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# Regioisomerism in coordination chemistry: oxidative addition of bifunctional ligand to palladium, stabilized with 1,2-bis(diphenylphosphino)ethane

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## Synthetic procedures:

Reagents and solvents were used as purchased or purified by standard procedures.[1] All synthetic procedures were carried out under vacuum. 2,5-di-tert-butyl-7,8-dithiabicyclo[4.2.0]octa-1,5-diene-3,4-dione **1** was prepared according to literature procedure.[2] Syntheses of tris(dibenzylideneacetone)dipalladium(0) (*Pd₂dba₃*) and [1,2-bis(diphenylphosphino)ethane] dichloropalladium(II) (*(dppe)PdCl₂*) were carried out according to [3] and [4], respectively.

Instrumentation: IR spectra were recorded on a FSM-1201 FTIR spectrometer. $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectra were obtained on a Bruker Avance III 400 MHz instrument. The chemical shifts are expressed in parts per million downfield. X-band EPR spectra were recorded with Bruker EMX spectrometer. The samples for EPR study were prepared according to procedures described by Prokof'ev et al. [5] Elemental analysis was carried out with a EURO EA machine.

*1,2-bis(diphenylphosphino)ethane palladium (II) 2,5-di-tert-butyl-7,8-dithiabicyclo[4.2.0]octa-1(6),2,4-triene-3,4-bis(olate)* ($\mathbf{3^{Cat}}$): A toluene solution of 2,5-di-tert-butyl-7,8-dithiabicyclo[4.2.0]octa-1,5-diene-3,4-dione (**1**, 0.564 g, 2 mmol), dppe (0.796 g, 2 mmol) and $Pd_2dba_3$ (0.921 g, 1 mmol) was stirred within 45 minutes at 25°C under vacuum. Brown-green precipitate was filtered, washed with hexane and dried in vacuum. Crude product was recrystallized by slow mixing of THF solution with toluene to form brown crystals, suitable for X-ray diffraction (0.585 g, 0.74 mmol, 37,2%). $^{1}H$ NMR (400 MHz, THF-$d_8$, 25°C): $\delta$ = 1.35 (s, $18H_{tBu}$), 2.74 (d, J=19.3 Hz, $4H_{CH2\text{-}CH2}$), 7.41-7.47 (m, $12H_{o+p}$), 8.11-8.15 (m, $8H_m$); $^{13}C$ NMR (100 MHz, THF-$d_8$, 25°C): $\delta$ = 28.87 (C(*C*H3)3), 31.27 (*C*H₂-CH₂), 32.24 (CH₂-*C*H₂), 36.18 (*C*(CH3)3), 127.69-136.40 (C=C of phenyl and o-benzoquinone rings), 161.66 ppm (*C*=O); $^{31}P$ NMR (161.97 MHz, 25°C): $\delta$ = 52.81 (THF), 52.45 ($CH_2Cl_2$), 54.62 (acetone); IR (nujol): 1436, 1359, 1256 (C-O), 1104, 1027, 997, 981, 967, 850, 743, 717, 690, 591, 524 cm$^{-1}$; elemental analysis: calculated (%, for $\mathbf{3^{Cat}}\cdot 2PhCH_3$ ($C_{54}H_{58}O_2P_2PdS_2$)):C, 66.76; H, 6.02; P, 6.38; Pd, 10.95; S, 6.60; found (%): C, 65.90; H, 5.78; P, 6.42; Pd, 11.05; S, 6.80

*1,2-bis(diphenylphosphino)ethane palladium (II) 3,6-di-tert-butyl-4,5-dioxocyclohexa-2,6-diene-1,2-bis(thiolate)* ($\mathbf{3^{Dit}}$): A THF solution of 2,5-di-tert-butyl-7,8-dithiabicyclo[4.2.0]octa-1,5-diene-3,4-dione (1, 0.564 g, 2 mmol), (dppe)$PdCl_2$ (1.15 g, 2 mmol) and excess of thallium amalgam was stirred within 30 minutes at 25°C under vacuum until the color of solution turned from violet to green. The resulting solution was filtered and evaporated. Crude product was crystallized by slow cooling of THF solution and isolated (1.17 g, 1.49 mmol, 74.6% yield) as green crystals. $^{1}H$ NMR (400 MHz, THF-$d_8$, 25°C): $\delta$ = 1.36 (s, $18H_{tBu}$), 2.71 (d, J=19.7 Hz, $4H_{CH2\text{-}CH2}$), 7.47-7.53 (m, $12H_{o+p}$), 7.82-7.87 (m, $8H_m$); $^{13}C$ NMR (100 MHz, THF-$d_8$, 25°C): $\delta$ = 26.30 (*C*H₂-CH₂), 26.53 (CH₂-*C*H₂), 29.57 (C(*C*H3)3), 35.89 (*C*(CH3)3), 128.81-137.44 (C=C of phenyl and o-benzoquinone rings), 187.28 ppm (*C*=O); $^{31}P$ NMR (161.97 MHz, 25°C): $\delta$ = 50.17 (THF), 49.83 ($CH_2Cl_2$), 52.32 (acetone); IR (nujol): 1614 (C=O), 1434, 1358, 1314, 1219, 1193, 1107, 1078, 1020, 998, 875, 842, 817, 800, 748, 719, 691, 654, 527 cm$^{-1}$; elemental analysis: calculated (%, for $\mathbf{3^{Dit}}\cdot 2THF$ ($C_{48}H_{58}O_4P_2PdS_2$)):C, 61.89; H, 6.28; P, 6.65; Pd, 11.42; S, 6.88; found (%): C, 61.65; H, 6.03; P, 6.87; Pd, 11.88; S, 7.14

# X-ray crystallography

The X-ray diffraction data were collected on Agilent Xcalibur Eos (**3**$^{\mathbf{Cat}}$) and Bruker D8 Quest (**3**$^{\mathbf{Dit}}$) diffractometers (Mo-K$_{\alpha}$ radiation, ω-scan technique, λ = 0.71073 Å). The intensity data were integrated by CrysAlisPro[6] (**3**$^{\mathbf{Cat}}$) and SAINT[7] (**3**$^{\mathbf{Dit}}$) programs. SCALE3 ABSPACK[8] (**3**$^{\mathbf{Cat}}$) and SADABS[9] (**3**$^{\mathbf{Dit}}$) were used to perform area-detector scaling and absorption corrections. The structures were solved by direct method using dual-space algorithm [10] and were refined on $F^2$ using all reflections with the SHELXTL package[11]. All non-hydrogen atoms were refined anisotropically. H atoms were placed in calculated positions and refined in the "riding model". Disordered solvate molecules of toluene and THF were found in crystals of **3**$^{\mathbf{Cat}}$ and **3**$^{\mathbf{Dit}}$ respectively. The details of crystallographic, collection and refinement data are presented in Table SI1. CCDC-1577236 (**3**$^{\mathbf{Cat}}$) and 1577237 (**3**$^{\mathbf{Dit}}$) 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.

