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SUPPORTING INFORMATION

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Title: Coordinative Flexibility of a Thiophenolate Oxazoline Ligand in Nickel(II), Palladium(II), and Platinum(II) Complexes

Author(s): Lydia M. Peschel, Christof Holzer, Ljiljana Mihajlović-Lalić, Ferdinand Belaj, Nadia C. Mösch-Zanetti*

This supporting information contains further details on the calculation of the number of unpaired electrons of **2** and the X-ray structure determinations of all compounds (**1a**,**1b**, **2**, **3a**,**3b**, **4**, **5**). In addition, compounds **3a**, **3b** and **5** were found to crystallize in a second conformation. Crystallographic data of these structure determinations are described.

Calculation of the number of unpaired electrons

The balance was calibrated against $[HgCo(SCN)_4]$ and the volume susceptibility χ^V of the sample was measured. From χ^V and the density of the solid the mass susceptibility χ_g can be calculated according to Equation 1. The the molar susceptibility χ_m in SI units is calculated from χ_g and the molecular weight of the sample using Equation 2. The molar susceptibility χ_m could then be corrected from all diamagnetic contributions using Equation 3. With the corrected molar susceptibility χ_{corr} the effective magnetic moment μ_{eff} can be obtained using Equation 4, which can then be simplified according to Equation 5. From the effective magnetic moment μ_{eff} the number of unpaired electrons n is finally obtained via Equation 6.

Three measurements were performed and their mean value is presented in the publication.

$$\chi_g = \frac{\chi_V}{d} \qquad \text{Equation 1.}$$

$$\chi_m = \chi_g \cdot M_w \cdot \frac{4\pi}{1 \cdot 10^6} \qquad \text{Equation 2.}$$

$$\chi_{corr} = \chi_m - \chi_{dia} \frac{4\pi}{1 \cdot 10^6} \qquad \text{Equation 3.}$$

$$\mu_{eff} = \sqrt{\frac{3k}{N_A \cdot \mu 0 \cdot \mu^2{}_B} \cdot \sqrt{\chi_{corr} \cdot T}} \frac{4\pi}{1 \cdot 10^6} \qquad \text{Equation 4.}$$

$$\mu_{eff} = 797.5 \cdot \sqrt{\chi_{corr} \cdot T} \frac{4\pi}{1 \cdot 10^6} \qquad \text{Equation 5.}$$

$$n = \sqrt{\mu^2{}_{eff} + 1} - 1 \frac{4\pi}{1 \cdot 10^6} \qquad \text{Equation 6.}$$

Crystallographic Data and Structure Refinement Details

Table S1. Crystallographic Data and Structure Refinement for Complexes *trans*-$[Pt(S\text{-}Phoz)_2]$ (**1a**), *trans*-$[Pd(S\text{-}Phoz)_2]$ (**1b**) and $[Ni(S\text{-}Phoz)_2]$ (**2**).

	1a	1b	2
Empirical formula	$C_{22}H_{24}N_2O_2PtS_2$	$C_{22}H_{24}N_2O_2PdS_2$	$C_{22}H_{24}N_2NiO_2S_2$
Formula weight	607.64	518.95	471.26
Crystal description	block, yellow	needle, orange	plate, black
Crystal size	0.27 x 0.17 x 0.12mm	0.28 x 0.07 x 0.06mm	0.32 x 0.28 x 0.06mm
Crystal system, space group	monoclinic, $P\ 2_1/n$	monoclinic, $P\ 2_1/n$	orthorhombic, P b c a
Unit cell dimensions	a = 18.2384(7) Å	a = 9.6915(5) Å	a = 9.4137(4) Å
	b = 11.0364(4) Å	b = 10.9547(5) Å	b = 20.0986(9) Å
	c = 22.0408(8) Å	c = 20.6209(10) Å	c = 22.8459(9) Å
	β = 106.8150(10)°	β = 90.443(2)°	
Volume	4246.8(3) $Å^3$	2189.20(18) $Å^3$	4322.5(3) $Å^3$
Z	8	4	8
Calculated density	1.901 Mg/m^3	1.575 Mg/m^3	1.448 Mg/m^3
F(000)	2368	1056	1968
Linear absorption coefficient μ	6.826 mm^{-1}	1.059 mm^{-1}	1.112 mm^{-1}
Max. and min. transmission	0.7461 and 0.3697	1.0000 and 0.7760	0.9657 and 0.8183
Θ range for data collection	2.18 to 30.00°	2.32 to 27.00°	2.21 to 30.00°
Index ranges	$-25 \le h \le 20, -15 \le k \le 14, -29 \le l \le 31$	$-12 \le h \le 11, -13 \le k \le 13, -20 \le l \le 26$	$-13 \le h \le 13, -25 \le k \le 28, -32 \le l \le 26$
Reflections collected/ unique	35116/ 12365	13570/ 4757	74158/ 6302
Significant unique reflections	10781 with $I > 2\sigma(I)$	4361 with $I > 2\sigma(I)$	5565 with $I > 2\sigma(I)$
R(int), R(sigma)	0.0308, 0.0335	0.0352, 0.0401	0.0276, 0.0128
Completeness to Θ = 30.0°	99.9%	99.5%	100.0%
Data/ parameters/ restraints	12365/ 547/ 0	4757/ 303/ 43	6302/ 274/ 0
Goodness-of-fit on F^2	1.094	1.168	1.074
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0382, wR2 = 0.0894	R1 = 0.0502, wR2 = 0.1070	R1 = 0.0228, wR2 = 0.0609
R indices (all data)	R1 = 0.0470, wR2 = 0.0931	R1 = 0.0562, wR2 = 0.1099	R1 = 0.0292, wR2 = 0.0654
Weighting scheme	$w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P = (F_o^2+2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P = (F_o^2+2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P = (F_o^2+2F_c^2)/3$
Largest difference peak and hole	6.745 and -2.509 $e/Å^3$	1.427 and -1.012 $e/Å^3$	0.438 and -0.237 $e/Å^3$
CCDC deposition number	1015350	1015351	1015352

