/cm³ (the density of Pd) and an atomic surface that is simplified to squares with edges that are equal to the atomic diameter of Pd, we estimate that about 4% of the Pd atoms are on the outside of the particle. The percentage of Pd that is active for such NPs is even lower. Not all of the metal on the outside of a particle can be catalytically active, since there are also coordinating “ligands” and other stabilizing species present on the surface of the particle. Additionally, the substrates have what is called a footprint\(^{18}\) meaning that a coordinating substrate molecule blocks neighboring surface Pd atoms. When 30% of the metal on the surface of a NP is active, this is a high amount for NPs this size.\(^{19,20}\) Assuming that such an amount of the surface Pd atoms is active less than 1.5% of the Pd of the observed NPs is expected to be active. This is in strong contrast to the observed 40% of Pd that is active based on the partial poisoning experiments.

SI8. Complex synthesis of 2, 6, 8 and 9

\textbf{[Palladium(II)phenanthroline(tetramethylthiourea)(methyl)] hexafluorophosphate (2).} To a solution of [Pd(phenanthroline)(Me)Cl] (0.21 mmol) in DCM (6 mL) a solution of TMTU (0.42 mmol) in DCM (1 mL) was added leading to a clear solution. To the latter a solution of AgPF\(_6\) (0.24 mmol) in DCM (1.5 mL) was added. The system was stirred at room temperature for 30 min leading to the precipitation of AgCl. The suspension was filtered over Celite, and washed with DCM. The filtrate was concentrated up to one third of volume and a yellow solid was isolated upon addition of diethyl ether. The solid was filtered and dried under vacuum. The NMR analysis indicates that the solid is a mixture of the desired product and of the unreacted starting Pd-complex. The solid was purified by completing the reaction. The solid (0.0122 mmol) was dissolved in DCM (6 mL). To this solution TMTU (0.0244 mmol) dissolved in DCM (0.5 mL) was added. To the obtained solution, a solution of AgPF\(_6\) in DCM (0.01403 in 0.5 mL) was added. The final solution was stirred for 30 min, afterwards the precipitated AgCl was filtered over Celite, washed with DCM. The filtrate was concentrated under vacuum and the product precipitated upon addition of diethyl ether. The yellow solid was filtered and dried under vacuum. Total yield: 46 %. \(^{1}H\)-NMR (500MHz, CD\(_2\)Cl\(_2\)) \(\delta = 9.08 \) (d, 1H, Phen(H\(^\text{9}\))), 8.98 (d, 1H, Phen(H\(^\text{2}\))), 8.68 (dd, 1H, Phen(H\(^\text{4}\))), 8.64 (dd, 1H, Phen(H\(^\text{7}\))), 8.09 (s, 2H, Phen(H\(^\text{5,6}\))), 7.97 (m, 2H, Phen(H\(^\text{3,8}\))), 3.31 (12H, s, NCH\(_3\)), 0.80 (s, 3H, Pd-CH\(_3\)).

\textbf{(1,4-Ditertbutyl-diazobuadiene)(maleic anhydride)palladium(0) (6).} The compound was synthesized according to the procedure of Cavell et al.\(^{21}\) Further purification was performed by flash column chromatography. The compound was dissolved in a minimum amount of 1:1 DCM THF and brought on the column. The compound was then eluted with pure THF. The fractions were collected and the solvent was removed giving the compound in a 90% yield. Subsequently, no particles were observed by DLS indicating that the compound is devoid of NPs.
Bis-{palladium(0)-(1,3-dimesityl-imidazolylidene)-μ(x-S,η²)-carbon disulfide} (8). The corresponding imidazolium salt (0.15 g, 0.44 mmol) was stripped twice with 3 mL toluene and suspended in THF (30 mL). Potassium tert-butoxide (65 mg, 0.53 mmol) was added and a lightly discolored solution was obtained. Subsequently, [Pd(DVTMS)] in solution (10.87 mass % Pd) (0.431 g, 0.44 mmol) was added and an orange solution was obtained. The solution was stirred for an hour and CS₂ (5M in THF, 4.4 mmol, 0.9 mL) was added. Upon addition the solution turned yellow, but in time the color changed to orange again. The solution was stirred overnight. Then 10 mL of pentane was added and the solution was filtered over Celite (in air). The solution was concentrated to ca 3 mL. The product was precipitated with pentane and washed with pentane twice, yielding a yellow powder. This was dissolved in DCM with 1% 5M CS₂ solution in THF and was flashed over a silica column 0.183 g (83% yield). A DLS measurement was performed, which showed that the sample was devoid of particles. X-ray quality crystals were obtained by slow diffusion of pentane 2 mL to 0.5 mL THF with 15 mg compound. ¹H-NMR (300MHz, CD₂Cl₂) δ 7.11 (s, 2H, Im-bb), 7.01 (s, 4H, Mes), 2.37 (s, 6H, Mes(p-Me)), 2.14 (s, 12H, Mes(o-Me)). ¹³C-NMR (75 MHz, CDCl₃) δ (CS₂ ¹³C not observed), 188.19 (NCN), 139.57 (p-Mes), 136.54 (i-Mes), 135.77 (o-Mes), 129.66 (m-Mes), 123.51 (Im-bb), 21.64 (Mes(p-Me)), 18.33 (Mes(o-Me)). IR: 1119 cm⁻¹ CS (s), 716 cm⁻¹ CS (s).

Palladium(0)-((1,3-Mesityl)-imidazolylidene)(maleic anhydride)(tetramethyl-thiourea) (9). 1,3-Dimesitylimidazolium chloride (0.200 g, 0.58 mmol) was stripped with toluene three times and, subsequently, suspended in 30 mL THF. First potassium tert-butoxide (0.093 g, 0.76 mmol), second [Pd(BuDAB)(MA)] 8 (0.218 g, 0.58 mmol) and third, TMTU (0.100 g, 0.76 mmol) were added. The solution was stirred for one hour, after which it was filtered over a thick layer of Celite and rinsed with an additional 10 mL of THF. The solution was concentrated to approximately 2 mL and 2 mL of Et₂O was added. While stirring 20 mL pentane was added drop-wise, upon which the compound precipitated as a light yellow powder. The precipitation step was repeated, but ¹H NMR showed that an unidentified byproduct was still present. The compound was further purified by column chromatography over silica (in air) using a 5% acetone in DCM eluent and 0.19 g of a yellow powder, (0.30 mmol) was obtained, which corresponds to a yield of 51%. ¹H NMR (300 MHz, CD₂Cl₂) δ 7.09 (s, 2H, Im-bb), 7.01 (s, 4H, Mes), 3.01 (d, J = 3.7 Hz, 1H, MA), 2.90 (s, 12H, NMe₃), 2.83 (d, J = 3.7 Hz, 1H, MA), 2.36 (s, 6H, Mes(p-Me)), 2.19 (s+s, 12H, Mes(o-Me)). ¹³C-NMR 75 MHz (CDCl₃) δ: 191.14 (NCN), 190.74 (thiourea), 172.71 (C=O), 172.21 (C=O), 138.17 (p-Mes), 136.97 (i-Mes), 136.11 (o-Mes), 128.57 (m-Mes), 128.51 (m-Mes), 122.36 (Im-bb), 43.68 (MA C=C), 43.04 (NCMe), 42.65 (MA C=C), 39.34 (MA C=C), 38.34 (MA C=C), 20.76 (MA C=C).
References