Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Evidence for "cocktail"-type catalysis in Buchwald-Hartwig reaction. A mechanistic study

Darya O. Prima[§], Malena Madiyeva[†§], Julia V. Burykina[§], Mikhail E. Minyaev[§], Daniil A. Boiko,[†§] Valentine P. Ananikov[†§*]

[§]*Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky prospekt 47, Moscow, 119991, Russia;*

[§] *Department of Chemistry, Lomonosov Moscow State University, Moscow, Russia*

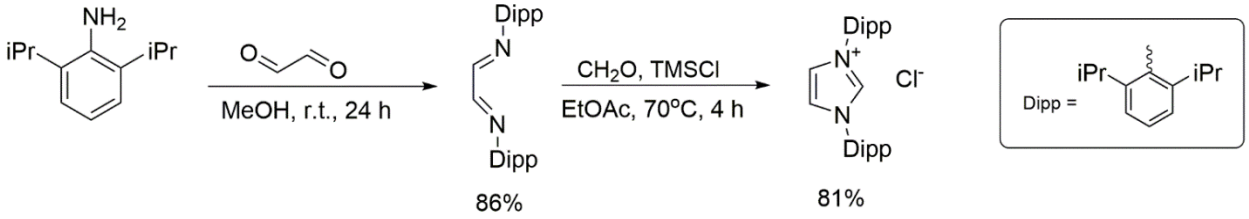
**e-mail: val@ioc.ac.ru;*

http://AnanikovLab.ru

Contents

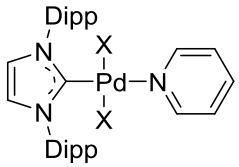
Experimental Section....3
NMR spectra of the obtained compounds....5
ESI-HRMS spectra of the obtained compounds....11
Palladium nanoparticles found in the Buchwald-Hartwig reaction mixture....20
X-ray crystallographic data and refinement details....23
The structure of 2a....26
The structure of 2b....29
The structure of 2c....32
The structure of 3a....37
The structure of 3b....44
The structure of 3c....55

Experimental Section



Scheme S1. Synthesis of imidazolium salt.

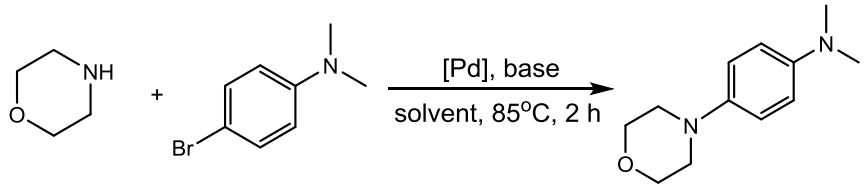
Results of the Buchwald-Hartwig reaction.[a]



entry	[Pd]	time, min	yield, %
1	1a	10	48
2		60	67
3		120	68
4		240	72
5	**1b**	10	48
6		60	70
7		120	72
8		**240**	**72**
9	1c	10	46
10		60	49
11		120	49
12		240	60

[a] Reaction conditions: 1 mmol 4-Bromo-*N*,*N*-dimethylaniline, 1.2 mmol morpholine, 1.5 mmol *t*BuOK and 0.5 mol% of corresponding [Pd] complex in the 1 ml toluene, 85°C. Reactions were performed five times and the yields were averaged. The yields were determined by ^{1}H NMR.

Optimization of the model Buchwald-Hartwig reaction of morpholine and 4-bromo-*N,N*-dimethylaniline (the yields were determined by ^{1}H NMR).



Solvent	Base	[Pd] 1b, mol%	Yield, %	Solvent	Base	[Pd] 2b, mol%	Yield, %
Toluene	*t*BuOK	1	79	Acetonitrile	*t*BuOK	2	<1
Toluene	*t*BuOK	0.5	72	THF	*t*BuOK	2	49
Acetonitrile	*t*BuOK	1	-	Dioxane	*t*BuOK	2	54
Dioxane	*t*BuOK	1	48	Toluene	PhONa	2	<1
THF	*t*BuOK	1	39	Toluene	K_2CO_3	2	-
Toluene	*t*BuONa	2	27	Toluene	DBU	2	-
				Toluene	*t*BuONa	2	27
				Toluene	*t*BuOK	2	>99
				Toluene	*t*BuOK	1	97
				Toluene	*t*BuOK	0.5	97
				Toluene	*t*BuOK	0.2	43

Solvent	Base	[Pd] 3b, mol%	Yield, %
Toluene	*t*BuOK	1	81
Toluene	*t*BuOK	0.5	74
Toluene	DBU	1	-
Toluene	K_2CO_3	1	-
Toluene	PhONa	1	<1
Toluene	*t*BuOK	2	>99

NMR spectra of the obtained compounds

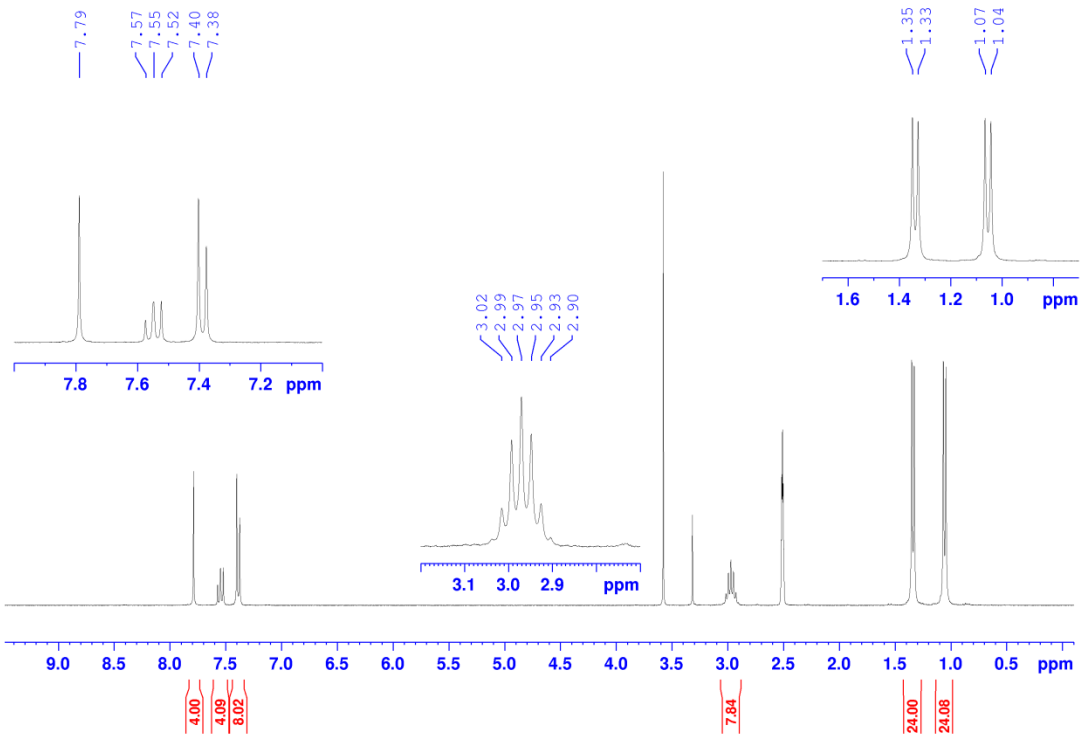


Figure S1. ^{1}H NMR spectra of **2a**. Solvent: DMSO-*d*6.

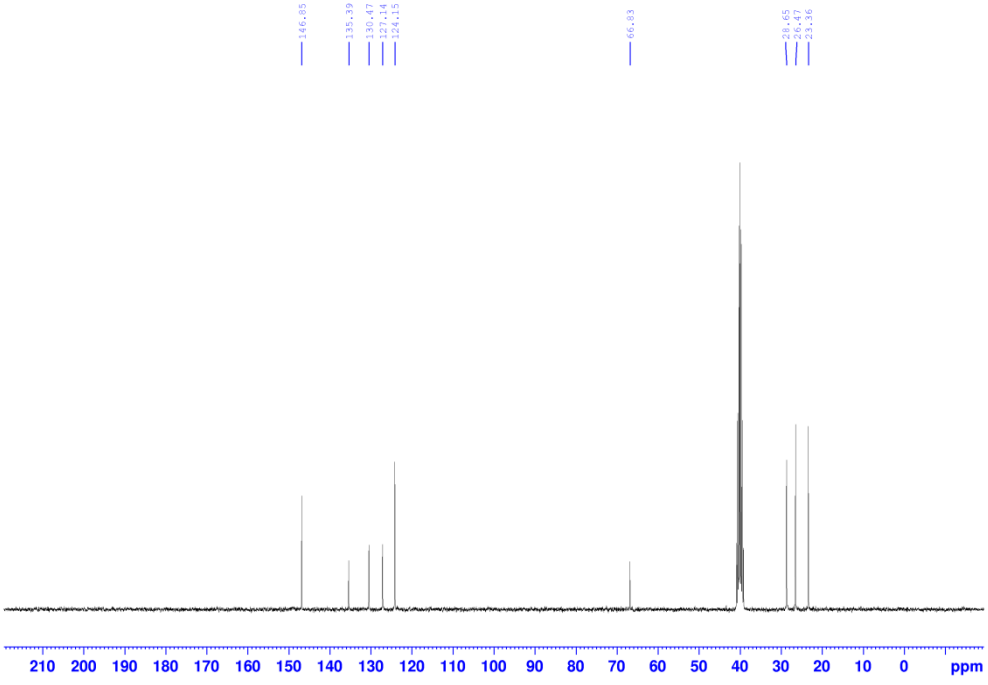


Figure S2. ^{13}C {^{1}H} NMR spectra of **2a**. Solvent: DMSO-*d*6.

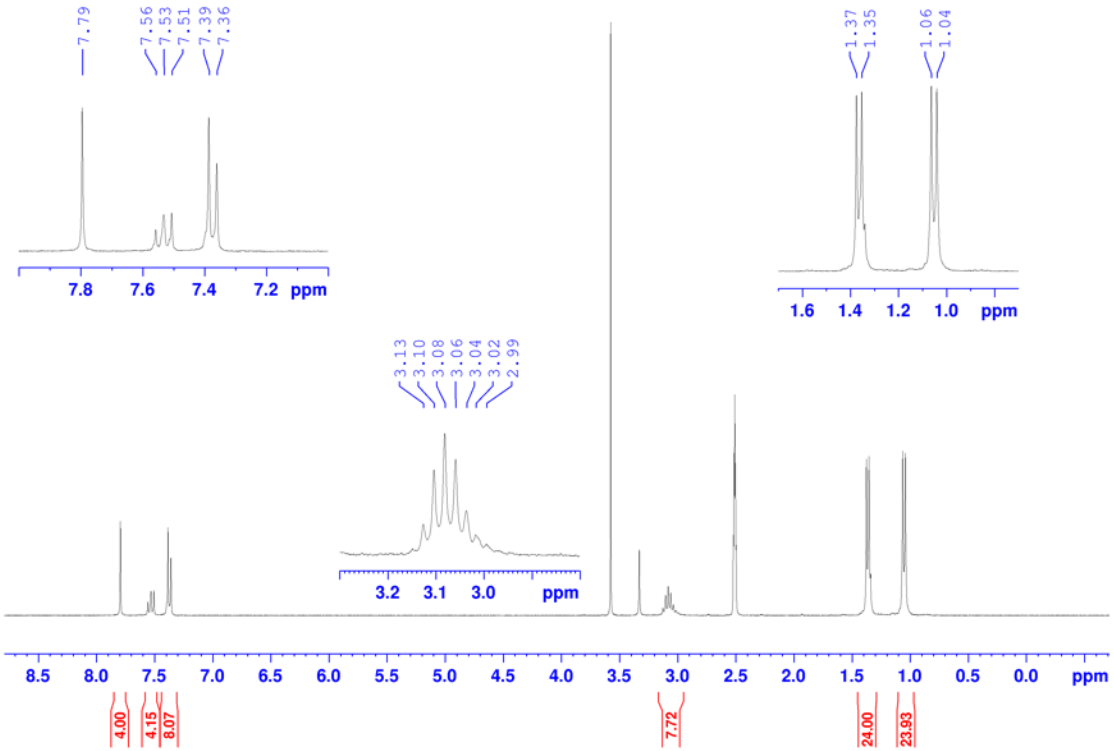


Figure S3. ^{1}H NMR spectra of **2b**. Solvent: DMSO-*d*6.

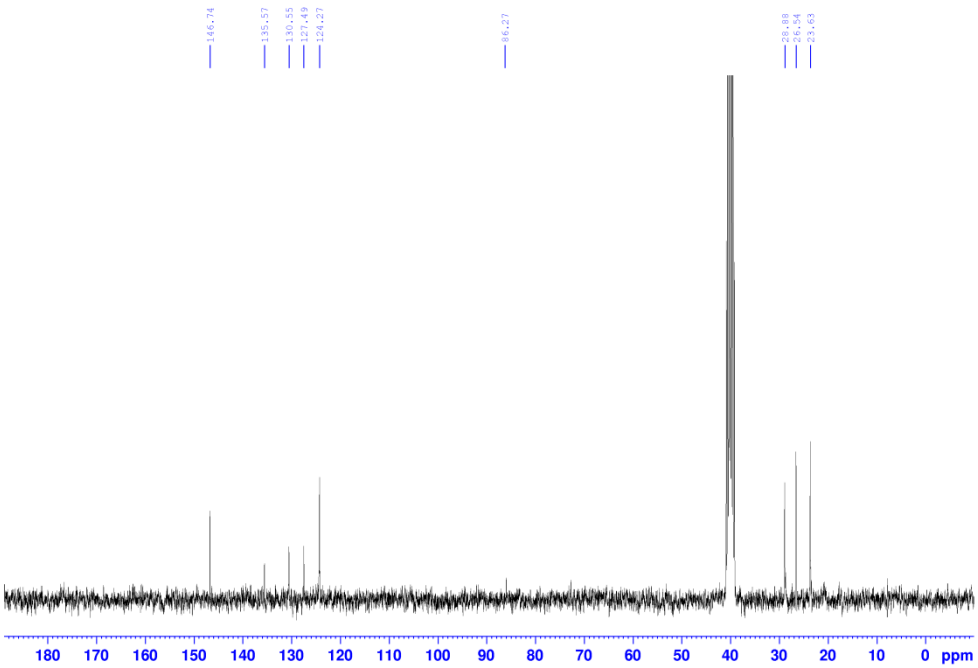


Figure S4. ^{13}C {^{1}H} NMR spectra of **2b**. Solvent: DMSO-*d*6.

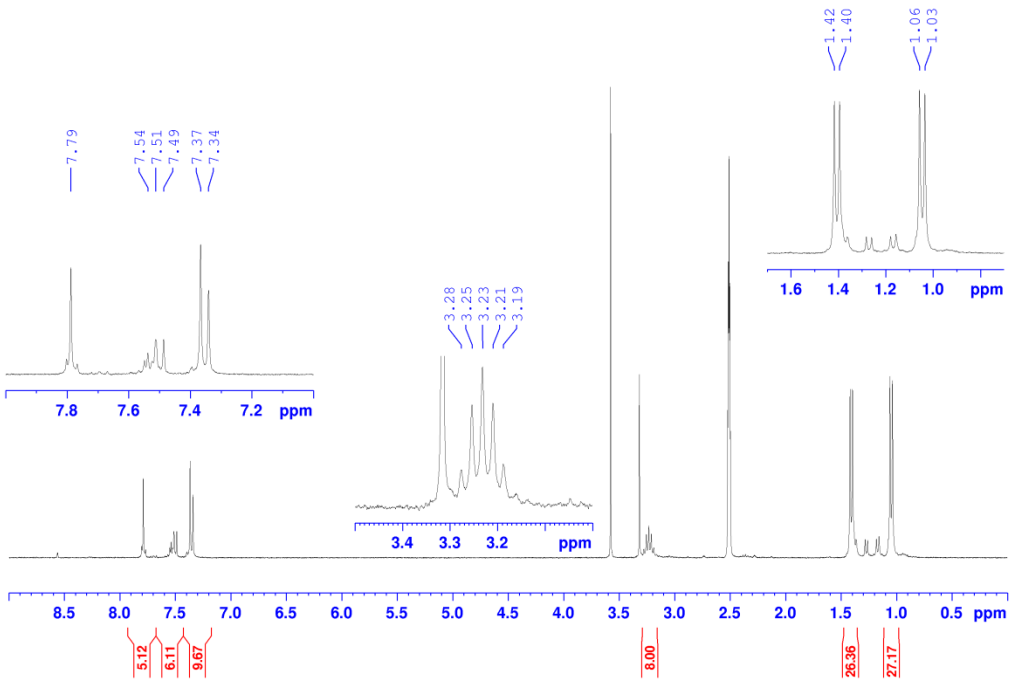


Figure S5. ^{1}H NMR spectra of **2c**. Solvent: DMSO-*d*6.