Table S2. Crystallographic Data and Structure Refinement Details for [Pt(η^2-S-Phoz)(η^1-S-Phoz)(PPh_3)] (**3a**) and [Pd(η^2-S-Phoz)(η^1-S-Phoz)(PPh_3)] (**3b**).

	3a	3b
Empirical formula	$C_{40}H_{39}N_2O_2PPtS_2$	$C_{40}H_{39}N_2O_2PPdS_2$
Formula weight	869.91	781.22
Crystal description	block, orange	block, red
Crystal size	0.33 x 0.31 x 0.28mm	0.26 x 0.21 x 0.16mm
Crystal system, space group	monoclinic, P 2_1/n	monoclinic, P 2_1/n
Unit cell dimensions:	a = 19.1704(9) Å	a = 19.1853(6) Å
	b = 8.6867(4) Å	b = 8.6988(3) Å
	c = 22.8310(11) Å	c = 22.8924(8) Å
	β = 111.3460(10)°	β = 111.5480(10)°
Volume	3541.2(3) $Å^3$	3553.5(2) $Å^3$
Z	4	4
Calculated density	1.632Mg/m^3	1.460Mg/m^3
F(000)	1736	1608
Linear absorption coefficient μ	4.164mm^{-1}	0.723mm^{-1}
Max. and min. transmission	0.2611 and 0.1571	0.7461 and 0.5794
Θ range for data collection	2.53 to 30.00°	2.38 to 30.00°
Index ranges	$-26 \leq h \leq 25, -12 \leq k \leq 10, -30 \leq l \leq 32$	$-26 \leq h \leq 26, -9 \leq k \leq 12, -16 \leq l \leq 32$
Reflections collected/ unique	53067/ 10337	25656/ 10368
Significant unique reflections	9350 with $I > 2\sigma(I)$	8853 with $I > 2\sigma(I)$
R(int), R(sigma)	0.0359, 0.0271	0.0299, 0.0385
Completeness to Θ = 30.0°	99.9%	99.9%
Data/ parameters/ restraints	10337/ 448/ 0	10368/ 448/ 0
Goodness-of-fit on F^2	1.038	1.035
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0200, wR2 = 0.0445	R1 = 0.0281, wR2 = 0.0721
R indices (all data)	R1 = 0.0237, wR2 = 0.0453	R1 = 0.0354, wR2 = 0.0753
Weighting scheme	$w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P = (F_o^2+2F_c^2)/3$	w = 1/[σ2(Fo2)+(aP)2+bP] where P = (Fo2+2Fc2)/3
Largest difference peak and hole	1.190 and -1.325$e/Å^3$	0.927 and -0.916$e/Å^3$
CCDC deposition number	1015354	1015356

Table S3. Crystallographic Data and Structure Refinement Details for [{PdCl(S-Phoz)}$_2$] (**4**) and [PdCl(S-Phoz)(PPh$_3$)] (**5**).