Table SI1. Crystallographic data and refinement parameters for **3**$^{\mathbf{Cat}}$ and **3**$^{\mathbf{Dit}}$.

| | **3**$^{\mathbf{Cat}}$ | **3**$^{\mathbf{Dit}}$ |
|---|---|---|
| Formula | C54 H58 O2 P2 Pd S2 | C46 H54 O3.50 P2 Pd S2 |
| MW | 971.46 | 895.35 |
| Crystal system | Tetragonal | Triclinic |
| Space group | P4(1)2(1)2 | P-1 |
| a, Å | 17.9561(1) | 10.9560(3) |
| b, Å | 17.9561(1) | 12.6502(4) |
| c, Å | 14.8394(1) | 17.8929(6) |
| α, ° | 90 | 100.177(1) |
| β, ° | 90 | 106.263(1) |
| γ, ° | 90 | 108.579(1) |
| V, Å$^3$ | 4784.54(6) | 2158.08(12) |
| Z, | 4 | 2 |
| $\rho_{calcd.,}$ g·cm$^{-3}$ | 1.349 | 1.378 |
| μ, mm$^{-1}$ | 0.582 | 0.641 |
| F(000) | 2024 | 932 |
| Crystal dimension, mm | 0.80 x 0.20 x 0.20 | 0.40 x 0.15 x 0.10 |
| 2θ range, ° | 2.971 - 29.997 | 2.102 - 27.997 |
| Reflections measured | 101714 | 25642 |
| Reflections unique ($R_{int}$) | 6979 (0.0509) | 10402 (0.0133) |
| $R_1$ (all data) | 0.0255 | 0.0261 |
| $R_1$ with $I \geq 2\sigma(I)$ | 0.0219 | 0.0247 |
| $wR_2$ (all data) | 0.0499 | 0.0664 |
| $wR_2$ with $I \geq 2\sigma(I)$ | 0.0487 | 0.0656 |
| Goodness-of-fit on $F^2$ | 1.094 | 1.010 |
| Absolute structure parameter | -0.030(6) | - |
| Highest residue, e·Å$^{-3}$ | 0.489 | 0.760 |
| Lowest residue, e·Å$^{-3}$ | -0.378 | -0.674 |

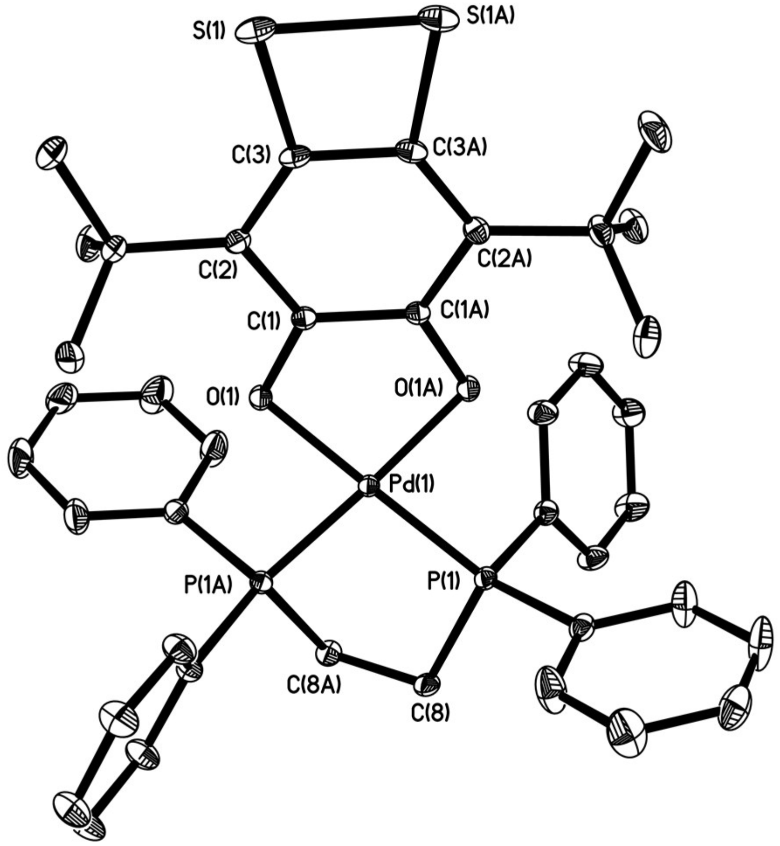


Table SI2. Selected bond lengths (Å) and angles (°) for ($\mathbf{3}^{\mathbf{Cat}}$)

| | |
|---|---|
| Pd(1)-O(1) | 2.0132(13) |
| Pd(1)-P(1) | 2.2197(5) |
| O(1)-C(1) | 1.350(2) |
| S(1)-C(3) | 1.784(2) |
| S(1)-S(1A) | 2.1331(11) |
| C(1)-C(2) | 1.407(3) |
| C(1)-C(1A) | 1.429(4) |
| C(2)-C(3) | 1.400(3) |
| C(3)-C(3A) | 1.400(4) |
| P(1)-C(8) | 1.8364(19) |
| C(8)-C(8A) | 1.537(4) |
| | |
| O(1)-Pd(1)-O(1A) | 83.00(8) |
| P(1)-Pd(1)-P(1A) | 86.40(3) |