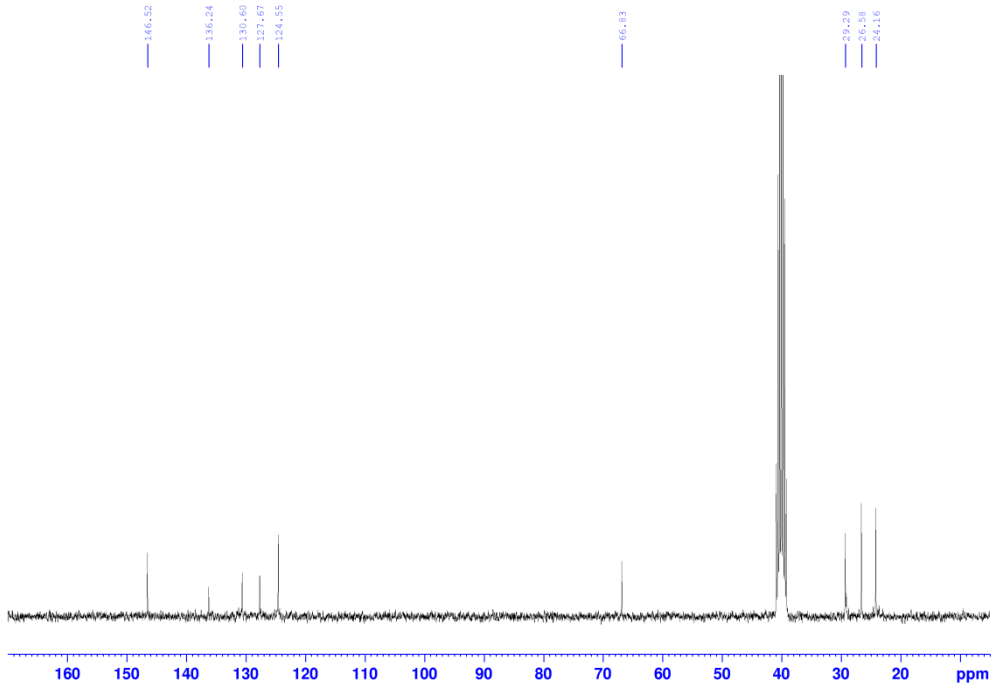


Figure S6. ^{13}C {^{1}H} NMR spectra of **2c.** Solvent: DMSO-*d*6.

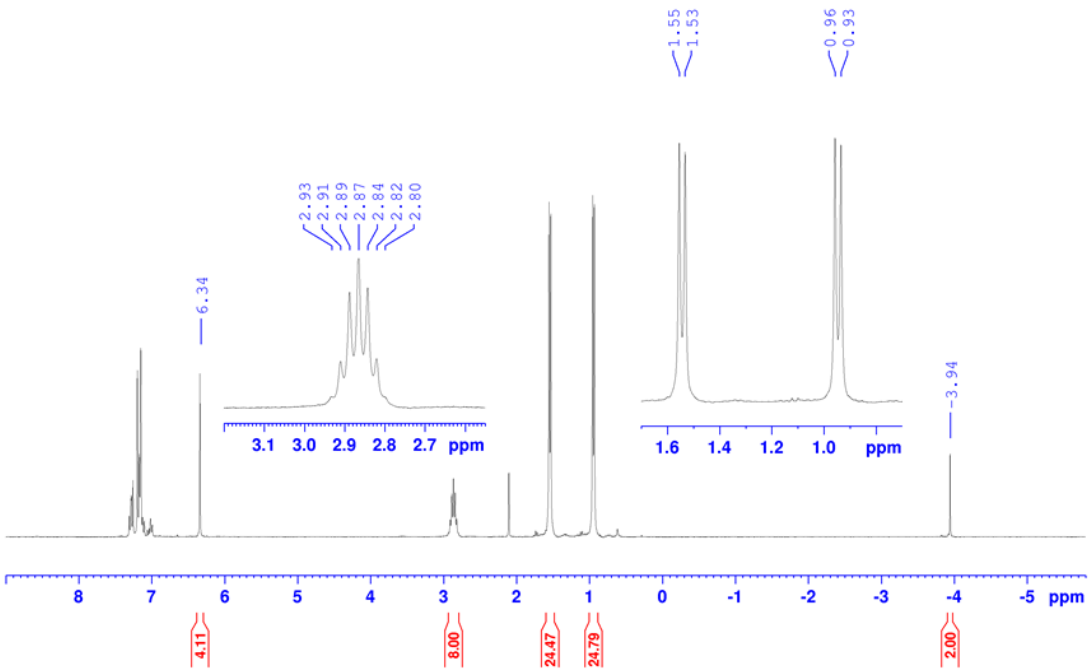


Figure S7. ^{1}H NMR spectra of **3a**. Solvent: benzene-*d*6.

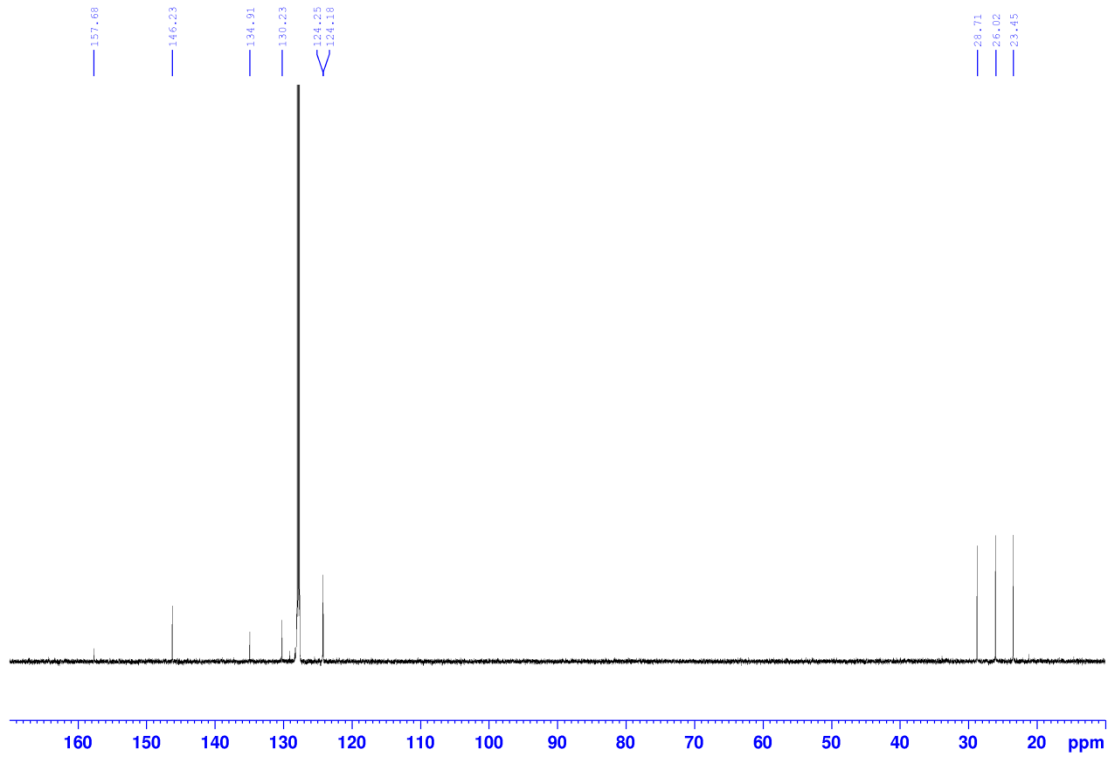


Figure S8. ^{13}C {^{1}H} NMR spectra of **3a**. Solvent: benzene-*d*6.

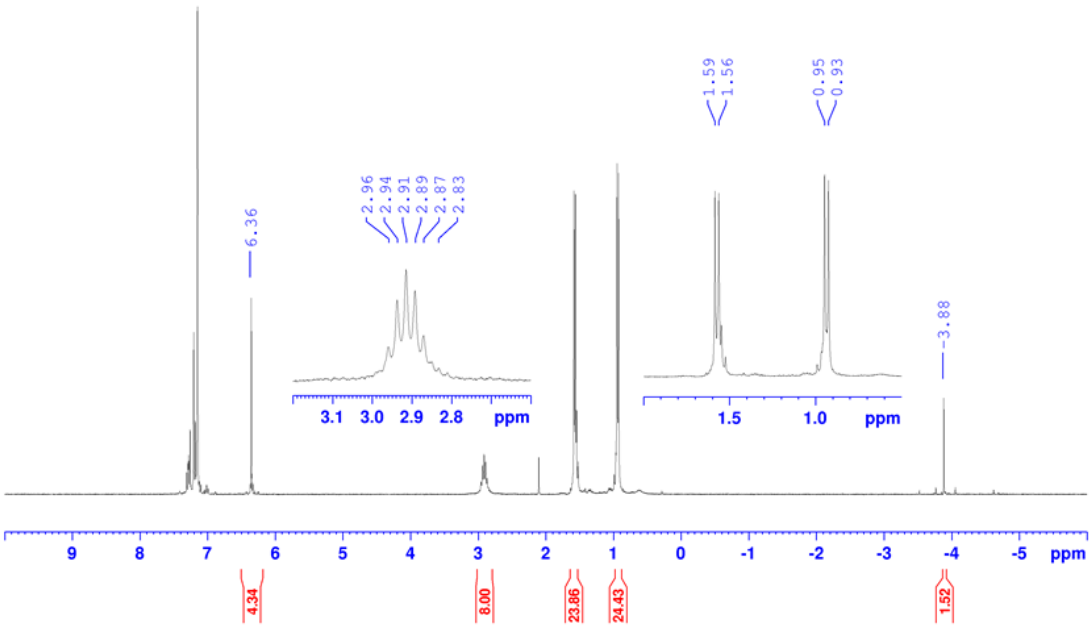


Figure S9. ^{1}H NMR spectra of **3b**. Solvent: benzene-*d*6.

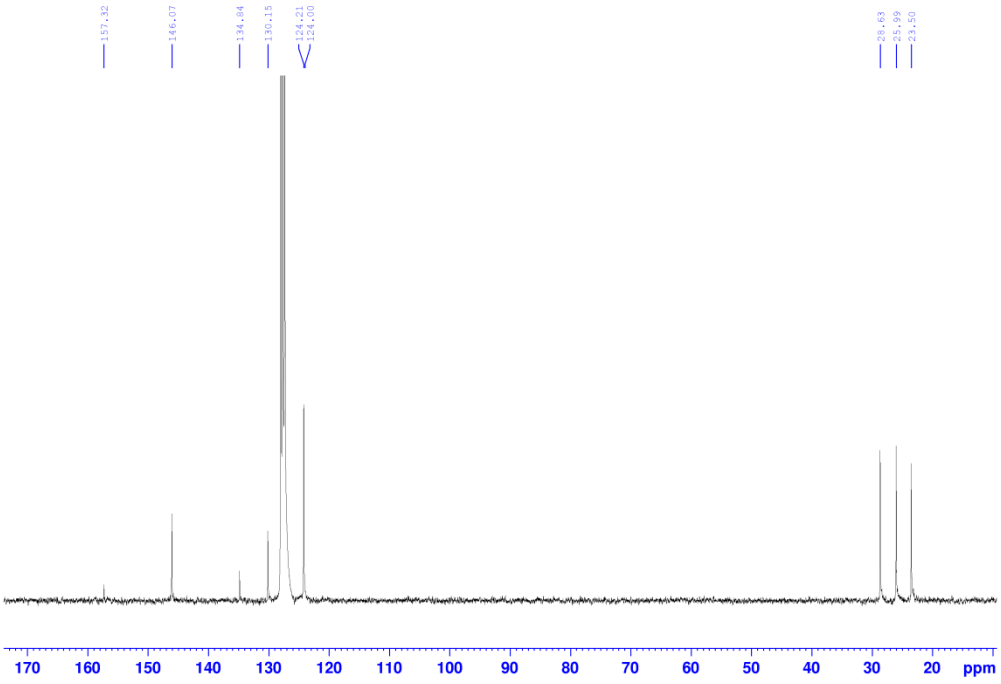


Figure S10. ^{13}C {^{1}H} NMR spectra of **3b**. Solvent: benzene-*d*6.

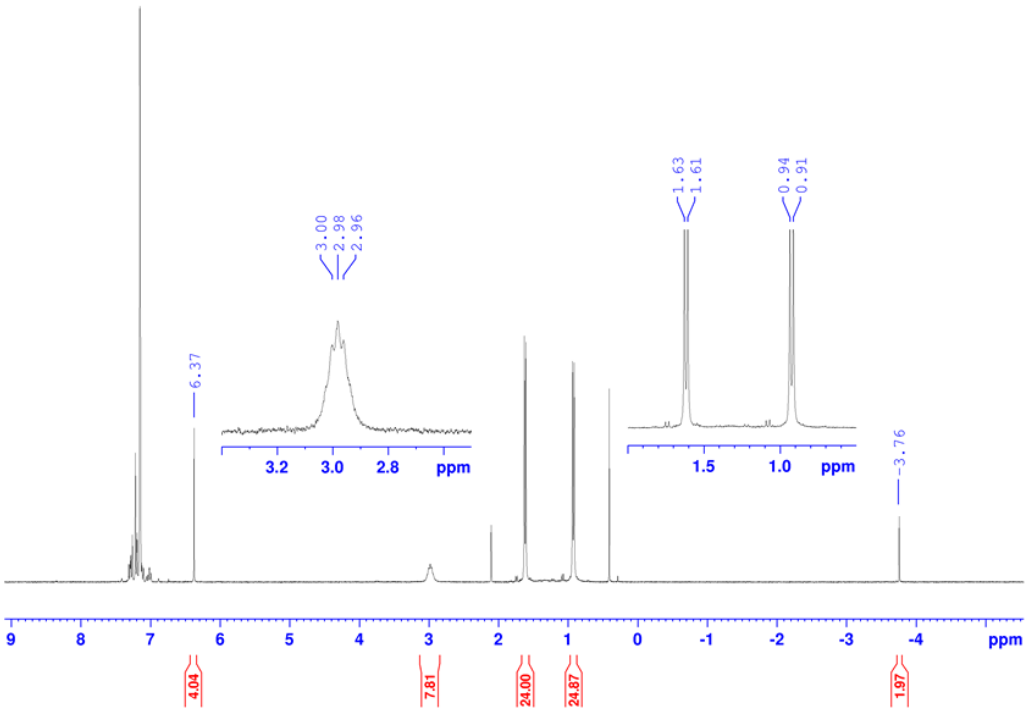


Figure S11. ^{1}H NMR spectra of **3c**. Solvent: benzene-*d*6.