	4	5
Empirical formula	$C_{22}H_{24}Cl_2N_2O_2Pd_2S_2 \cdot 0.590(8)CH_2Cl_2$	$C_{29}H_{27}ClNOPPdS$
Formula weight	746.45	610.40
Crystal description	plate, orange	block, orange
Crystal size	0.28 x 0.17 x 0.07mm	0.19 x 0.17 x 0.12mm
Crystal system, space group	orthorhombic, P c c n	monoclinic, P 2_1/c
Unit cell dimensions:	a = 15.0475(5) Å	a = 14.9793(7) Å
	b = 23.4300(7) Å	b = 10.9549(5) Å
	c = 7.6521(2) Å	c = 17.4456(8) Å
		β = 114.3340(10)°
Volume	2697.85(14) Å^3	2608.4(2) Å^3
Z	4	4
Calculated density	1.838Mg/m^3	1.554Mg/m^3
F(000)	1475.1	1240
Linear absorption coefficient μ	1.827mm^{-1}	0.979mm^{-1}
Max. and min. transmission	1.0000 and 0.7685	0.9922 and 0.8008
Θ range for data collection	2.71 to 30.00°	2.26 to 30.00°
Index ranges	$-21 \le h \le 21$, $-32 \le k \le 32$, $-10 \le l \le 10$	$-21 \le h \le 16$, $-9 \le k \le 15$, $-21 \le l \le 24$
Reflections collected/ unique	28367/ 3937	20782/ 7608
Significant unique reflections	3219 with $I > 2\sigma(I)$	6792 with $I > 2\sigma(I)$
R(int), R(sigma)	0.0447, 0.0274	0.0265, 0.0277
Completeness to Θ = 30.0°	99.8%	99.9%
Data/ parameters/ restraints	3937/ 179/ 0	7608/ 325/ 0
Goodness-of-fit on F^2	1.330	1.043
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0436, wR2 = 0.0957	R1 = 0.0264, wR2 = 0.0683
R indices (all data)	R1 = 0.0606, wR2 = 0.1028	R1 = 0.0311, wR2 = 0.0707
Weighting scheme	$w = 1/[\sigma_2(F_o^2)+(aP)^2+bP]$ where $P = (F_o^2+2F_c^2)/3$	$w = 1/[\sigma_2(F_o^2)+(aP)^2+bP]$ where $P = (F_o^2+2F_c^2)/3$
Largest difference peak and hole	0.958 and -1.016e/Å^3	0.870 and -0.545e/Å^3
CCDC Deposition number	1015357	1015358

[Pt(S-Phoz)$_2$] (1a)

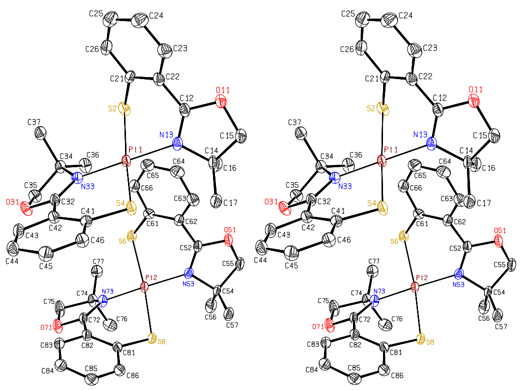


Figure S 1. Stereoscopic ORTEP plot of **1a** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms were omitted for clarity reasons.

The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the CH_2 groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and C–H distances of 0.99Å. The H atoms of the phenyl rings were put at the external bisectors of the C–C–C angles at C–H distances of 0.95Å and common isotropic displacement parameters were refined for the H atoms of the same phenyl group. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bond, and C–H distances of 0.98Å.

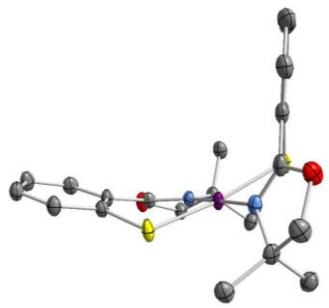


Figure S 2. View of **1a** showing the acute angle between the two planes spanned by the ligands.

[Pd(S-Phoz)$_2$] (1b)

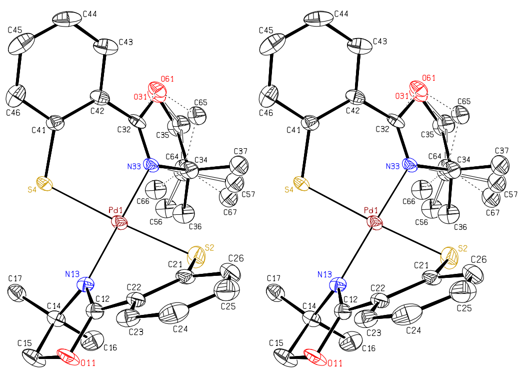


Figure S 3. Stereoscopic ORTEP plot of **1b** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms were omitted for clarity reasons. The disordered 1,3-oxazole ring was plotted with full, open, and dashed bonds for the parts with site occupation factors of 0.4066(3), 0.3625(10), and 0.2309(11), respectively.