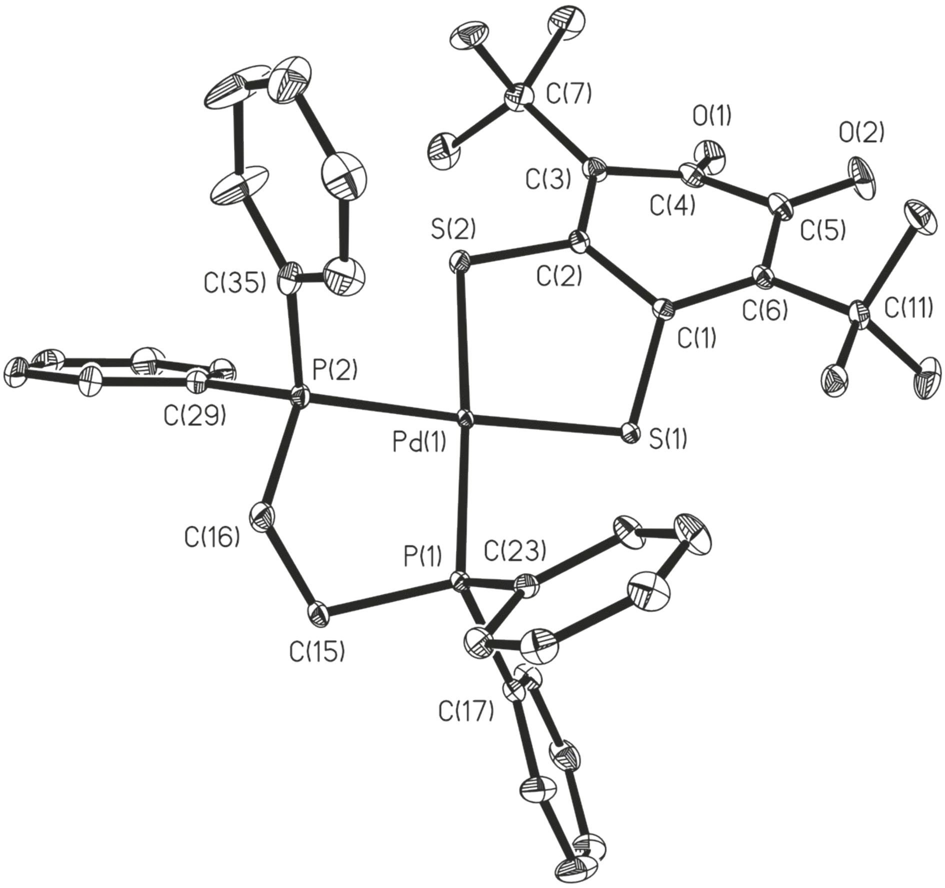
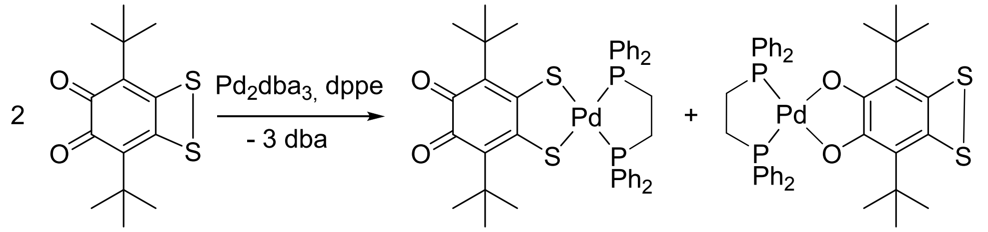


Table SI3. Selected bond lengths (Å) and angles (°) for (**$3^{\mathrm{Dit}}$**)

| | |
|---|---|
| Pd(1)-P(1) | 2.2753(4) |
| Pd(1)-P(2) | 2.2836(4) |
| Pd(1)-S(2) | 2.2980(3) |
| Pd(1)-S(1) | 2.3026(3) |
| S(1)-C(1) | 1.7367(14) |
| S(2)-C(2) | 1.7457(14) |
| P(1)-C(15) | 1.8233(14) |
| P(2)-C(29) | 1.8066(15) |
| P(2)-C(16) | 1.8405(15) |
| C(15)-C(16) | 1.527(2) |
| O(1)-C(4) | 1.2215(18) |
| O(2)-C(5) | 1.2298(19) |
| C(1)-C(6) | 1.3786(19) |
| C(1)-C(2) | 1.5108(19) |
| C(2)-C(3) | 1.3721(19) |
| C(3)-C(4) | 1.460(2) |
| C(4)-C(5) | 1.541(2) |
| C(5)-C(6) | 1.4540(19) |
| | |
| S(1)-Pd(1)-S(2) | 86.825(12) |
| P(1)-Pd(1)-P(2) | 84.346(13) |

# NMR studies



**1** **$3^{Dit}$** **$3^{Cat}$**

Scheme SI1. Interaction of o-quinone **1** with $Pd_2(dba)_3$ and dppe.

$^{31}$P-NMR monitoring was carried out to determine the ratio of products **$3^{Cat}$/$3^{Dit}$**, produced in the synthesis: compound **1** was mixed with 0.5 eq of $Pd_2dba_3$ and 1 eq. of dppe in various solvents.