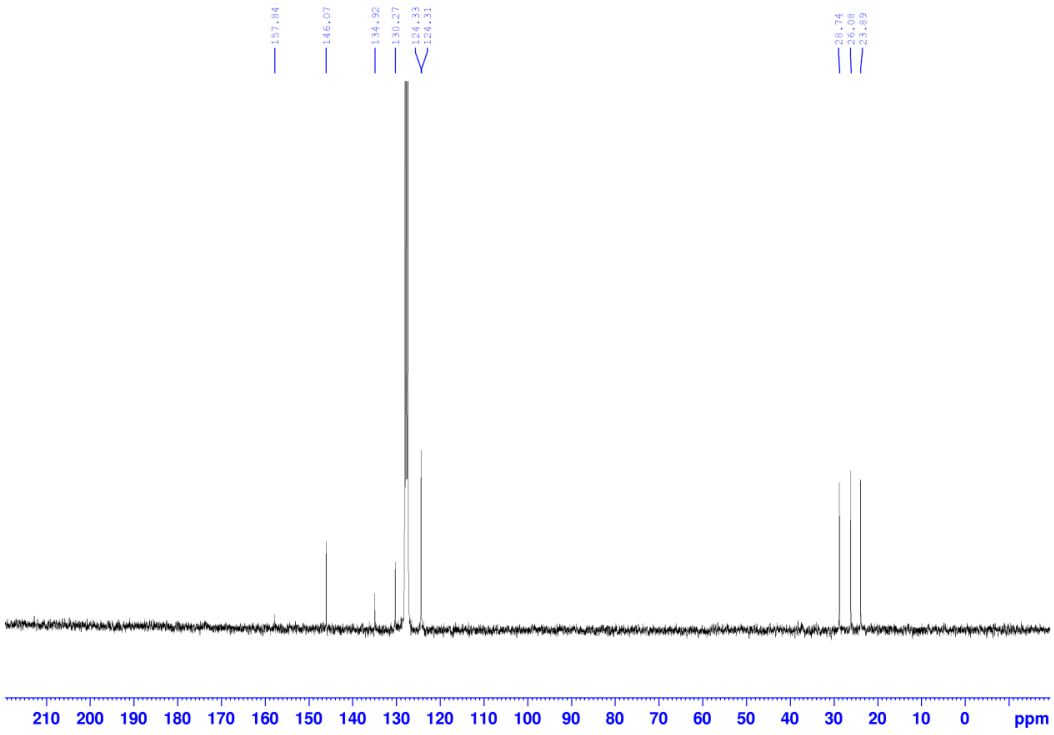


Figure S12. ^{13}C {^{1}H} NMR spectra of **3c**. Solvent: benzene-*d*6.

ESI-HRMS spectra of the obtained compounds

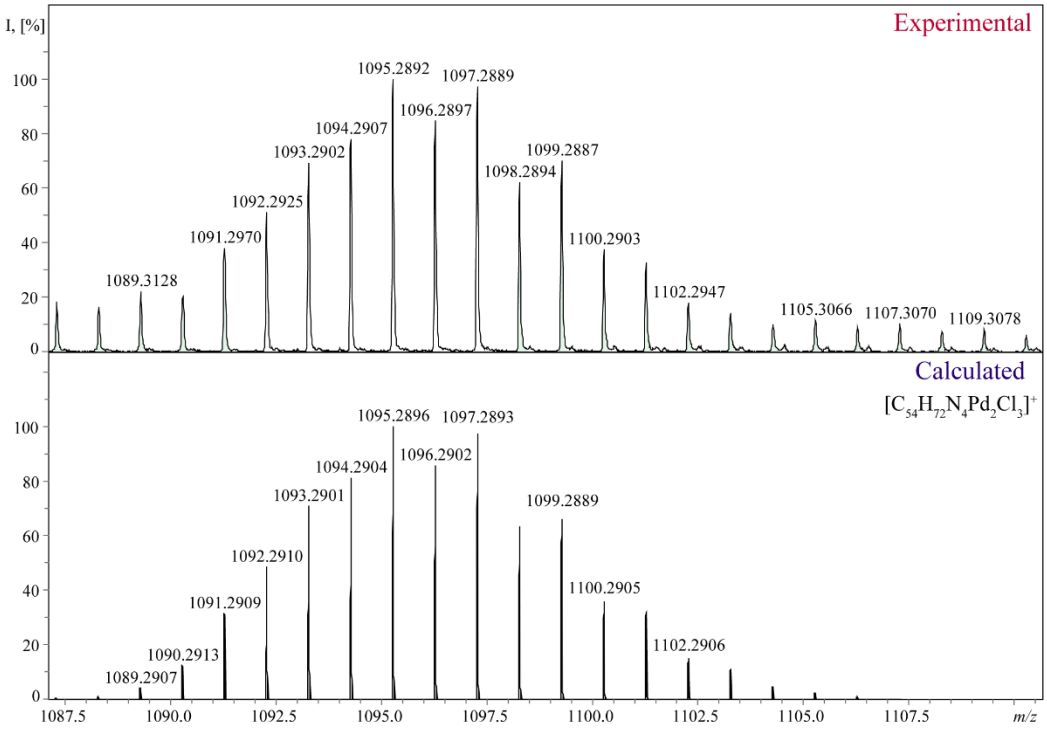


Figure S13. Experimental and theoretical ESI-(+)HRMS spectrum of **2a** in CH_3CN solution: experimental peak $[M]^+$ = 1095.2892 Da, calculated for $C_{54}H_{72}N_4Pd_2Cl_3$ = 1095.2896, Δ = 0.3 ppm,

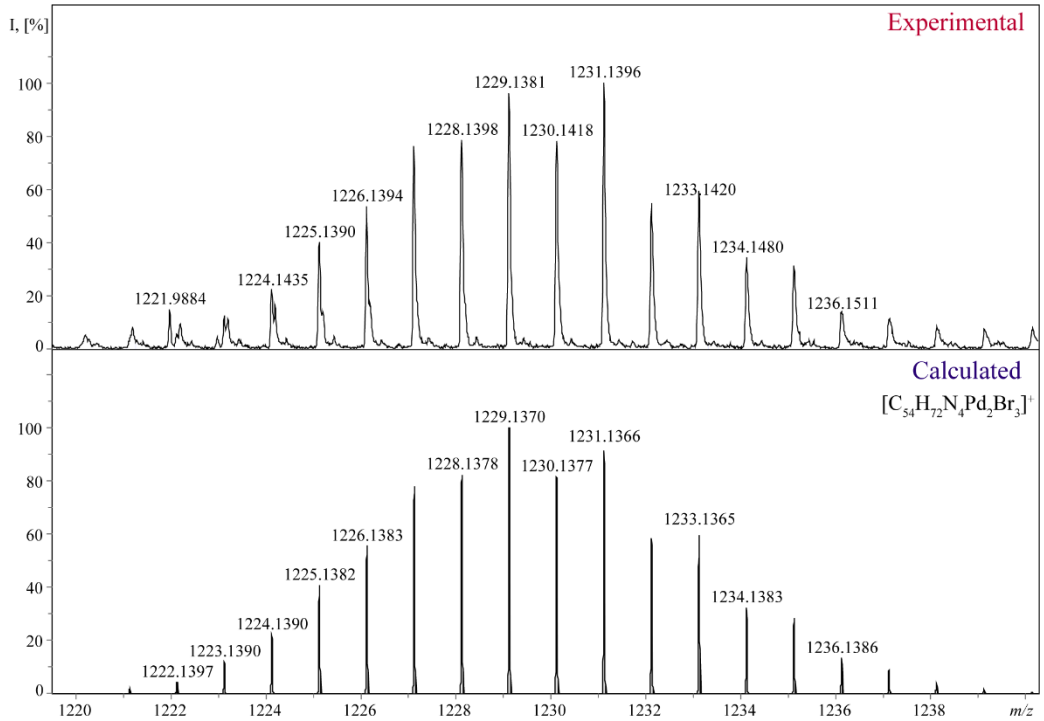


Figure S14. Experimental and theoretical ESI-(+)HRMS spectrum of **2b** in CH_3CN solution; experimental peak $[M]^+$ = 1229.1381 Da, (C) calculated for $C_{54}H_{72}N_4Pd_2Br_3$ = 1229.1370, Δ = 0.9 ppm.

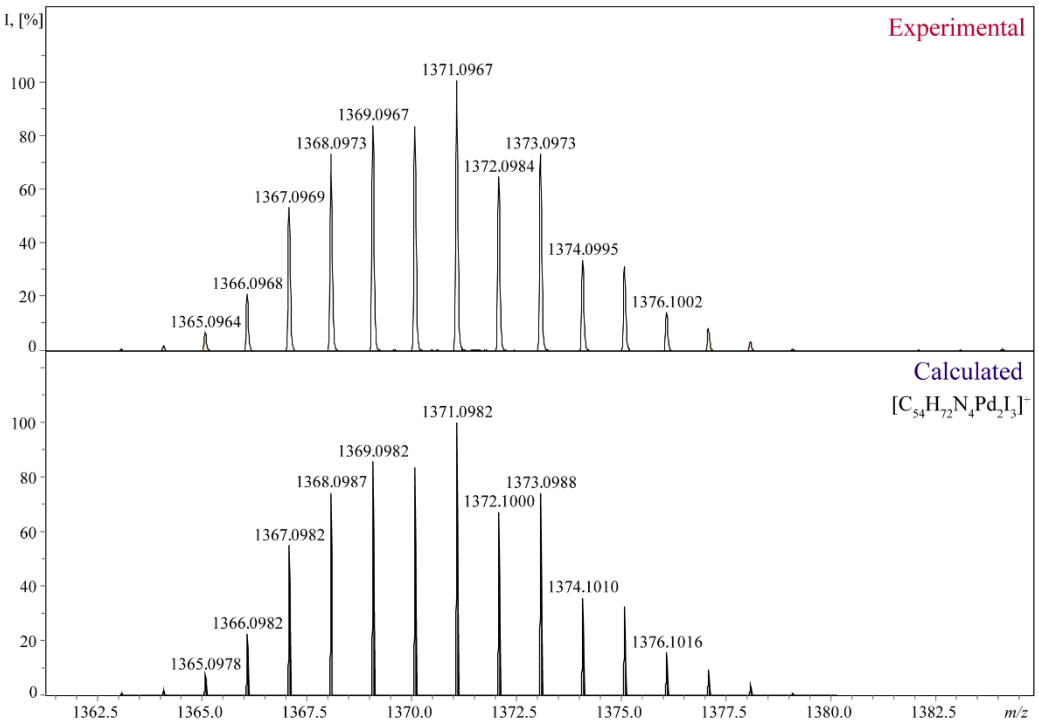


Figure S15. Experimental and theoretical ESI-(+)HRMS spectrum of **2c** in CH_3CN solution; experimental peak $[M]^+$ = 1371.0967 Da, calculated for $C_{54}H_{72}N_4Pd_2I_3$ = 1371.0982, Δ = 1.1 ppm.

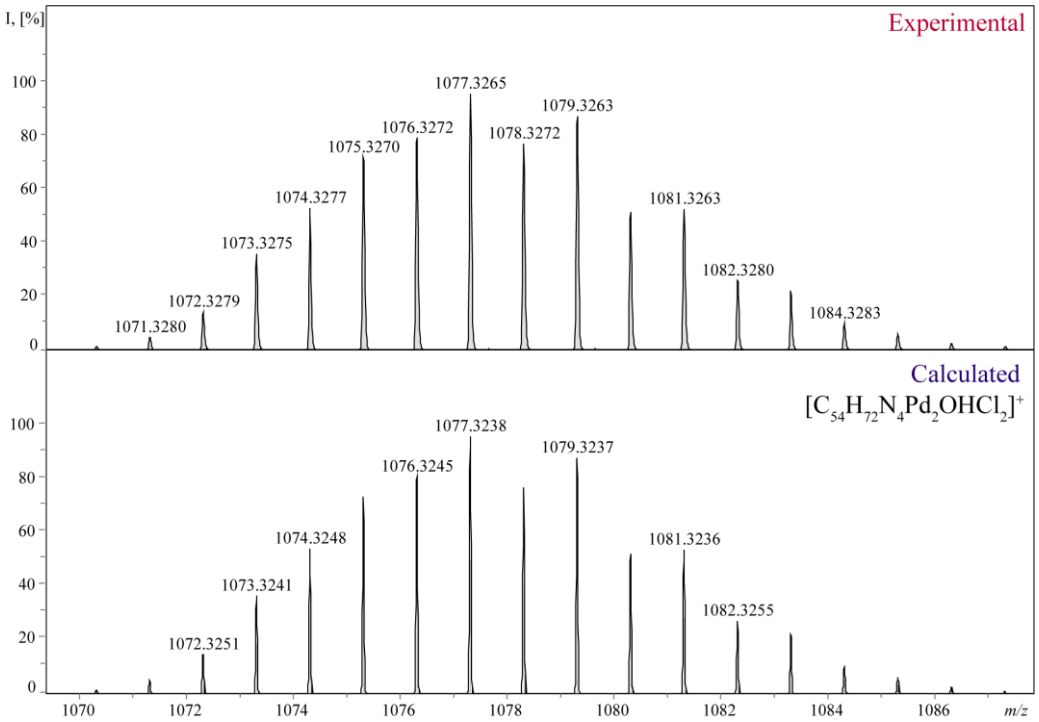


Figure S16. Experimental and theoretical ESI-(+)HRMS spectrum of **3a** in CH_3CN solution; experimental peak $[M]^+$ = 1077.3267 Da, calculated for $C_{54}H_{72}N_4Pd_2OHCl_2$ = 1077.3240, Δ = 2.3 ppm.

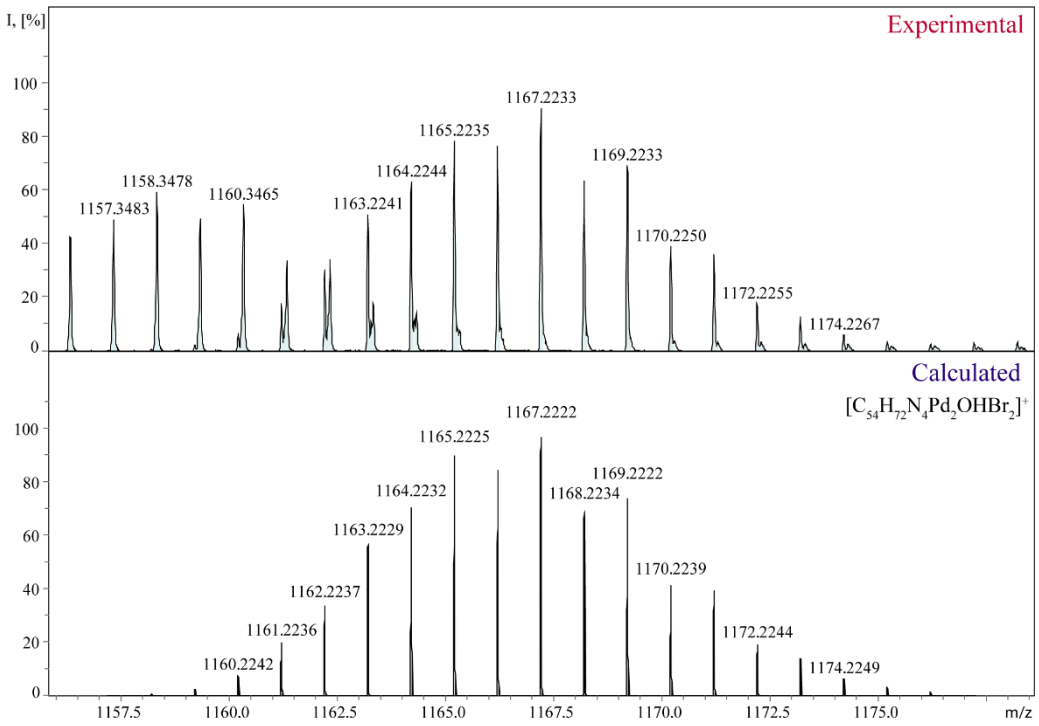


Figure S17. Experimental and theoretical ESI-(+)HRMS spectrum of **3b** in CH_3CN solution; experimental peak $[M]^+$ = 1167.2233 Da, calculated for $C_{54}H_{72}N_4Pd_2OHBr_2$ = 1167.2222, Δ = 0.9 ppm (partial signal overlap does not interfere with the correct interpretation of the spectrum).