Since racemic twinning was detected a twin matrix (-1 0 0/ 0 -1 0/ 0 0 -1) was applied and a scale factor was refined [0.2182(11)] between the two unequal components lowering the R factor from 0.156 to 0.050. One of the 1,3-oxazole rings was disordered over three orientations and refined with site occupation factors of 0.4066(3), 0.3625(10), and 0.2309(11), respectively. The equivalent bonds in these fragments were restrained to have the same lengths and the same anisotropic displacement parameters were used for equivalent atoms. The disordered atoms were restrained to have similar U_{ij} components. The other non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the phenyl rings were put at the external bisectors of the C–C–C angles at C–H distances of 0.95Å and common isotropic displacement parameters were refined for the H atoms of the same phenyl group. The H atoms of the ordered CH_2 group were refined with a common isotropic displacement parameter and an idealized geometry with approximately tetrahedral angles and C–H distances of 0.99Å. The H atoms of the disordered CH_2 group were included at calculated positions with their isotropic displacement parameters fixed to 1.2 times U_{eq} of the C atom they are bonded to. The H atoms of the ordered methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bond, and C–H distances of 0.98Å. The H atoms of the disordered methyl groups were included with idealized geometries with tetrahedral angles, staggered conformations, and C–H distances of 0.98Å with their isotropic displacement parameters fixed to 1.3 times U_{eq} of the C atom they are bonded to

[Ni(S-Phoz)$_2$] (2)

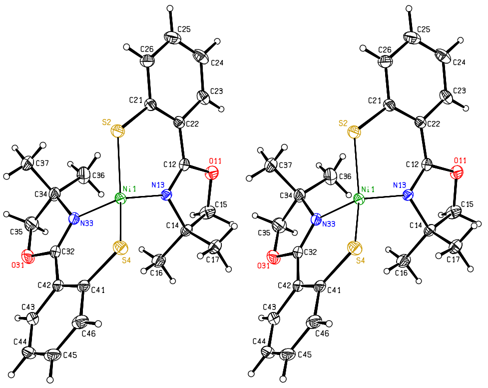
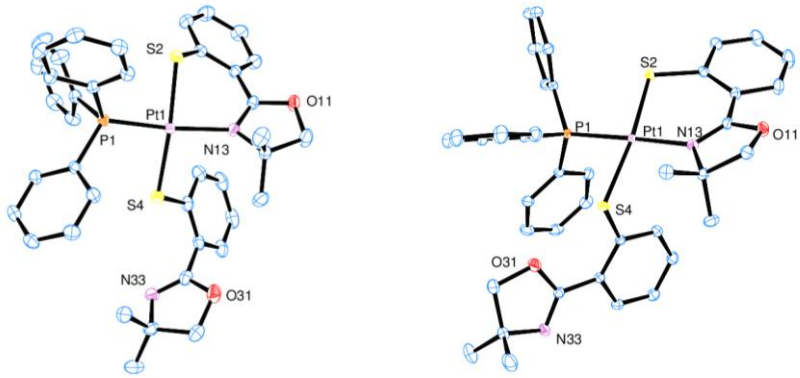


Figure S 4. Stereoscopic ORTEP plot of **2** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms are drawn with arbitrary radii.

The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the CH_2 groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and C–H distances of 0.99Å. The H atoms of the phenyl rings were put at the external bisectors of the C–C–C angles at C–H distances of 0.95Å and common isotropic displacement parameters were refined for the H atoms of the same phenyl group. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bond, and C–H distances of 0.98Å.

[Pt(κ^2-S-Phoz)(κ^1-S-Phoz)(PPh$_3$)] (3a)



modification **A**:crystallized from acetonitrile modification **B**:crystallized from diethyl ether

Figure S 5. ORTEP plots of two modifications of [Pt(κ^2-S-Phoz)(κ^1-S-Phoz)(PPh$_3$)] (**3a**) showing the atomic numbering schemes. The probability ellipsoids are drawn at the 50% probability level. Left: modification A, crystallized from acetonitrile (described in the manuscript). Right: modification B, crystallized from diethyl ether. The major difference between the two identified modifications is the orientation of the dangling oxazoline ring being in plane with the aromatic ring (right) or perpendicular to it (left).