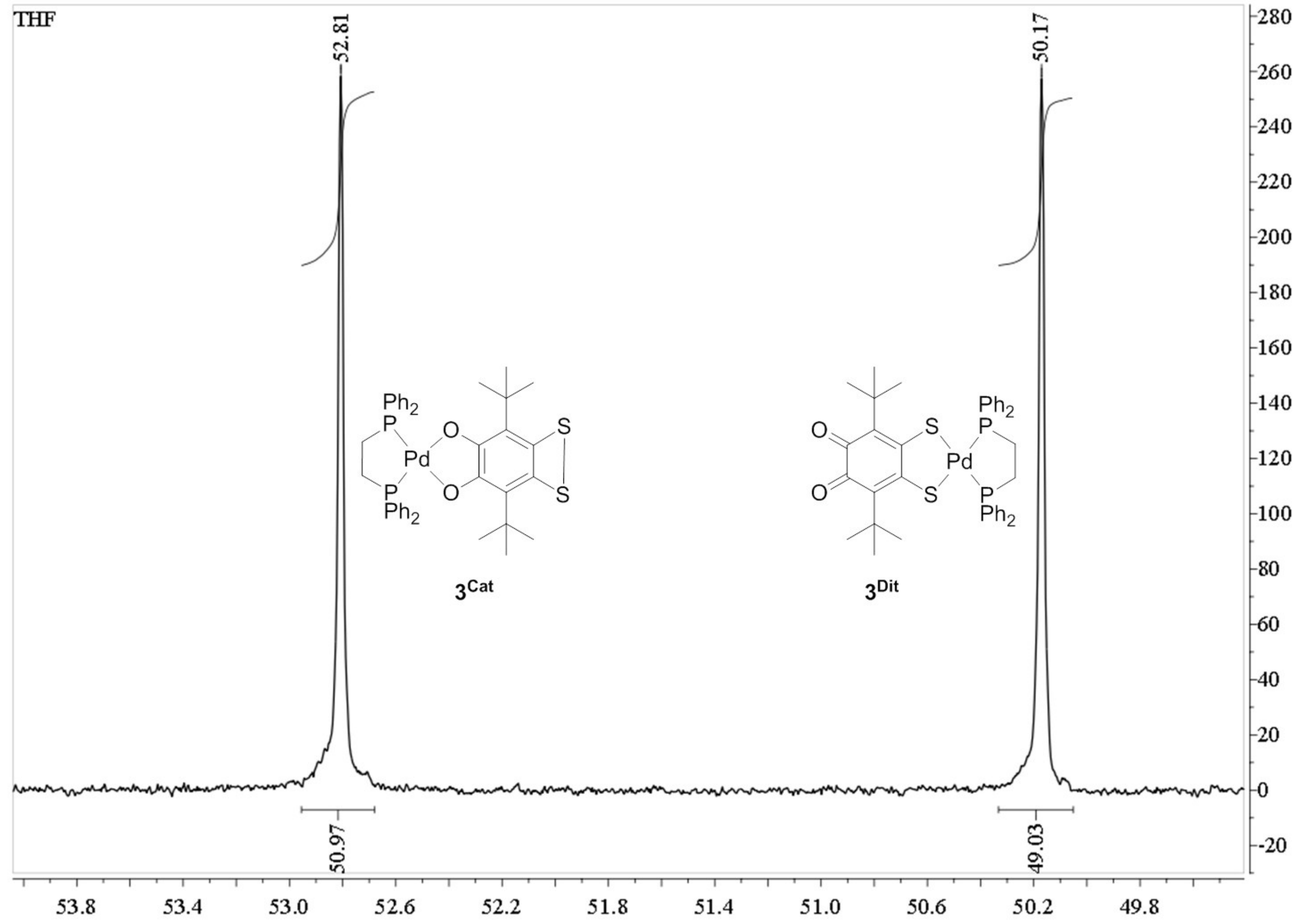


Figure SI1. $^{31}$P NMR spectrum of reaction mixture in THF: $\delta$ = 52.81 (**$3^{Cat}$**), 50.17 ppm (**$3^{Dit}$**), **$3^{Cat}$/$3^{Dit}$** = 1.04