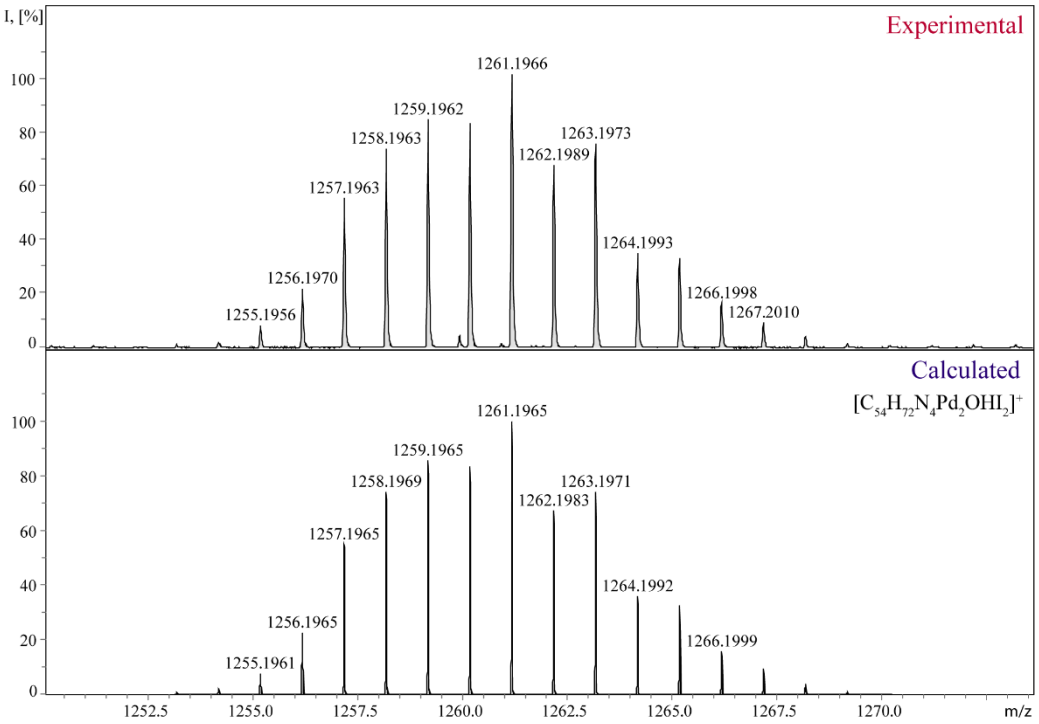


Figure S18. Experimental and theoretical ESI-(+)HRMS spectrum of **3c** in CH_3CN solution; experimental peak $[M]^+$ = 1261.1966 Da, calculated for $C_{54}H_{72}N_4Pd_2(OH)I_2$= 1261.1965, Δ = 0.01 ppm.

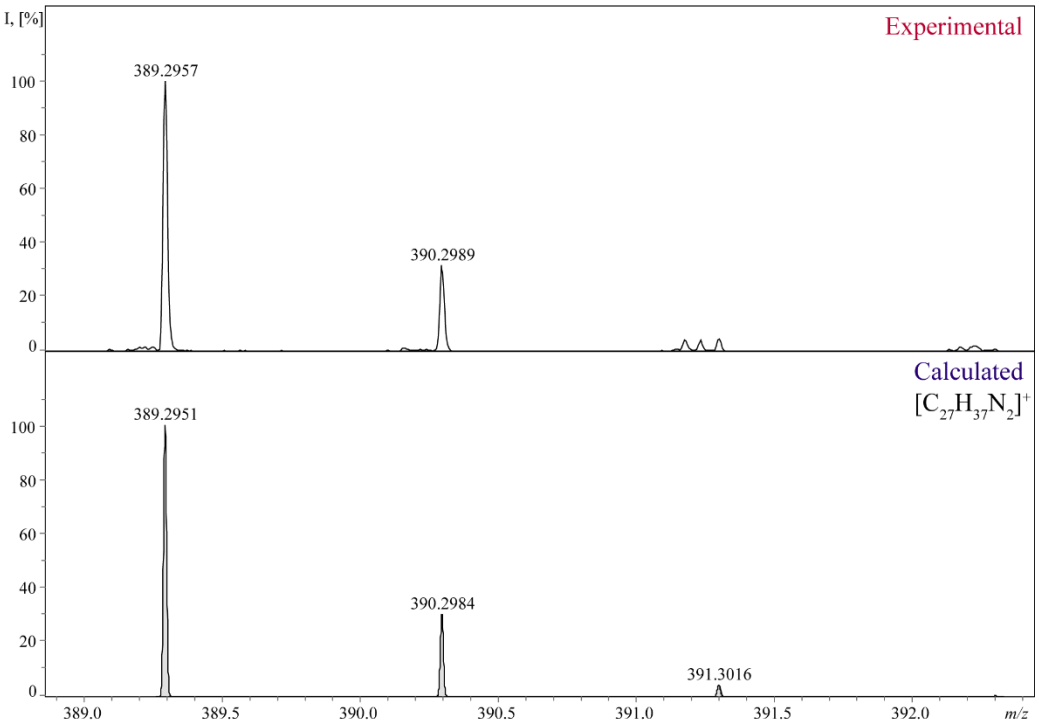


Figure S19. Experimental peak $[M]^+$ = 389.2957 Da, calculated for $C_{27}H_{37}N_2$ = 389.2951, Δ = 1.5 ppm detected in the reaction mixture with **1b**.

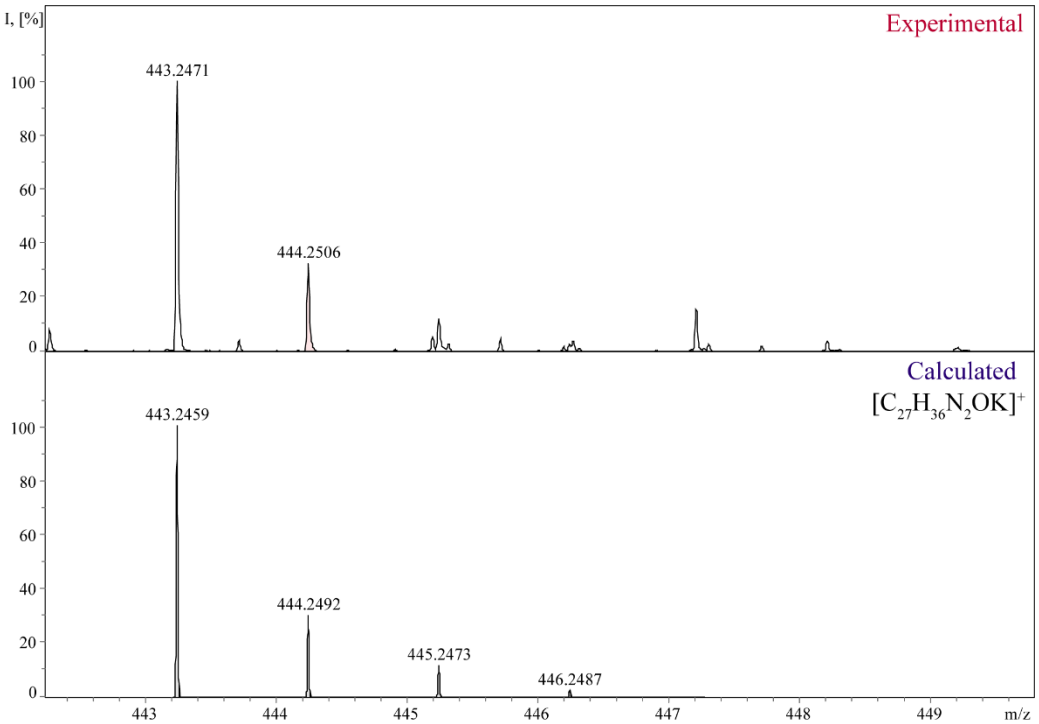


Figure S20. Experimental peak $[M]^+$ = 443.2471 Da, calculated for $C_{27}H_{36}N_2OK$ = 443.2459, Δ = 2.7 ppm detected in the reaction mixture with **1b**.

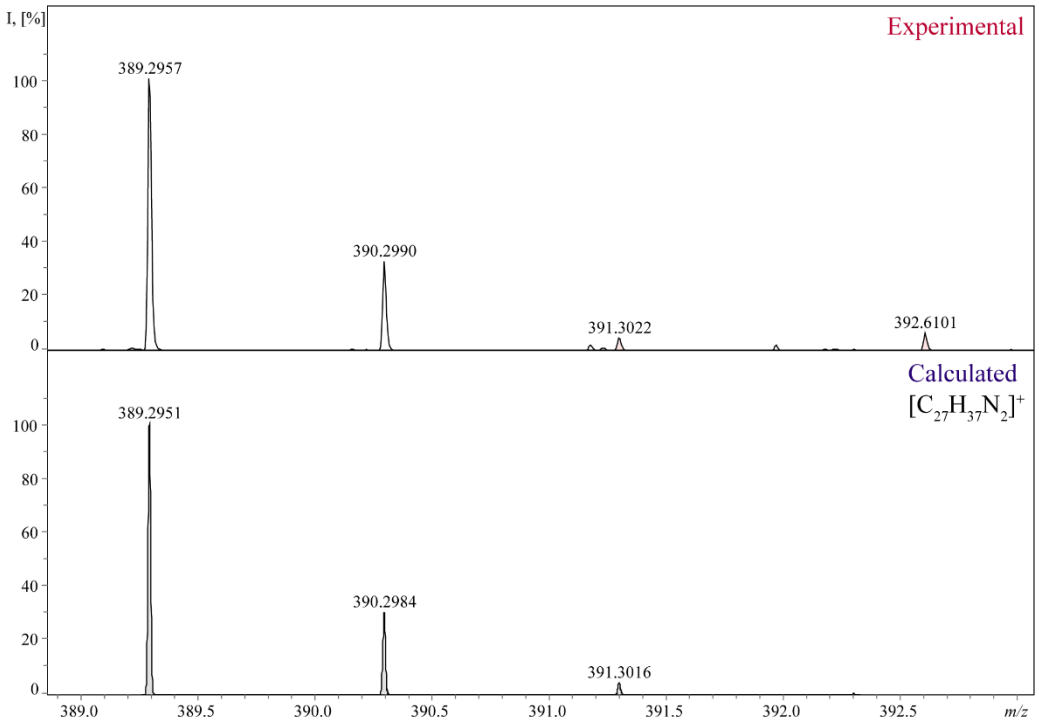


Figure S21. Experimental peak $[M]^+$ = 389.2957 Da, calculated for $C_{27}H_{37}N_2$ = 389.2951, Δ = 1.5 ppm detected in the reaction mixture with **2b**.

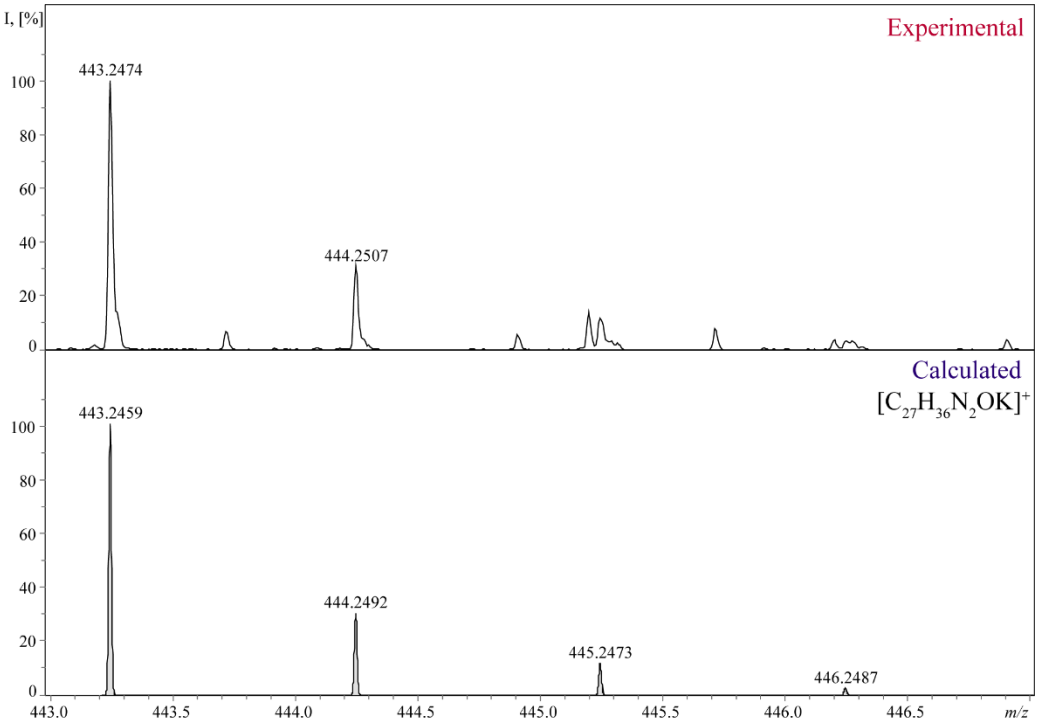


Figure S22. Experimental peak $[M]^+$ = 443.2474 Da, calculated for $C_{27}H_{36}N_2OK$ = 443.2459, Δ = 3.4 ppm detected in the reaction mixture with **2b**.

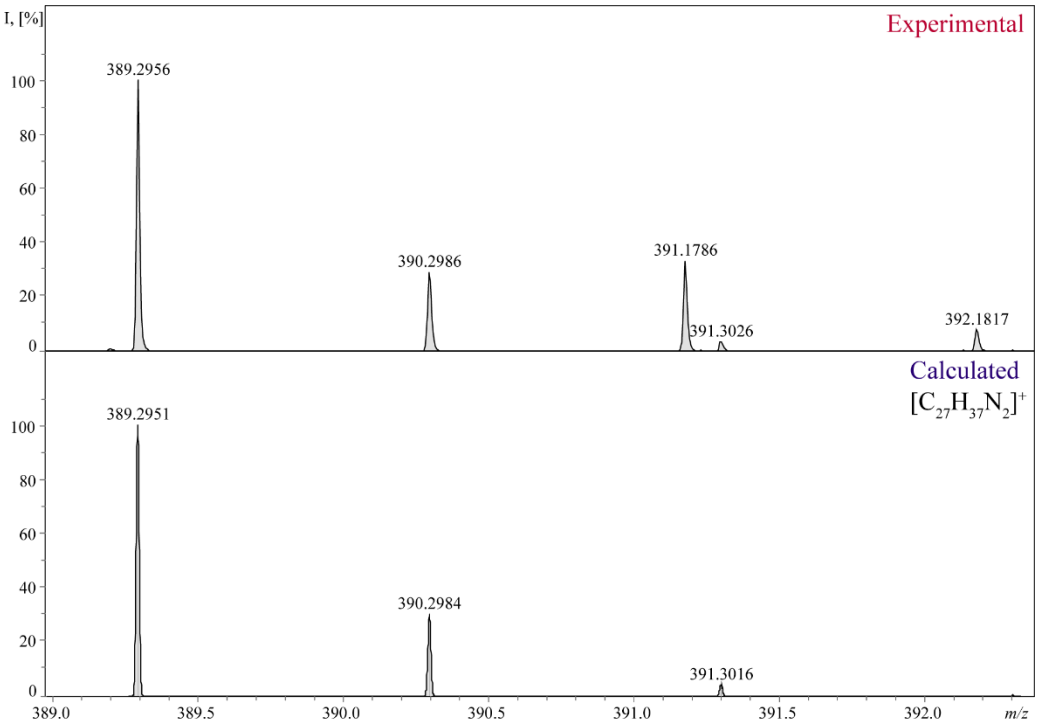


Figure S23. Experimental peak $[M]^+$ = 389.2956 Da, calculated for $C_{27}H_{37}N_2$ = 389.2951, Δ = 1.3 ppm detected in the reaction mixture with **3b**.