[Pt(κ[2]-S-Phoz)(κ[1]-S-Phoz)(PPh$_3$)] (3a)- Modification A

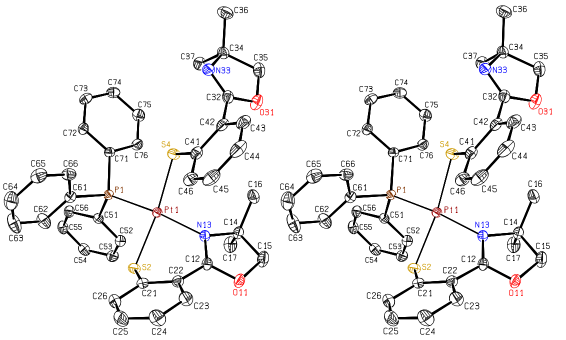


Figure S 6. Stereoscopic ORTEP plot of **3a-modification A.**

The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the CH_2 groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and C–H distances of 0.99Å. The H atoms of the phenyl rings were put at the external bisectors of the C–C–C angles at C–H distances of 0.95Å and common isotropic displacement parameters were refined for the H atoms of the same phenyl group. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bond, and C–H distances of 0.98Å.

[Pt(κ[2]-S-Phoz)(κ[1]-S-Phoz)(PPh$_3$)] (3a)- Modification B

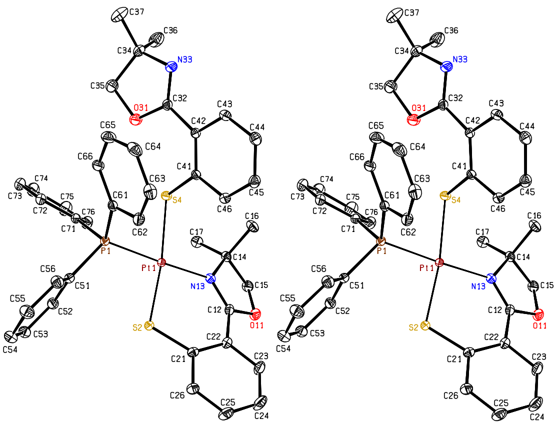
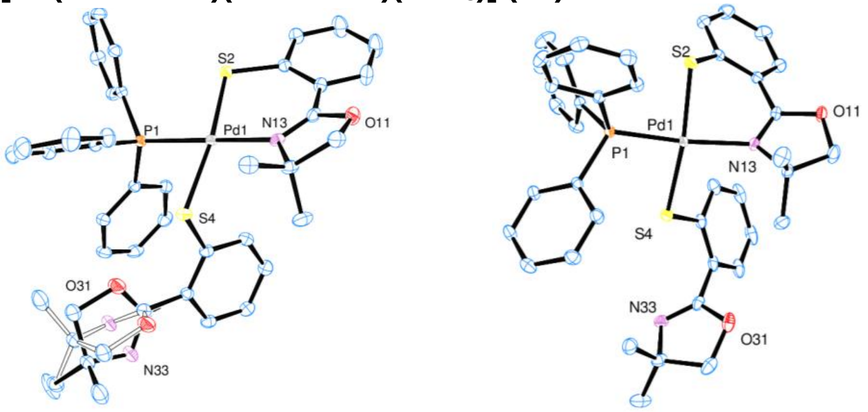


Figure S 7. Stereoscopic ORTEP plot of **3a-modification B.**

The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the CH_2 groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and C–H distances of 0.99Å. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bond (or with staggered conformations for the ether molecule), and C–H distances of 0.98Å. The H atoms of the phenyl rings were put at the external bisectors of the C–C–C angles at C–H distances of 0.95Å and common isotropic displacement parameters were refined for the H atoms of the same phenyl group.

[Pd(κ^2-S-Phoz)(κ^1-S-Phoz)(PPh_3)] (3b)



modification **A**:crystallized from acetonitrile   modification **B**:crystallized from acetone

Figure S 8. ORTEP plot of two modifications of [Pd(κ^2-S-Phoz)(κ^1-S-Phoz)(PPh_3)] (**3b**) showing the atomic numbering schemes. The probability ellipsoids are drawn at the 50% probability level. Left: crystallized from acetonitrile (described in the manuscript). Right: crystallized from acetone. In the conformation on the left side the dangling 1,3-oxazoline ring is disordered indicating the presence of the conformation on the right side, which was refined with a site occupation factor of 0.163(3).