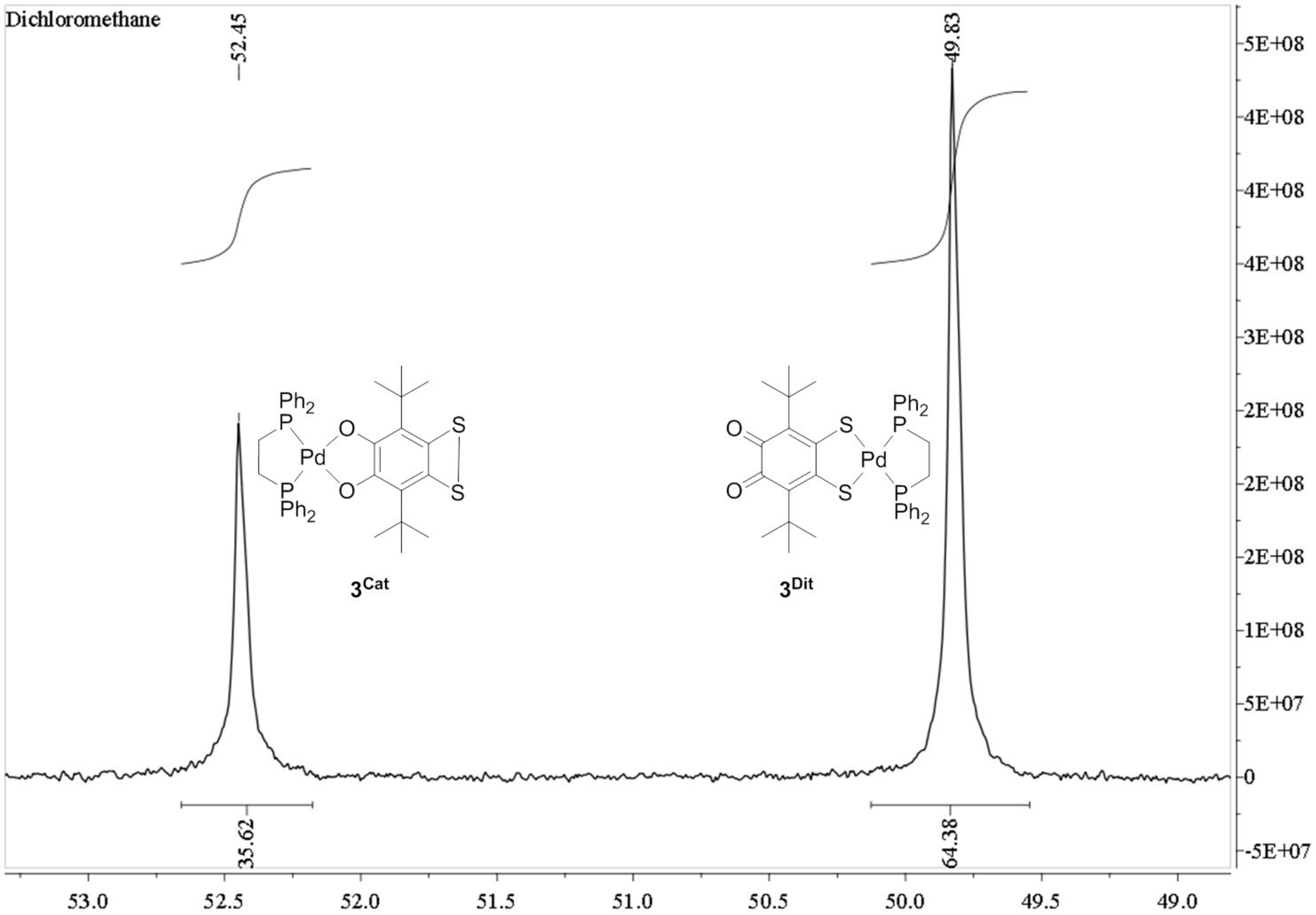


Figure SI2. $^{31}$P NMR spectrum of reaction mixture in $CH_2Cl_2$: δ= 52.45 (**3**$^{Cat}$), 49.83 ppm (**3**$^{Dit}$), **3**$^{Cat}$/**3**$^{Dit}$ = 0.55

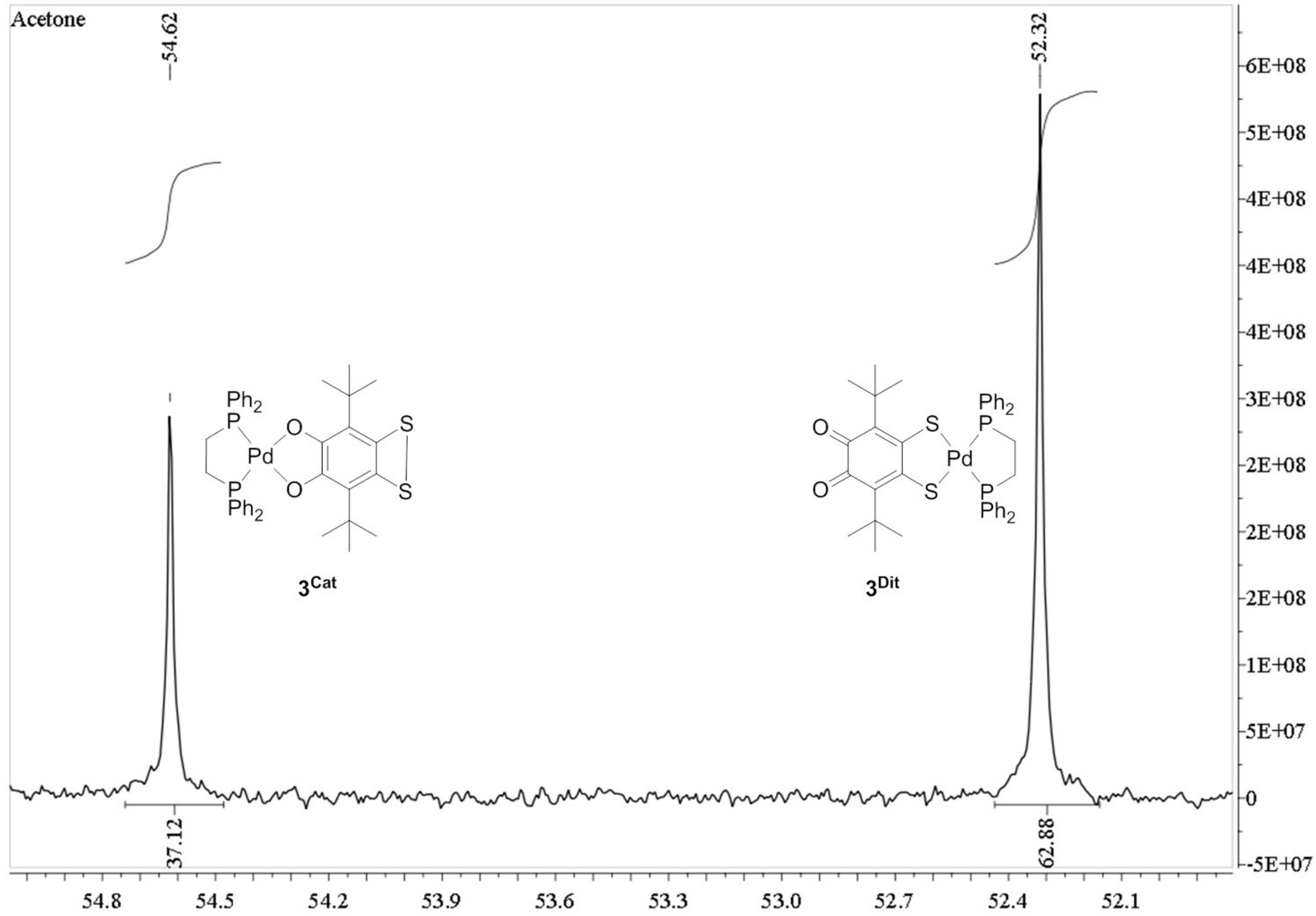
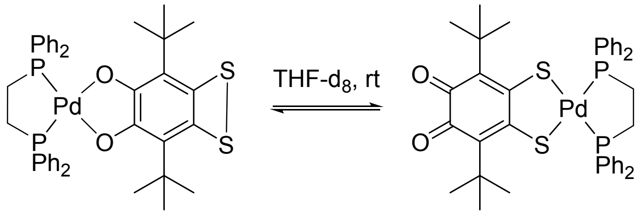


Figure SI3. $^{31}$P NMR spectrum of reaction mixture in acetone: $\delta$= 54.62 ($\mathbf{3^{Cat}}$), 52.32 ppm ($\mathbf{3^{Dit}}$), $\mathbf{3^{Cat}/3^{Dit}}$ = 0.59



$\mathbf{3^{Cat}}$ $\mathbf{3^{Dit}}$

Scheme SI2. Isomerization of $\mathbf{3^{Cat}}$ to $\mathbf{3^{Dit}}$.

Pure sample of $\mathbf{3^{Cat}}$ was dissolved in THF-d8, and $^1$H-NMR monitoring of isomerization was carried out at room temperature. Quantitative estimations were done using signals of m-Ph protons of phosphine ligands that are resolved and are not overlapped in NMR spectra.