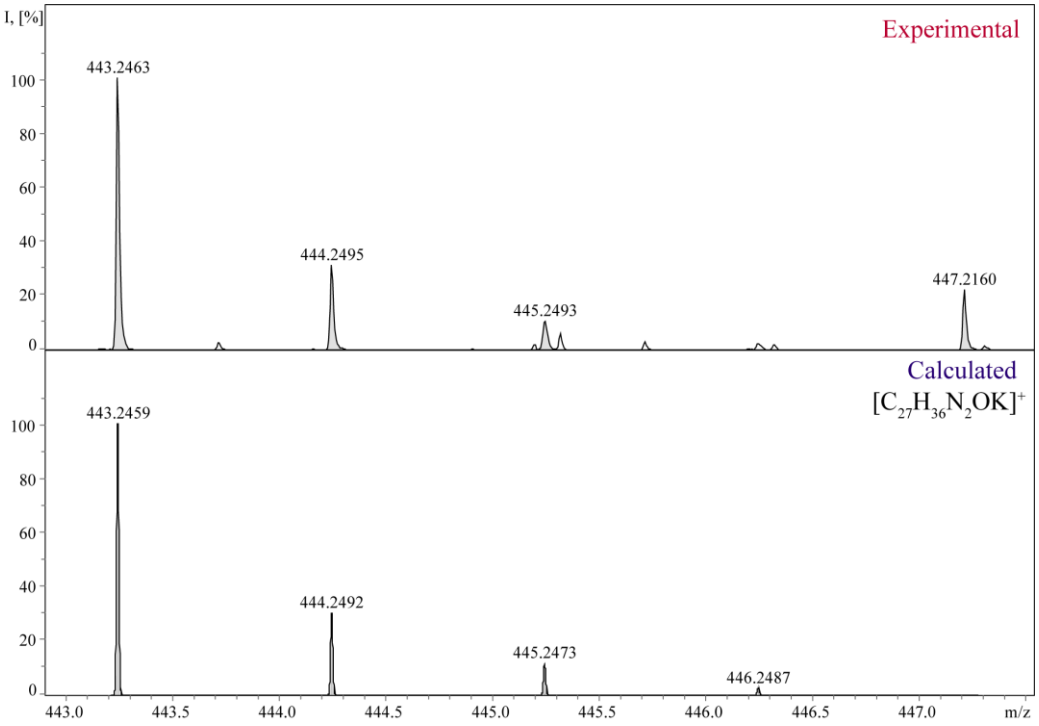


Figure S24. Experimental peak $[M]^+$ = 443.2463 Da, calculated for $C_{27}H_{36}N_2OK$ = 443.2459, Δ = 0.9 ppm detected in the reaction mixture with **3b**.

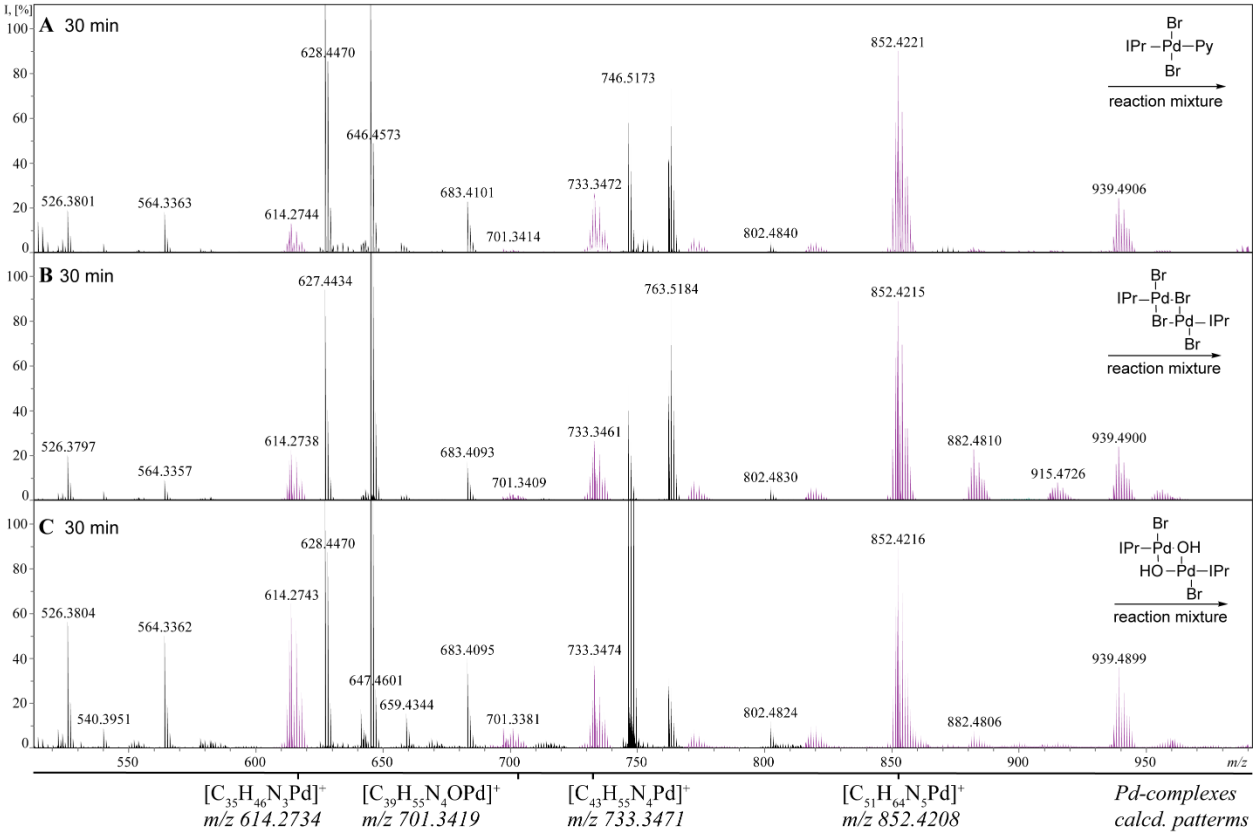


Figure S25. ESI-(+)HRMS study of Buchwald-Hartwig reaction mixtures with different palladium precursors: (A) **1b**; (B) **2b**; (C) **3b**. **Reaction conditions:** 1 mmol 4-bromo-*N*,*N*-dimethylaniline, 1.5 mmol morpholine, 1.5 mmol *t*BuOK, 1 ml toluene and 0.5 mol% [Pd], 85°C, 30 min. Calculated patterns for $[C_{35}H_{46}N_3Pd]^+$ = 614.2734 Da, $[C_{39}H_{55}N_4OPd]^+$ = 701.3419 Da, $[C_{43}H_{55}N_4Pd]^+$ = 733.3471 Da, $[C_{51}H_{64}N_5Pd]^+$ = 852.4208 Da were colored in purple.

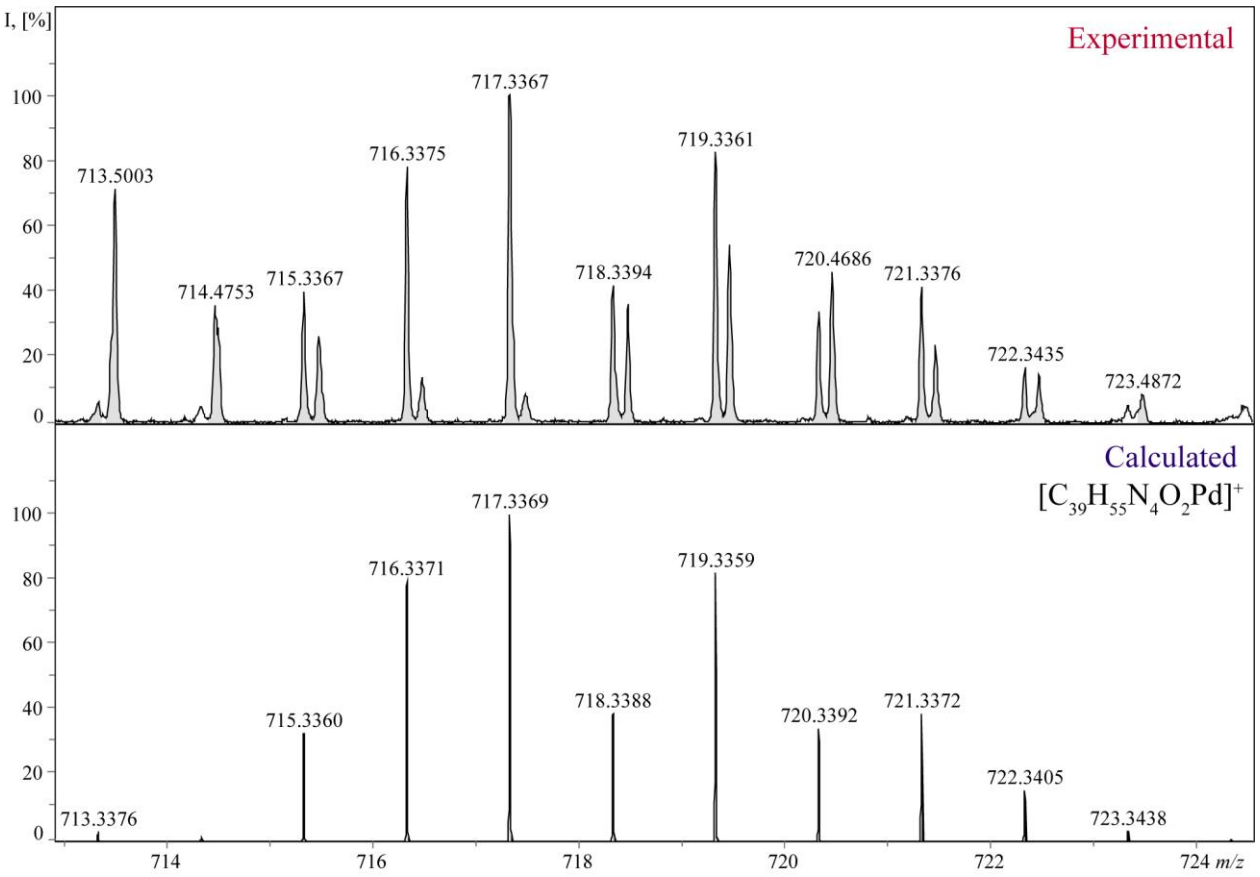


Figure S26. Experimental and theoretical ESI-(+)HRMS spectrum of the reaction mixture with precipitate from **2b** in CH_3CN solution: experimental peak $[M]^+$ = 717.3367 Da, calculated for $C_{39}H_{55}N_4O_2Pd$ = 717.3369, Δ = 0.3 ppm (partial signal overlap does not interfere with the correct interpretation of the spectrum).

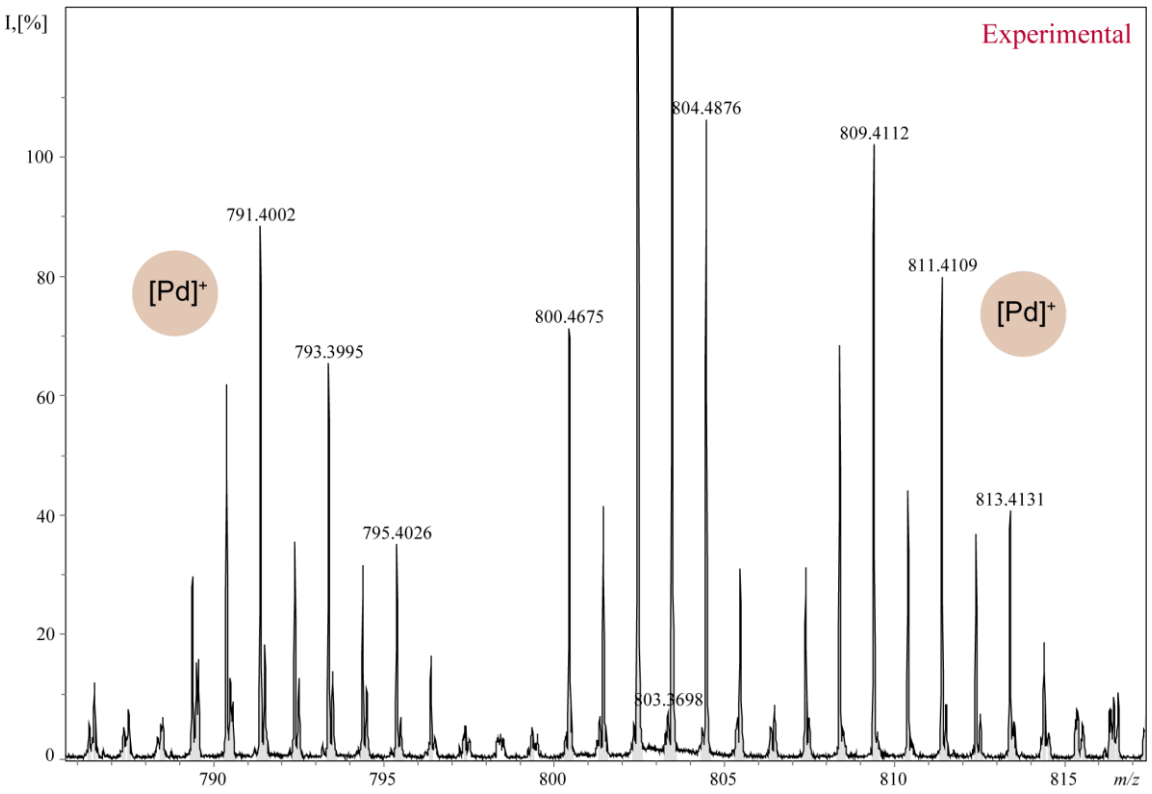


Figure S27. Experimental ESI-(+)HRMS spectrum of the reaction mixture with precipitate from **2b** in CH_3CN solution.

Palladium nanoparticles found in the Buchwald-Hartwig reaction mixture

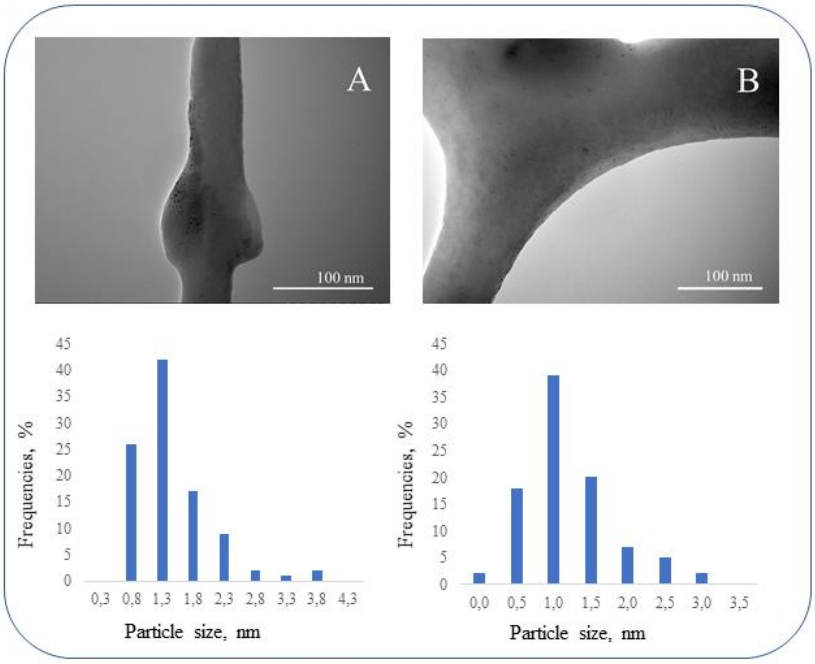


Figure S28. TEM images and the size distribution of palladium nanoparticles in the initial catalyst before the Buchwald-Hartwig reaction. Pd-NHC complexes: (A) **1b**; (B) **2b**. **3b** – it is not reliable to calculate the distribution because there are too few particles.

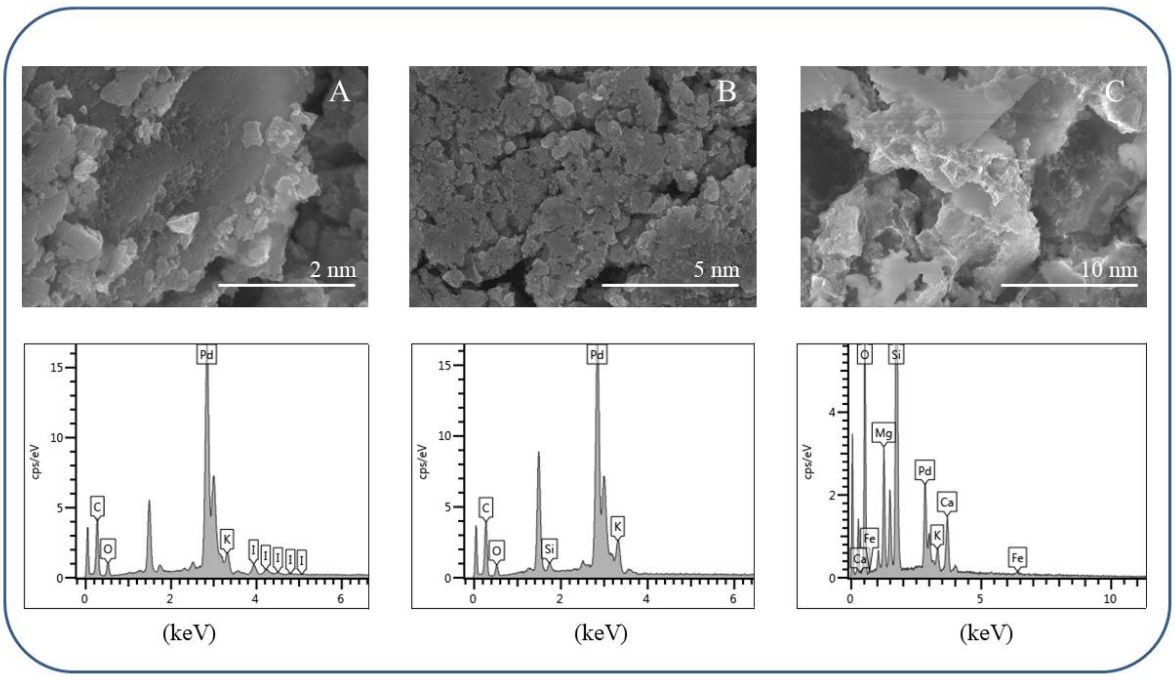


Figure S29. SEM images of separated Pd nanoparticles after the Buchwald-Hartwig reaction (**A-C**) and their EDX spectra.