[Pd(κ^2-S-Phoz)(κ^1-S-Phoz)(PPh_3)] (3b)- Modification A

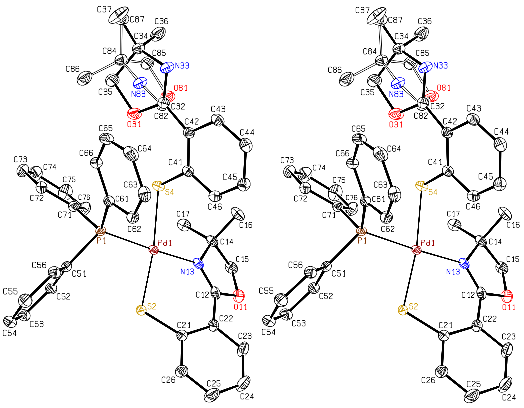


Figure S 9. Stereoscopic ORTEP plot of **3b-modification A.** The H atoms as well as the solvent molecule were omitted for clarity reasons. The bonds to atoms with site occupation factors less than 0.5 are plotted with open bonds.

The 1,3-oxazole ring not coordinating to Pd is disordered over two orientations which were refined with site occupation factors of 0.837(3) and 0.163(3), respectively. The equivalent bonds in this part were restrained to have the same lengths and the atoms with low site occupation factors were refined with the same displacement parameters of appropriate atoms. The other non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the CH_2 groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and C–H distances of 0.99Å. The H atoms of the phenyl rings were put at the external bisectors of the C–C–C angles at C–H distances of 0.95Å and common isotropic displacement parameters were refined for the H atoms of the same phenyl group. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bond, and C–H distances of 0.98Å.

[Pd(κ^2-S-Phoz)(κ^1-S-Phoz)(PPh_3)] (3b)- Modification B

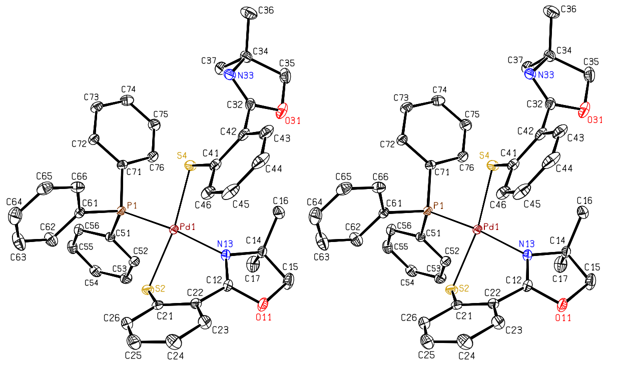


Figure S 10. Stereoscopic ORTEP plot of **1b-modification B.**

The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the CH_2 groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and C–H distances of 0.99Å. The H atoms of the phenyl rings were put at the external bisectors of the C–C–C angles at C–H distances of 0.95Å and common isotropic displacement parameters were refined for the H atoms of the same phenyl group. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bond, and C–H distances of 0.98Å.

Table S4. Selected Bond Lengths [Å] and Angles [°] for[Pd(κ^2-S-Phoz)(κ^1-S-Phoz)(PPh_3)] (3b)- Modification B and [Pd(κ^2-S-Phoz)(κ^1-S-Phoz)(PPh_3)] (3b)- Modification B

Crystal data		
Identification	**3a-modification B**	**3b-modification B**
	crystallized from diethyl ether	crystallized from acetone
Empirical formula	$C_{44}H_{49}N_2O_3PPtS_2$	$C_{40}H_{39}N_2O_2PPdS_2 \cdot C_3H_6O$
Formula weight	944.03	839.30
Crystal description	block, yellow	block, red
Crystal size	0.15 x 0.15 x 0.12mm	0.30 x 0.26 x 0.21mm
Crystal system, space group	triclinic, P -1	triclinic, P -1
Unit cell dimensions: a	11.2715(4)Å	11.2363(3)Å
b	13.1029(5)Å	12.9101(4)Å
c	14.2801(5)Å	14.3306(5)Å
α	73.9838(14)°	75.2998(14)°
β	82.3007(13)°	80.5655(12)°
γ	87.9455(13)°	88.1908(12)°
Volume	2008.88(13)Å^3	1983.47(11)Å^3
Z	2	2
Calculated density	1.561Mg/m^3	1.405Mg/m^3
F(000)	952	868
Linear absorp. coefficient μ	3.678mm^{-1}	0.655mm^{-1}
Max. and min. transmission	0.7461 and 0.5944	0.7461 and 0.6068
Θ range for data collection	2.44 to 30.00°	2.44 to 30.00°
Index ranges	$-15 \leq h \leq 15$, $-18 \leq k \leq 16$, $-19 \leq l \leq 20$	$-15 \leq h \leq 15$, $-15 \leq k \leq 18$, $-20 \leq l \leq 20$
Reflections collected/ unique	26716/ 11670	23428/ 11496
Significant unique reflections	11018 with I > 2σ(I)	10075 with I > 2σ(I)
R(int), R(sigma)	0.0231, 0.0292	0.0221, 0.0324
Completeness to Θ = 30.0°	99.6%	99.3%
Data/ parameters/ restraints	11670/ 495/ 0	11496/ 516/ 7
Goodness-of-fit on F^2	1.045	1.029
Final R indices [I > 2σ(I)]	R1 = 0.0240, wR2 = 0.0609	R1 = 0.0277, wR2 = 0.0691
R indices (all data)	R1 = 0.0262, wR2 = 0.0620	R1 = 0.0345, wR2 = 0.0728
Weighting scheme	$w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$ where	$w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$