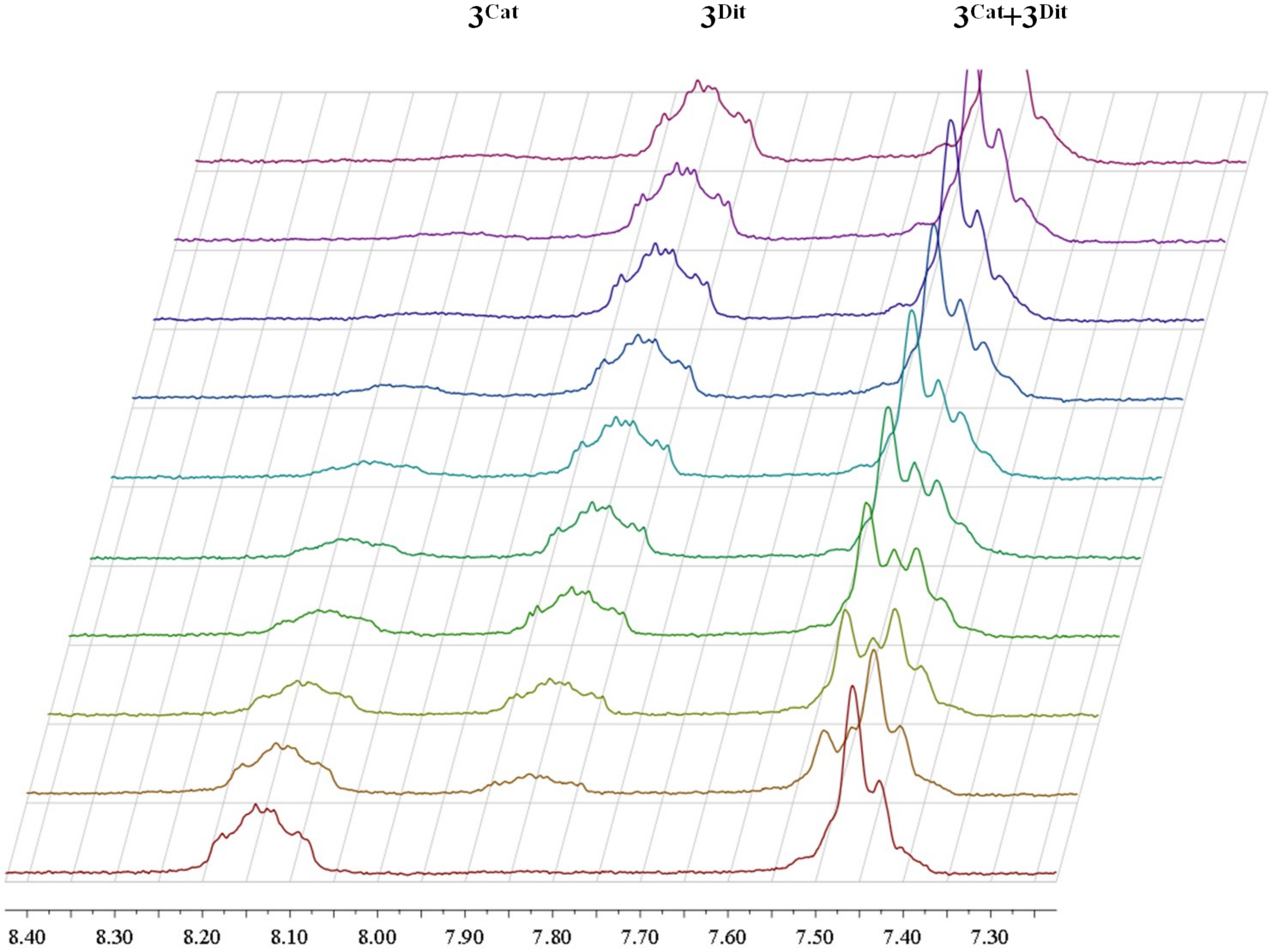


Figure SI4. $^1$H-NMR stack plot of isomerization of $\mathbf{3^{Cat}}$ to $\mathbf{3^{Dit}}$:

$\mathbf{3^{Cat}}$ **:** 7.41-7.47 (m, $12H_{o+p}$), 8.11-8.15 (m, $8H_m$);
$\mathbf{3^{Dit}}$ **:** 7.47-7.53 (m, $12H_{o+p}$), 7.82-7.87 (m, $8H_m$)