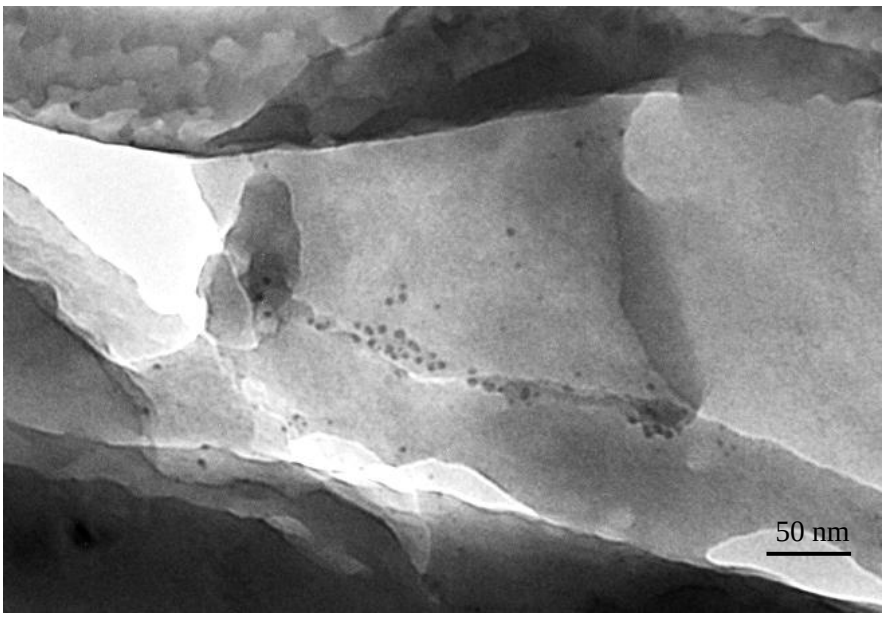


Figure S30. TEM image of palladium nanoparticles obtained at 19 h of the Buchwald-Hartwig reaction. 50k magnification.

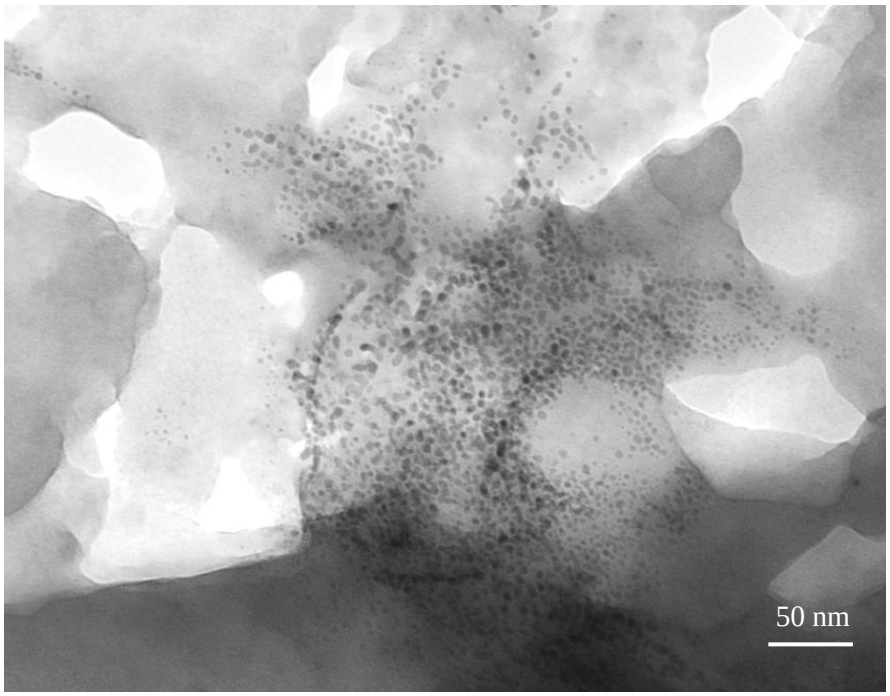


Figure S31. TEM image of palladium nanoparticles obtained at 19 h of the Buchwald-Hartwig reaction. 50k magnification.

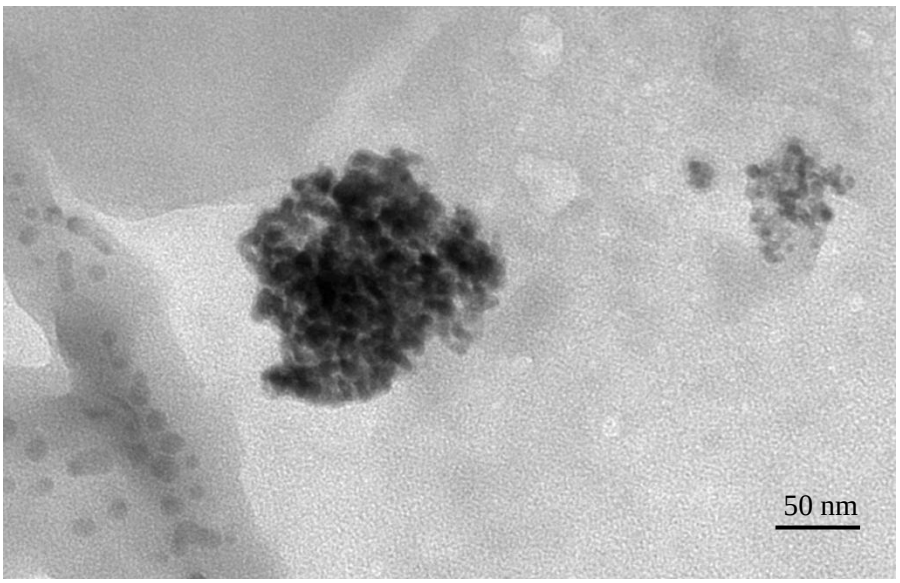


Figure S32. TEM image of palladium nanoparticles obtained at 19 h of the Buchwald-Hartwig reaction. 100k magnification.

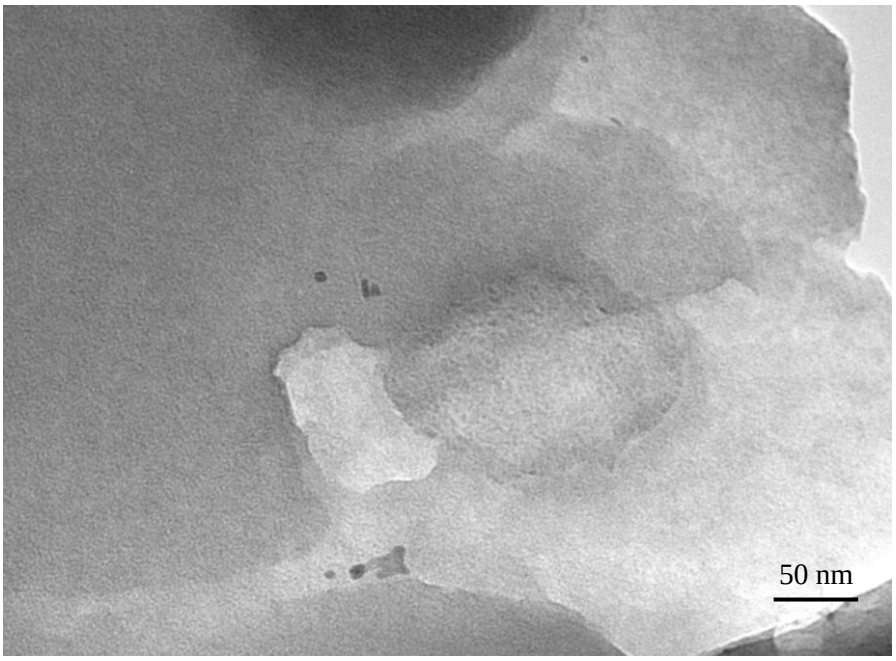


Figure S33. TEM image of palladium nanoparticles obtained at 19 h of the Buchwald-Hartwig reaction. 100k magnification.

X-ray crystallographic data and refinement details.

X-ray diffraction data were collected on a Bruker Quest D8 diffractometer equipped with a Photon-III area detector (shutterless φ- and ω-scan technique) using graphite-monochromatized Mo K_α-radiation (λ=0.71073 Å). The intensity data were integrated by the SAINT program[1] and semi-empirically corrected from equivalent reflections for absorption and decay with SADABS[2] (for **2a**, **2b**, **2c**, **3a** and **3b**) or with TWINABS[1] (for **3c**). The structures were solved by direct methods using SHELXT[3] and refined by full-matrix least-squares on F^2 using SHELXL.[4] All nonhydrogen atoms were refined with anisotropic displacement parameters. Positions of hydroxy hydrogen atoms in **3a** and **3c** were found from electron difference-density maps. In the case of **3a**, the positions of these atoms were restrained at a distance of 0.84 Å from the corresponding oxygen atoms. All other hydrogen atoms, including hydroxy atoms in **2b**, were placed in ideal calculated positions (C-H distance = 0.850 Å for hydroxy (in **3b)**, 0.950 Å for aromatic, 0.980 Å for methyl, 0.990 Å for methylene and 1.000 Å for tertiary hydrogen atoms) and refined as riding atoms with relative isotropic displacement parameters. (U_{iso}(H)=1.5 U_{eq}(C) for methyl, 1.2 U_{eq}(C) for other hydrogen atoms). A rotating group model was applied for methyl groups. The disordered fragments were modeled by applying similarity constraints on anisotropic displacement parameters on similar atoms and by constraining similar distances to be equal within the deviation of 0.003 Å. Crystal **3b** was refined as a 2-component twin with domain ratios of 0.5350(4):0.4650(4). Crystal voids in **3a** and **3b** contained unresolved highly disordered solvent molecules with partial occupancies, which were removed by the SQUEEZE method[5] implemented in the PLATON program.[6] The SHELXTL program suite[1] was used for molecular graphics herein. Crystal data, data collection and structure refinement details are summarized in Table S1.

Literature references:

1. Bruker. APEX-III. *Bruker AXS Inc.*, Madison, Wisconsin, USA, **2019**.
2. Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J. Appl. Cryst.* **2015**, 48, 3-10. http://doi.org/10.1107/S1600576714022985
3. Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, A71, 3-8. http://doi.org/10.1107/S2053273314026370
4. Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, C71, 3-8. http://doi.org/10.1107/S2053229614024218
5. Spek, A. L. PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Cryst.*, **2015**, C71, 9-18, http://doi.org/10.1107/S2053229614024929
6. Spek, A. L. Structure validation in chemical crystallography. *Acta Cryst.*, **2009**, D65, 148-155, http://doi.org/10.1107/S090744490804362X

Table S1. Crystal data, data collection and structure refinement details

Identification code	**2a**·2(CH_2Cl_2)	**2b**·2(CH_2Cl_2)	**2c**·CH_2Cl_2	**3a**·0.5(CH_2Cl_2)	**3b**	**3c**
Empirical formula	$C_{56}H_{76}Cl_8N_4Pd_2$	$C_{56}H_{76}Br_4Cl_4N_4Pd_2$	$C_{55}H_{74}Cl_2I_4N_4Pd_2$	$C_{54.5}H_{75}Cl_3N_4O_2Pd_2$	$C_{54}H_{74}Br_2N_4O_2Pd_2$	$C_{54}H_{74}I_2N_4O_2Pd_2$
Formula weight	1301.60	1479.44	1582.48	1137.33	1183.79	1277.77
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2) K	120(2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	Pbca	Pbca	$P2_1$	C2/c	$P2_1$	C2/c
Unit cell dimensions						
a (Å)	14.2641(3)	14.6417(4)	12.5373(3)	29.8011(4)	12.4263(3)	25.3642(7)
b (Å)	19.0639(4)	19.3275(6)	15.0465(3)	13.1568(2)	14.7841(4)	12.2415(3)
c (Å)	22.6150(5)	22.4789(7)	16.1547(3)	30.6277(4)	16.2288(4)	18.7483(5)
β (°)	90	90	100.0640(10)	95.8028(6)	103.5667(10)	105.0300(10)
Volume ($Å^3$)	6149.7(2)	6361.2(3)	3000.57(11)	11947.2(3)	2898.23(13)	5622.1(3)
Z	4	4	2	8	2	4
Calcd density (g/cm^3)	1.406	1.545	1.752	1.265	1.357	1.510
μ (mm^{-1})	0.970	3.282	2.783	0.775	2.038	1.778
F(000)	2672	2960	1540	4712	1208	2560
Crystal size (mm)	0.50×0.20×0.17	0.57×0.38×0.18	0.55×0.47×0.42	0.58×0.38×0.27	0.57×0.51×0.46	0.32×0.25×0.14
θ range (°)	2.137-34.648	2.284-34.998	2.258-36.347	2.114-34.499	2.321 to 33.998°.	2.250-34.348
Index ranges	-22<=h<=22, -30<=k<=30, -35<=l<=36	-18<=h<=23, -31<=k<=31, -36<=l<=30	-20<=h<=20, -25<=k<=25, -26<=l<=26	-47<=h<=47, -20<=k<=20, -48<=l<=48	-19<=h<=19, -23<=k<=23, -25<=l<=25	-40<=h<=38, 0<=k<=19, 0<=l<=29

Table S1. Crystal data, data collection and structure refinement details (cont.)