	$P = (F_o^2+2F_c^2)/3$	where $P = (F_o^2+2F_c^2)/3$
Largest diff. peak and hole	2.520 and -1.259e/Å^3	1.190 and -1.325e/Å^3
CCDC deposition number	1015353	1015355

Table S5. Selected Bond Lengths [Å] and Angles [°] for [Pt(κ^2-S-Phoz)(κ^1-S-Phoz)(PPh_3)] (**3a**)

Bond length/ distances [Å]	3a-Mod. A	3a-Mod. B	Angles [°]	3a-Mod. A	3a-Mod. B
Pt1-N13	2.104(2)	2.1078(16)	N13-Pt1-P1	173.51(5)	171.33(5)
Pt1-P1	2.2337(6)	2.2204(5)	S2-Pt1-S4	169.56(2)	168.67(2)
Pt1-S2	2.2886(5)	2.3198(5)	N13-Pt1-S2	92.49(5)	86.49(5)
Pt1-S4	2.3624(5)	2.3409(5)	P1-Pt1-S2	91.76(2)	87.497(18)
Pt1-O312	5.015	5.638	N13-Pt1-S4	97.33(5)	96.49(5)
Pt1-N334	6.687	5.788	P1-Pt1-S4	78.78(2)	90.612(18)
			O31-Pt1-N33	15.04	22.81

Table S6. Selected Bond Lengths [Å] and Angles [°] for [Pd(κ^2-S-Phoz)(κ^1-S-Phoz)(PPh_3)] (**3b**).

Bond length/ distances [Å]	3b-Mod. A	3b-Mod. B	Angles [°]	3b-Mod. A	3b-Mod. B
Pd1-N13	2.1153(13)	2.1168(13)	N13-Pd1-P1	172.62(4)	170.46(4)
Pd1-P1	2.2466(4)	2.2343(4)	S2-Pd1-S4	168.626(15)	167.092(16)
Pd1-S2	2.2934(4)	2.3228(4)	N13-Pd1-S2	92.47(4)	87.36(4)
Pd1-S4	2.3651(4)	2.3497(4)	P1-Pd1-S2	91.587(14)	86.274(15)
Pd1-O312	5.015	5.619	N13-Pd1-S4	98.33(4)	97.83(4)
Pd1-N334	6.687	5.792	P1-Pd1-S4	78.065(14)	89.876(15)
			O31-Pd1-N33	15.04	22.87

[{PdCl(S-Phoz)}$_2$] (4)

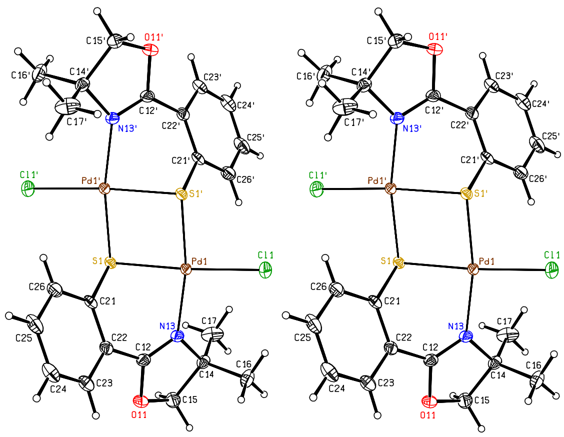


Figure S 2. Stereoscopic ORTEP plot of **4** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms are drawn with arbitrary radii. The disordered solvent molecule is omitted for clarity reasons.