# IR spectra

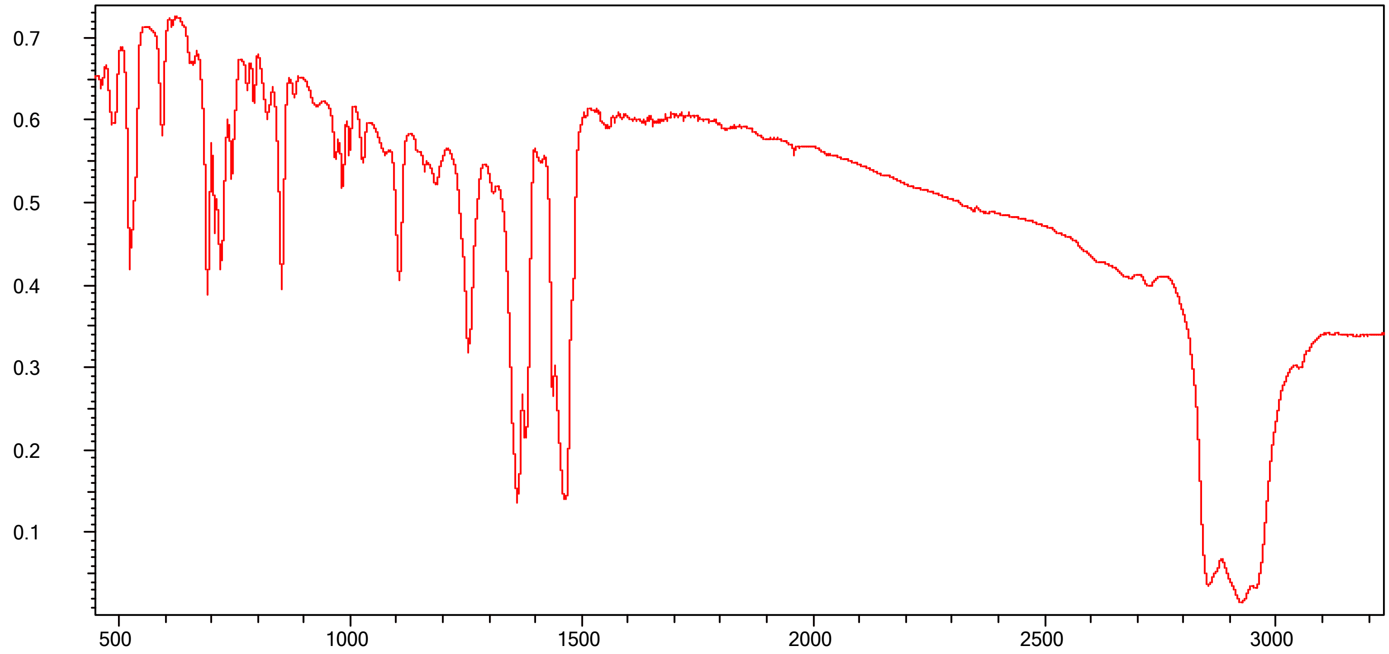


Figure SI5. IR spectrum of $\mathbf{3}^{\mathrm{Cat}}$ in nujol

ν = 1436, 1359, 1256 (C-O), 1104, 1027, 997, 981, 967, 850, 743, 717, 690, 591, 524 cm$^{-1}$

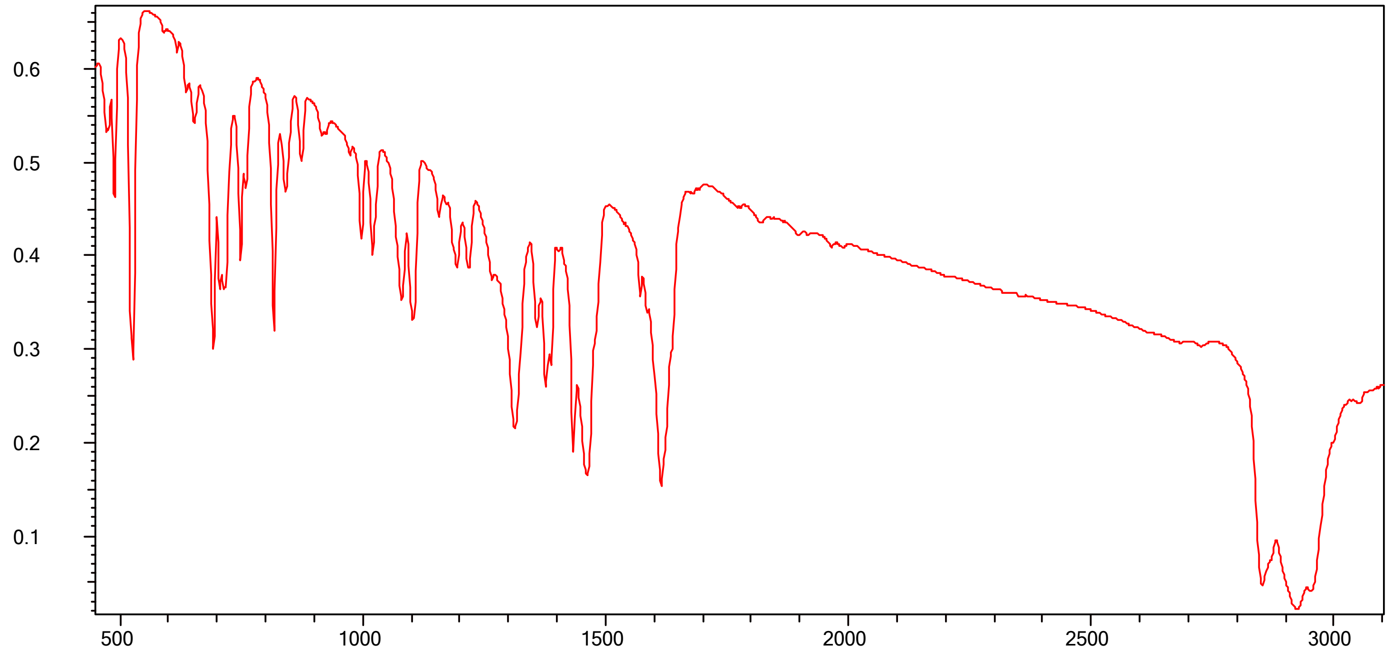


Figure SI6. IR spectrum of $\mathbf{3}^{\mathrm{Dit}}$ in nujol

ν = 1614 (C=O), 1434, 1358, 1314, 1219, 1193, 1107, 1078, 1020, 998, 875, 842, 817, 800, 748, 719, 691, 654, 527 cm$^{-1}$

## X-band EPR spectra

*Generation of semiquinonate complex* **4** *in solution.*

10 mg (0.01 mmol) of $3^{Cat}$ and 2 mg (0.01 mmol) of silver trifluoroacetate were dissolved in 5 mL of degassed THF, then poored to the ampoule with attached EPR tube. The ampoule was shaken for several times and then the solution was poured into the EPR tube.

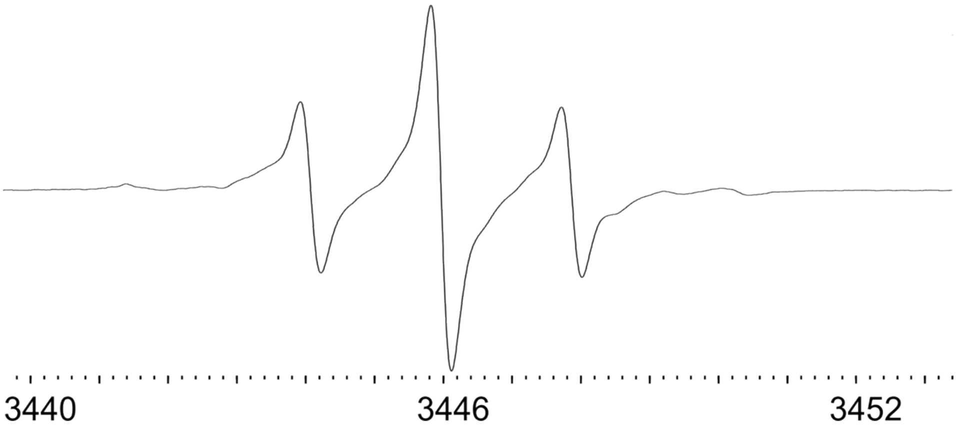


Figure SI7. X-band EPR spectra of **4** in THF, 298K.