Identification code	**2a**·2(CH_2Cl_2)	**2b**·2(CH_2Cl_2)	**2c**·CH_2Cl_2	**3a**·0.5(CH_2Cl_2)	**3b**	**3c**
Reflections						
collected	165577	120402	220125	237674	170408	21362
independent [R_{int}]	13189 [0.0439]	13997 [0.0268]	29074 [0.0297]	25307 [0.0368]	23690 [0.0411]	21362 [-]
observed	10792	12064	28350	21126	19373	18656
Completeness to θ_{max}	1.000	0.999	0.999	1.000	0.999	
T_{max} / T_{min}	0.3859 / 0.3093	0.1649 / 0.0846	0.7471 / 0.6088	0.4376 / 0.3541	0.2720 / 0.1529	0.1649 / 0.1027
Restraints / parameters	13189 /2 / 334	13997 / 2 / 334	29074 / 3 / 631	25307 / 30 / 697	23690 / 465 / 801	21362 / 5 / 317
Goodness-of-fit on F^2	1.075	1.037	1.086	1.017	1.022	1.059
R1 / wR2 [I>2σ(I)]	0.0286 / 0.0567	0.0304 / 0.0809	0.0185 / 0.0412	0.0375 / 0.0842	0.0404 / 0.0965	0.0337 / 0.0617
R1 / wR2 (all data)	0.0411 / 0.0628	0.0371 / 0.0849	0.0197 / 0.0417	0.0484 / 0.0920	0.0565 / 0.1079	0.0436 / 0.0661
Abs. struct. param.	-	-	0.010(3)	-	0.014(8)	-
Extinction coef.	-	-	0.00128(6)	-	-	-
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ ($\bar{e}$·Å^{-3})	0.753 / -0.751	1.276 / -1.181	0.775 / -0.640	1.340 / -1.416	0.952 / -1.273	1.232 / -0.705
CCDC number	2079916	2079917	2079918	2079919	2079920	2079921

The structure of 2a

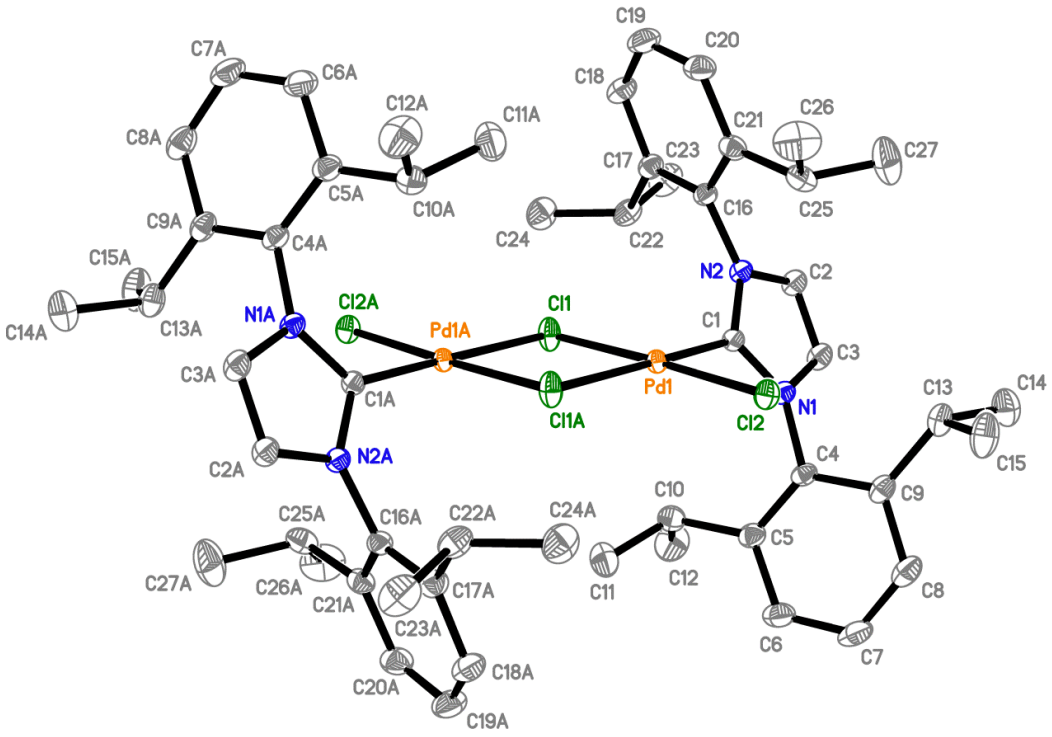


Figure S34. The molecular structure of **2a**. Hydrogen atoms are omitted. Thermal ellipsoids are set to a 50% probability level. Symmetry transformation to generate equivalent atoms: (A) -x+1, -y+1, -z+1.

Table S2. Selected bond distances for **2a** (Å).

Atoms	Distance	Atoms	Distance	Atoms	Distance
Pd(1)-C(1)	1.9512(12)	C(4)-C(9)	1.4070(18)	C(16)-C(21)	1.4054(18)
Pd(1)-Cl(2)	2.2737(3)	C(5)-C(6)	1.3990(19)	C(17)-C(18)	1.3950(19)
Pd(1)-Cl(1)	2.3153(3)	C(5)-C(10)	1.522(2)	C(17)-C(22)	1.520(2)
Pd(1)-Cl(1)#1	2.3976(3)	C(6)-C(7)	1.382(2)	C(18)-C(19)	1.378(2)
N(1)-C(1)	1.3565(16)	C(7)-C(8)	1.384(2)	C(19)-C(20)	1.386(2)
N(1)-C(3)	1.3894(16)	C(8)-C(9)	1.3965(19)	C(20)-C(21)	1.399(2)
N(1)-C(4)	1.4451(16)	C(9)-C(13)	1.517(2)	C(21)-C(25)	1.517(2)
C(1)-N(2)	1.3543(16)	C(10)-C(12)	1.531(2)	C(22)-C(24)	1.534(2)
N(2)-C(2)	1.3904(16)	C(10)-C(11)	1.533(2)	C(22)-C(23)	1.536(2)
N(2)-C(16)	1.4460(16)	C(13)-C(14)	1.534(2)	C(25)-C(26)	1.526(2)
C(2)-C(3)	1.3427(18)	C(13)-C(15)	1.535(2)	C(25)-C(27)	1.532(2)
C(4)-C(5)	1.3964(19)	C(16)-C(17)	1.4027(18)		

Symmetry transformation used to generate equivalent atoms: #1 -x+1, -y+1, -z+1

Table S3. Selected bond angles for **2a** (°).

Atoms	Angle	Atoms	Angle
C(1)-Pd(1)-Cl(2)	91.05(4)	C(8)-C(9)-C(4)	116.62(13)
C(1)-Pd(1)-Cl(1)	90.82(4)	C(8)-C(9)-C(13)	120.45(13)
Cl(2)-Pd(1)-Cl(1)	177.709(12)	C(4)-C(9)-C(13)	122.92(12)
C(1)-Pd(1)-Cl(1)#1	177.82(4)	C(5)-C(10)-C(12)	110.79(13)
Cl(2)-Pd(1)-Cl(1)#1	91.105(11)	C(5)-C(10)-C(11)	110.69(13)
Cl(1)-Pd(1)-Cl(1)#1	87.022(11)	C(12)-C(10)-C(11)	111.61(14)
Pd(1)-Cl(1)-Pd(1)#1	92.977(11)	C(9)-C(13)-C(14)	111.54(12)
C(1)-N(1)-C(3)	110.46(10)	C(9)-C(13)-C(15)	111.83(13)
C(1)-N(1)-C(4)	128.91(11)	C(14)-C(13)-C(15)	109.34(12)
C(3)-N(1)-C(4)	120.49(10)	C(17)-C(16)-C(21)	123.31(12)
N(2)-C(1)-N(1)	105.25(10)	C(17)-C(16)-N(2)	118.61(11)
N(2)-C(1)-Pd(1)	127.04(9)	C(21)-C(16)-N(2)	117.94(11)
N(1)-C(1)-Pd(1)	127.59(9)	C(18)-C(17)-C(16)	116.87(13)
C(1)-N(2)-C(2)	110.34(10)	C(18)-C(17)-C(22)	119.50(12)
C(1)-N(2)-C(16)	127.29(10)	C(16)-C(17)-C(22)	123.58(12)
C(2)-N(2)-C(16)	122.17(10)	C(19)-C(18)-C(17)	121.39(14)
C(3)-C(2)-N(2)	107.09(11)	C(18)-C(19)-C(20)	120.61(13)
C(2)-C(3)-N(1)	106.86(11)	C(19)-C(20)-C(21)	120.87(14)
C(5)-C(4)-C(9)	123.48(12)	C(20)-C(21)-C(16)	116.95(13)
C(5)-C(4)-N(1)	119.04(11)	C(20)-C(21)-C(25)	120.92(13)
C(9)-C(4)-N(1)	117.18(12)	C(16)-C(21)-C(25)	122.03(12)
C(4)-C(5)-C(6)	117.10(13)	C(17)-C(22)-C(24)	112.71(12)
C(4)-C(5)-C(10)	123.06(12)	C(17)-C(22)-C(23)	110.40(13)
C(6)-C(5)-C(10)	119.84(13)	C(24)-C(22)-C(23)	109.18(13)
C(7)-C(6)-C(5)	120.95(14)	C(21)-C(25)-C(26)	113.54(13)
C(6)-C(7)-C(8)	120.52(13)	C(21)-C(25)-C(27)	110.48(12)
C(7)-C(8)-C(9)	121.28(14)	C(26)-C(25)-C(27)	110.72(14)

Symmetry transformation used to generate equivalent atoms: #1 -x+1, -y+1, -z+1

Table S4. Torsion angles for **2a** (°).

Atoms	Angle	Atoms	Angle
C(3)-N(1)-C(1)-N(2)	-0.70(14)	C(4)-C(5)-C(10)-C(11)	-122.31(15)
C(4)-N(1)-C(1)-N(2)	174.96(12)	C(6)-C(5)-C(10)-C(11)	58.60(18)
C(3)-N(1)-C(1)-Pd(1)	175.58(9)	C(8)-C(9)-C(13)-C(14)	76.56(17)
C(4)-N(1)-C(1)-Pd(1)	-8.76(19)	C(4)-C(9)-C(13)-C(14)	-102.67(15)
N(1)-C(1)-N(2)-C(2)	0.29(14)	C(8)-C(9)-C(13)-C(15)	-46.24(18)

Pd(1)-C(1)-N(2)-C(2)	-176.02(9)	C(4)-C(9)-C(13)-C(15)	134.54(14)
N(1)-C(1)-N(2)-C(16)	-174.58(11)	C(1)-N(2)-C(16)-C(17)	-115.18(14)
Pd(1)-C(1)-N(2)-C(16)	9.11(18)	C(2)-N(2)-C(16)-C(17)	70.51(16)
C(1)-N(2)-C(2)-C(3)	0.23(15)	C(1)-N(2)-C(16)-C(21)	69.04(17)
C(16)-N(2)-C(2)-C(3)	175.41(12)	C(2)-N(2)-C(16)-C(21)	-105.27(14)
N(2)-C(2)-C(3)-N(1)	-0.65(15)	C(21)-C(16)-C(17)-C(18)	-0.1(2)
C(1)-N(1)-C(3)-C(2)	0.86(15)	N(2)-C(16)-C(17)-C(18)	-175.69(12)
C(4)-N(1)-C(3)-C(2)	-175.22(12)	C(21)-C(16)-C(17)-C(22)	177.09(13)
C(1)-N(1)-C(4)-C(5)	82.41(17)	N(2)-C(16)-C(17)-C(22)	1.55(19)
C(3)-N(1)-C(4)-C(5)	-102.31(15)	C(16)-C(17)-C(18)-C(19)	-0.6(2)
C(1)-N(1)-C(4)-C(9)	-103.59(15)	C(22)-C(17)-C(18)-C(19)	-177.92(14)
C(3)-N(1)-C(4)-C(9)	71.68(16)	C(17)-C(18)-C(19)-C(20)	0.7(2)
C(9)-C(4)-C(5)-C(6)	-2.3(2)	C(18)-C(19)-C(20)-C(21)	-0.2(2)
N(1)-C(4)-C(5)-C(6)	171.27(12)	C(19)-C(20)-C(21)-C(16)	-0.5(2)
C(9)-C(4)-C(5)-C(10)	178.57(13)	C(19)-C(20)-C(21)-C(25)	175.88(14)
N(1)-C(4)-C(5)-C(10)	-7.83(19)	C(17)-C(16)-C(21)-C(20)	0.7(2)
C(4)-C(5)-C(6)-C(7)	0.6(2)	N(2)-C(16)-C(21)-C(20)	176.24(12)
C(10)-C(5)-C(6)-C(7)	179.75(14)	C(17)-C(16)-C(21)-C(25)	-175.67(12)
C(5)-C(6)-C(7)-C(8)	1.3(2)	N(2)-C(16)-C(21)-C(25)	-0.10(18)
C(6)-C(7)-C(8)-C(9)	-1.5(2)	C(18)-C(17)-C(22)-C(24)	-50.32(18)
C(7)-C(8)-C(9)-C(4)	-0.1(2)	C(16)-C(17)-C(22)-C(24)	132.51(14)
C(7)-C(8)-C(9)-C(13)	-179.34(14)	C(18)-C(17)-C(22)-C(23)	72.07(17)
C(5)-C(4)-C(9)-C(8)	2.05(19)	C(16)-C(17)-C(22)-C(23)	-105.10(15)
N(1)-C(4)-C(9)-C(8)	-171.66(12)	C(20)-C(21)-C(25)-C(26)	32.02(19)
C(5)-C(4)-C(9)-C(13)	-178.70(13)	C(16)-C(21)-C(25)-C(26)	-151.78(14)
N(1)-C(4)-C(9)-C(13)	7.60(18)	C(20)-C(21)-C(25)-C(27)	-93.04(17)
C(4)-C(5)-C(10)-C(12)	113.33(16)	C(16)-C(21)-C(25)-C(27)	83.15(17)
C(6)-C(5)-C(10)-C(12)	-65.76(18)		

Symmetry transformation used to generate equivalent atoms: #1 -x+1,-y+1,-z+1

The structure of 2b

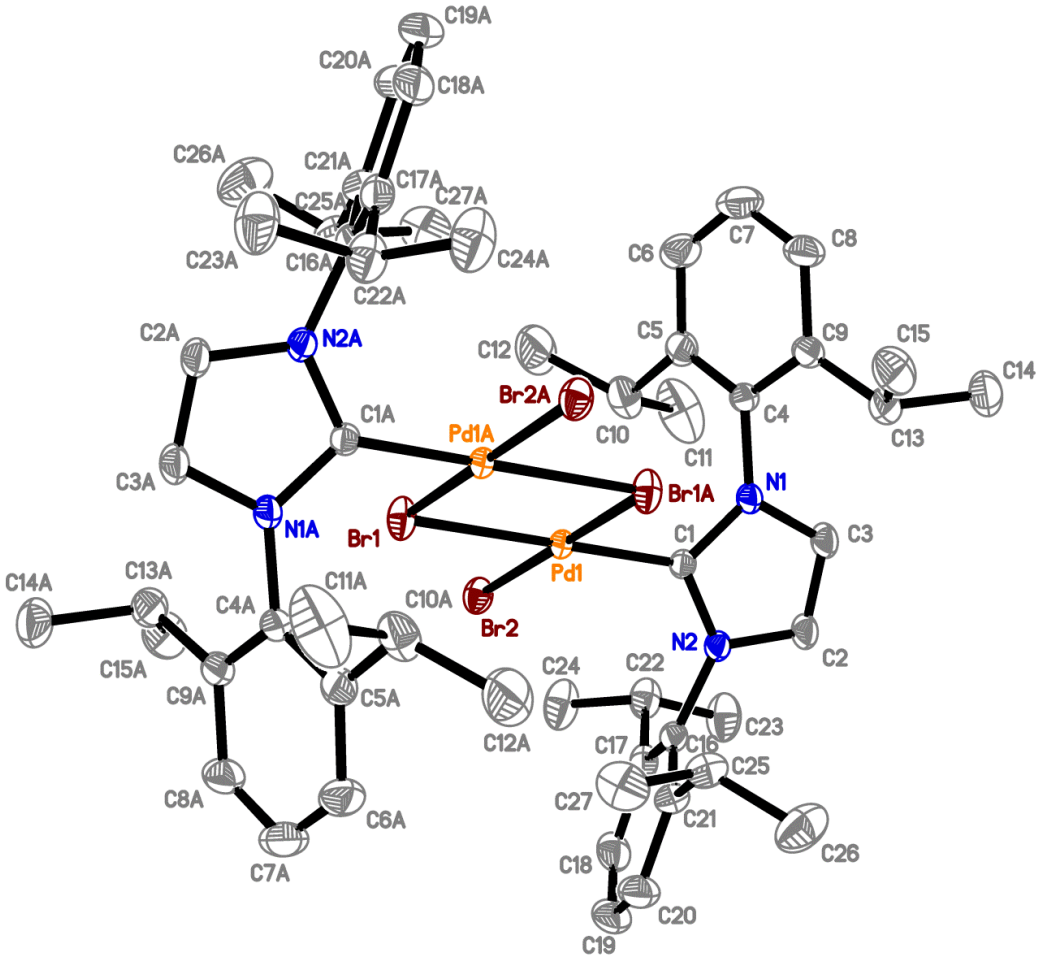


Figure S35. The molecular structure of **2b**. Hydrogen atoms are omitted. Thermal ellipsoids are set to a 50% probability level. Symmetry transformation to generate equivalent atoms: (A) -x+1, -y+1, -z+1.

Table S5. Selected bond distances for **2b** (Å).