The crystal structure contains voids of approx. 200Å^3 that are partially occupied by solvent molecules disordered over two orientations around two-fold rotation axes. Their site occupation factor refined to 0.295(4). The non-hydrogen atoms including those of the solvent molecule were refined with anisotropic displacement parameters without any constraints. The H atoms of the CH_2 group of the ligand were refined with common isotropic displacement parameters and idealized geometry with approximately tetrahedral angles and C–H distances of 0.99Å. The H atoms of the CH_2 groups of the solvent were included at calculated positions with their isotropic displacement parameters fixed to 1.2 times U_{eq} of the C atom they are bonded to. The H atoms of the phenyl ring were put at the external bisectors of the C–C–C angles at C–H distances of 0.95Å and a common isotropic displacement parameter was refined. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bond, and C–H distances of 0.98Å.

[PdCl(S-Phoz)(PPh_3)] (5)

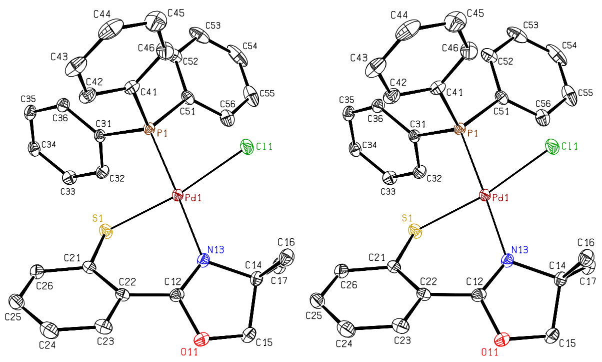


Figure S 3. Stereoscopic ORTEP plot of **5** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms were omitted for clarity reasons.

The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the CH_2 groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and C–H distances of 0.99Å. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bond, and C–H distances of 0.98Å. The H atoms of the phenyl rings were put at the external bisectors of the C–C–C angles at C–H distances of 0.95Å and common isotropic displacement parameters were refined for the H atoms of the same phenyl group.

[PdCl(S-Phoz)(PPh_3)] · ACN (5)

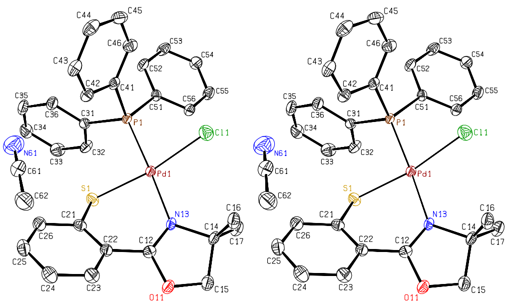


Figure S 4. Stereoscopic ORTEP plot of **5 · ACN** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms were omitted for clarity reasons.

The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the CH_2 groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and C–H distances of 0.99Å. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bond, and C–H distances of 0.98Å. The H atoms of the phenyl rings were put at the external bisectors of the C–C–C angles at C–H distances of 0.95Å and common isotropic displacement parameters were refined for the H atoms of the same phenyl group.

Crystal data	
Identification	**5 · ACN**
Empirical formula	$C_{29}H_{27}ClNOPPdS \cdot CH_3CN$
Formula weight	651.45
Crystal description	plate, orange
Crystal size	0.17 x 0.14 x 0.06mm
Crystal system, space group	monoclinic, P 2_1/c
Unit cell dimensions: a	16.1253(12)Å
b	9.7152(7)Å
c	19.3494(13)Å
β	111.930(2)°
Volume	2811.9(3)$Å^3$
Z	4
Calculated density	1.539Mg/m^3
F(000)	1328
Linear absorption coefficient μ	0.914mm^{-1}

Θ range for data collection	2.38 to 26.00°
Index ranges	$-14 \le h \le 19$, $-10 \le k \le 11$, $-23 \le l \le 22$
Reflections collected/ unique	11075/ 5475
Significant unique reflections	4648 with $I > 2\sigma(I)$
R(int), R(sigma)	0.0265, 0.0389
Completeness to Θ = 30.0°	99.3%
Data/ parameters/ restraints	5475/ 354/ 0
Goodness-of-fit on F^2	1.072
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0395, wR2 = 0.0951
R indices (all data)	R1 = 0.0497, wR2 = 0.1009
Weighting scheme	$w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P = (F_o^2+2F_c^2)/3$
Largest difference peak and hole	0.923 and -0.764e/Å^3
CCDC deposition number	1015359