$g_{iso}$ = 2.0021, $a_P$ = 1.89 G (2*P)

*Generation of semiquinonate complex* **5** *in solution.*

10 mg (0.01 mmol) of $3^{Dit}$ and thallium amalgam (excess) were placed into ampoule. Then 5 mL of degassed THF were added. The ampoule was shaken for several times and then the solution was poured into the EPR tube.

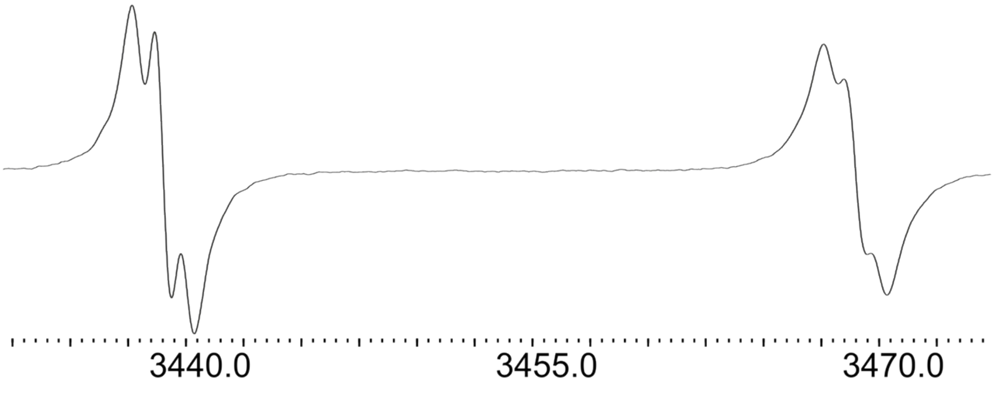


Figure SI8. X-band EPR spectra of **5** in $CH_2Cl_2$, 298K.

$g_{iso}$ = 1.9964, $a_{Tl}$ = 30.3 G, $a_P$ = 1.3 G (2*P)

# DFT calculations data

DFT calculations were performed by Gaussian 09[12]. The following levels of theory for a full geometry optimization were used: B3LYP/def2tzvp, M062X/def2tzvp, CAM-B3LYP/def2svp, M062X/def2tzvp (IEFPCM, Solv=THF), M062X/def2tzvpp and TPSSh/def2tzvp. Obtained data are presented in Table SI4.

| | E ($\mathbf{3}^{Cat}$), a.u.<br>E ($\mathbf{3}^{Dit}$), a.u. | **ΔE, kcal/mol** |
|---|---|---|
| B3LYP/def2tzvp | -3307.851530 | |
| | -3307.867293 | **-9.9** |
| M062X/def2tzvp | -3306.852322 | |
| | -3306.859963 | **-4.8** |
| M062X/def2tzvp IEFPCM, THF | -3306.876304 | |
| | -3306.887147 | **-6.8** |
| M062X/def2tzvpp | -3306.873126 | |
| | -3306.879023 | **-3.7** |
| CAM-B3LYP/def2svp | -3306.778076 | |
| | -3306.787734 | **-6.1** |
| TPSSh/def2tzvp | -3307.894113 | |
| | -3307.906271 | **-7.6** |

Table SI4. Total (E) and relative (ΔE) energies of $\mathbf{3}^{Cat}$ and $\mathbf{3}^{Dit}$ calculated by the DFT method.

The best agreement of optimized parameters with experiment was obtained by using of M062X/def2tzvp approximation.

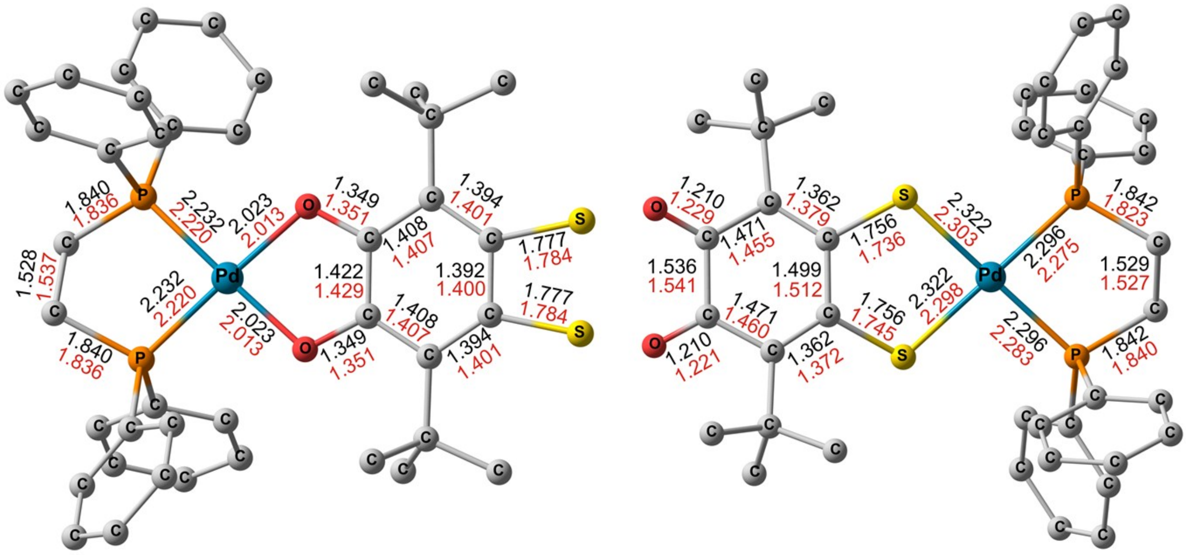


Figure SI9. Optimized geometries of $\mathbf{3}^{Cat}$ (left) and $\mathbf{3}^{Dit}$ (right) calculated by DFT M062X/def2tzvp method. X-ray data are shown in red colour. Bond lengths are given in Å, hydrogen atoms are omitted for clarity.

## Literature

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