Atoms	Distance	Atoms	Distance	Atoms	Distance
Pd(1)-C(1)	1.9614(14)	C(5)-C(6)	1.398(3)	C(17)-C(22)	1.517(3)
Pd(1)-Br(2)	2.3908(2)	C(5)-C(10)	1.519(3)	C(18)-C(19)	1.381(3)
Pd(1)-Br(1)#1	2.4309(2)	C(6)-C(7)	1.381(4)	C(19)-C(20)	1.383(3)
Pd(1)-Br(1)	2.5026(2)	C(7)-C(8)	1.379(3)	C(20)-C(21)	1.397(2)
N(1)-C(1)	1.3561(19)	C(8)-C(9)	1.394(2)	C(21)-C(25)	1.516(3)
N(1)-C(3)	1.393(2)	C(9)-C(13)	1.520(3)	C(22)-C(23)	1.531(3)
N(1)-C(4)	1.442(2)	C(10)-C(12)	1.528(3)	C(22)-C(24)	1.533(3)
N(2)-C(1)	1.3575(19)	C(10)-C(11)	1.534(4)	C(25)-C(26)	1.530(3)
N(2)-C(2)	1.389(2)	C(13)-C(15)	1.539(3)	C(25)-C(27)	1.540(3)
N(2)-C(16)	1.446(2)	C(13)-C(14)	1.541(3)	Cl(1A)-C(28A)	1.760(3)
C(2)-C(3)	1.344(2)	C(16)-C(21)	1.394(2)	Cl(2A)-C(28A)	1.774(4)

C(4)-C(9)	1.405(2)	C(16)-C(17)	1.408(2)	Cl(1B)-C(28B)	1.759(4)
C(4)-C(5)	1.406(2)	C(17)-C(18)	1.398(3)	Cl(2B)-C(28B)	1.774(5)

Symmetry transformation used to generate equivalent atoms: #1 -x+1, -y+1, -z+1

Table S6. Selected bond angles for **2b** (°).

Atoms	Angle	Atoms	Angle
C(1)-Pd(1)-Br(2)	91.30(4)	C(8)-C(9)-C(4)	117.12(17)
C(1)-Pd(1)-Br(1)#1	91.22(4)	C(8)-C(9)-C(13)	119.38(17)
Br(2)-Pd(1)-Br(1)#1	176.920(8)	C(4)-C(9)-C(13)	123.46(15)
C(1)-Pd(1)-Br(1)	178.77(4)	C(5)-C(10)-C(12)	113.6(2)
Br(2)-Pd(1)-Br(1)	89.823(7)	C(5)-C(10)-C(11)	110.29(17)
Br(1)#1-Pd(1)-Br(1)	87.642(6)	C(12)-C(10)-C(11)	111.2(2)
Pd(1)#1-Br(1)-Pd(1)	92.357(7)	C(9)-C(13)-C(15)	113.12(17)
C(1)-N(1)-C(3)	110.40(13)	C(9)-C(13)-C(14)	110.17(18)
C(1)-N(1)-C(4)	127.28(12)	C(15)-C(13)-C(14)	108.93(17)
C(3)-N(1)-C(4)	122.17(13)	C(21)-C(16)-C(17)	123.59(15)
C(1)-N(2)-C(2)	110.42(13)	C(21)-C(16)-N(2)	118.91(14)
C(1)-N(2)-C(16)	129.31(13)	C(17)-C(16)-N(2)	117.18(15)
C(2)-N(2)-C(16)	120.14(13)	C(18)-C(17)-C(16)	116.32(18)
N(1)-C(1)-N(2)	105.25(12)	C(18)-C(17)-C(22)	120.25(17)
N(1)-C(1)-Pd(1)	127.20(11)	C(16)-C(17)-C(22)	123.43(16)
N(2)-C(1)-Pd(1)	127.46(11)	C(19)-C(18)-C(17)	121.48(18)
C(3)-C(2)-N(2)	107.08(14)	C(18)-C(19)-C(20)	120.51(18)
C(2)-C(3)-N(1)	106.85(14)	C(19)-C(20)-C(21)	120.9(2)
C(9)-C(4)-C(5)	122.96(15)	C(16)-C(21)-C(20)	117.21(17)
C(9)-C(4)-N(1)	118.84(14)	C(16)-C(21)-C(25)	123.21(15)
C(5)-C(4)-N(1)	118.06(15)	C(20)-C(21)-C(25)	119.57(17)
C(6)-C(5)-C(4)	116.91(18)	C(17)-C(22)-C(23)	111.71(17)
C(6)-C(5)-C(10)	121.19(18)	C(17)-C(22)-C(24)	112.07(18)
C(4)-C(5)-C(10)	121.79(16)	C(23)-C(22)-C(24)	108.75(16)
C(7)-C(6)-C(5)	121.18(19)	C(21)-C(25)-C(26)	110.93(17)
C(8)-C(7)-C(6)	120.57(18)	C(21)-C(25)-C(27)	110.98(17)
C(7)-C(8)-C(9)	121.24(19)	C(26)-C(25)-C(27)	111.18(19)

Symmetry transformation used to generate equivalent atoms: #1 -x+1, -y+1, -z+1

Table S7. Torsion angles for **2b** (°).

Atoms	Angle	Atoms	Angle
C(3)-N(1)-C(1)-N(2)	-0.17(17)	C(6)-C(5)-C(10)-C(11)	92.8(3)
C(4)-N(1)-C(1)-N(2)	175.43(15)	C(4)-C(5)-C(10)-C(11)	-83.4(2)
C(3)-N(1)-C(1)-Pd(1)	176.49(12)	C(8)-C(9)-C(13)-C(15)	47.4(2)
C(4)-N(1)-C(1)-Pd(1)	-7.9(2)	C(4)-C(9)-C(13)-C(15)	-135.10(18)
C(2)-N(2)-C(1)-N(1)	0.74(18)	C(8)-C(9)-C(13)-C(14)	-74.7(2)
C(16)-N(2)-C(1)-N(1)	-174.96(15)	C(4)-C(9)-C(13)-C(14)	102.72(19)
C(2)-N(2)-C(1)-Pd(1)	-175.92(12)	C(1)-N(2)-C(16)-C(21)	-81.2(2)
C(16)-N(2)-C(1)-Pd(1)	8.4(2)	C(2)-N(2)-C(16)-C(21)	103.48(19)
C(1)-N(2)-C(2)-C(3)	-1.0(2)	C(1)-N(2)-C(16)-C(17)	105.05(19)
C(16)-N(2)-C(2)-C(3)	175.11(15)	C(2)-N(2)-C(16)-C(17)	-70.3(2)
N(2)-C(2)-C(3)-N(1)	0.9(2)	C(21)-C(16)-C(17)-C(18)	-1.4(2)
C(1)-N(1)-C(3)-C(2)	-0.5(2)	N(2)-C(16)-C(17)-C(18)	172.00(15)
C(4)-N(1)-C(3)-C(2)	-176.32(16)	C(21)-C(16)-C(17)-C(22)	179.42(16)
C(1)-N(1)-C(4)-C(9)	114.92(18)	N(2)-C(16)-C(17)-C(22)	-7.1(2)
C(3)-N(1)-C(4)-C(9)	-70.0(2)	C(16)-C(17)-C(18)-C(19)	0.1(3)
C(1)-N(1)-C(4)-C(5)	-69.3(2)	C(22)-C(17)-C(18)-C(19)	179.31(18)
C(3)-N(1)-C(4)-C(5)	105.84(18)	C(17)-C(18)-C(19)-C(20)	1.4(3)
C(9)-C(4)-C(5)-C(6)	-1.8(3)	C(18)-C(19)-C(20)-C(21)	-1.8(3)
N(1)-C(4)-C(5)-C(6)	-177.39(15)	C(17)-C(16)-C(21)-C(20)	1.1(3)
C(9)-C(4)-C(5)-C(10)	174.54(16)	N(2)-C(16)-C(21)-C(20)	-172.21(16)
N(1)-C(4)-C(5)-C(10)	-1.1(2)	C(17)-C(16)-C(21)-C(25)	-179.81(16)
C(4)-C(5)-C(6)-C(7)	1.1(3)	N(2)-C(16)-C(21)-C(25)	6.9(2)
C(10)-C(5)-C(6)-C(7)	-175.22(19)	C(19)-C(20)-C(21)-C(16)	0.5(3)
C(5)-C(6)-C(7)-C(8)	0.0(3)	C(19)-C(20)-C(21)-C(25)	-178.60(19)
C(6)-C(7)-C(8)-C(9)	-0.5(3)	C(18)-C(17)-C(22)-C(23)	-77.5(2)
C(7)-C(8)-C(9)-C(4)	-0.1(3)	C(16)-C(17)-C(22)-C(23)	101.6(2)
C(7)-C(8)-C(9)-C(13)	177.51(19)	C(18)-C(17)-C(22)-C(24)	44.8(2)
C(5)-C(4)-C(9)-C(8)	1.3(2)	C(16)-C(17)-C(22)-C(24)	-136.06(18)
N(1)-C(4)-C(9)-C(8)	176.86(15)	C(16)-C(21)-C(25)-C(26)	-112.7(2)
C(5)-C(4)-C(9)-C(13)	-176.22(17)	C(20)-C(21)-C(25)-C(26)	66.4(2)
N(1)-C(4)-C(9)-C(13)	-0.6(2)	C(16)-C(21)-C(25)-C(27)	123.2(2)
C(6)-C(5)-C(10)-C(12)	-32.8(3)	C(20)-C(21)-C(25)-C(27)	-57.7(2)
C(4)-C(5)-C(10)-C(12)	151.03(19)		

Symmetry transformation used to generate equivalent atoms: #1 -x+1,-y+1,-z+1

The structure of 2c

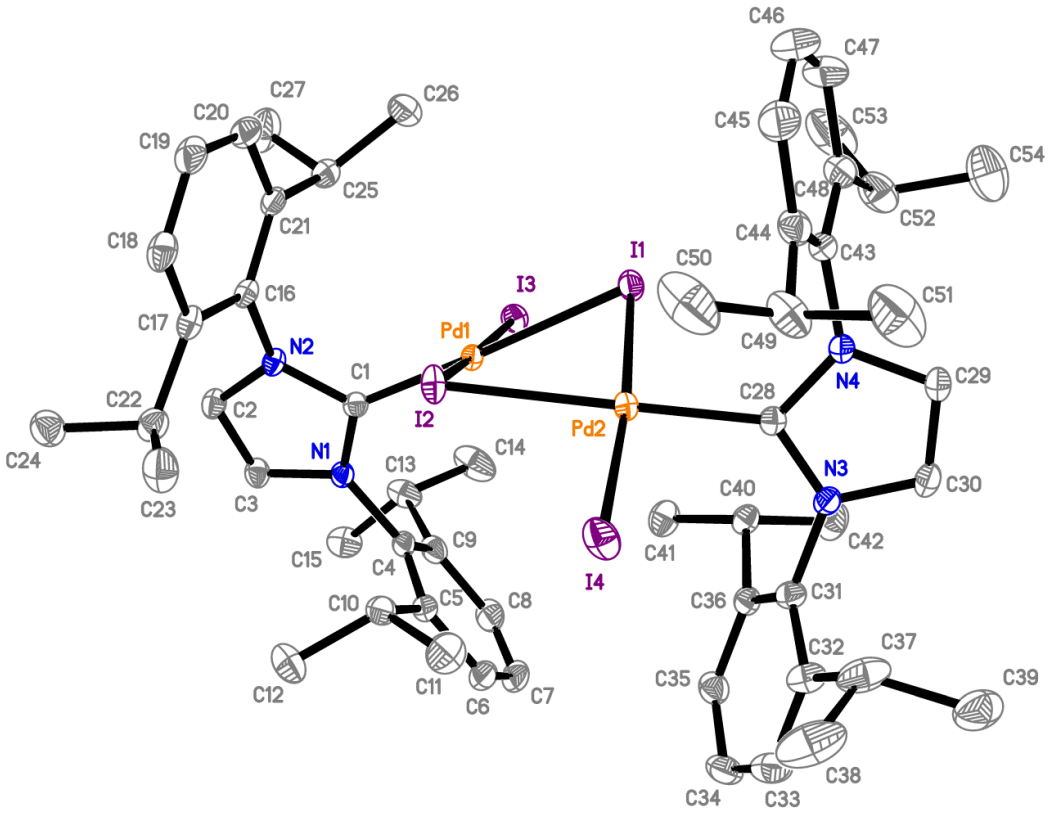


Figure S36. The molecular structure of **2c**. Hydrogen atoms are omitted. Thermal ellipsoids are set to a 50% probability level.

Table S8. Selected bond distances for **2c** (Å).

Atoms	Distance	Atoms	Distance	Atoms	Distance
I(1)-Pd(1)	2.6442(2)	C(5)-C(10)	1.518(3)	C(31)-C(32)	1.406(3)
I(2)-Pd(1)	2.6152(2)	C(6)-C(7)	1.380(4)	C(32)-C(33)	1.401(4)
I(3)-Pd(1)	2.5962(2)	C(7)-C(8)	1.383(4)	C(32)-C(37)	1.519(4)
I(1)-Pd(2)	2.6106(2)	C(8)-C(9)	1.399(3)	C(33)-C(34)	1.380(4)
I(2)-Pd(2)	2.6530(2)	C(9)-C(13)	1.518(4)	C(34)-C(35)	1.385(4)
I(4)-Pd(2)	2.5778(2)	C(10)-C(11)	1.532(3)	C(35)-C(36)	1.397(3)
Pd(1)-C(1)	1.994(2)	C(10)-C(12)	1.535(3)	C(36)-C(40)	1.516(3)
Pd(2)-C(28)	1.999(2)	C(13)-C(14)	1.534(4)	C(37)-C(38)	1.531(5)
N(1)-C(1)	1.365(3)	C(13)-C(15)	1.538(4)	C(37)-C(39)	1.551(5)
N(1)-C(3)	1.390(3)	C(16)-C(21)	1.402(3)	C(40)-C(41)	1.524(3)
N(1)-C(4)	1.449(3)	C(16)-C(17)	1.409(3)	C(40)-C(42)	1.533(3)
N(2)-C(1)	1.364(3)	C(17)-C(18)	1.396(3)	C(43)-C(44)	1.397(3)
N(2)-C(2)	1.393(3)	C(17)-C(22)	1.526(3)	C(43)-C(48)	1.411(3)
N(2)-C(16)	1.447(3)	C(18)-C(19)	1.384(4)	C(44)-C(45)	1.399(4)
N(3)-C(28)	1.362(3)	C(19)-C(20)	1.386(4)	C(44)-C(49)	1.514(4)
N(3)-C(30)	1.384(3)	C(20)-C(21)	1.395(3)	C(45)-C(46)	1.379(5)

N(3)-C(31)	1.441(3)	C(21)-C(25)	1.520(3)	C(46)-C(47)	1.380(5)
N(4)-C(28)	1.364(3)	C(22)-C(23)	1.531(4)	C(47)-C(48)	1.403(4)
N(4)-C(29)	1.385(3)	C(22)-C(24)	1.533(4)	C(48)-C(52)	1.518(4)
N(4)-C(43)	1.441(3)	C(25)-C(27)	1.529(4)	C(49)-C(50)	1.525(4)
C(2)-C(3)	1.350(3)	C(25)-C(26)	1.533(4)	C(49)-C(51)	1.534(4)
C(4)-C(9)	1.407(3)	C(29)-C(30)	1.351(3)	C(52)-C(53)	1.535(5)
C(4)-C(5)	1.413(3)	C(31)-C(36)	1.399(3)	C(52)-C(54)	1.536(5)
C(5)-C(6)	1.393(3)				

Table S9. Selected bond angles for **2c** (°).

Atoms	Angle	Atoms	Angle
Pd(2)-I(1)-Pd(1)	86.662(6)	C(16)-C(17)-C(22)	123.40(19)
Pd(1)-I(2)-Pd(2)	86.388(6)	C(19)-C(18)-C(17)	121.3(2)
C(1)-Pd(1)-I(3)	88.39(6)	C(18)-C(19)-C(20)	120.3(2)
C(1)-Pd(1)-I(2)	96.79(6)	C(19)-C(20)-C(21)	121.2(2)
I(3)-Pd(1)-I(2)	173.611(8)	C(20)-C(21)-C(16)	117.2(2)
C(1)-Pd(1)-I(1)	177.61(6)	C(20)-C(21)-C(25)	119.7(2)
I(3)-Pd(1)-I(1)	90.116(7)	C(16)-C(21)-C(25)	122.99(19)
I(2)-Pd(1)-I(1)	84.579(6)	C(17)-C(22)-C(23)	113.6(2)
C(28)-Pd(2)-I(4)	91.92(6)	C(17)-C(22)-C(24)	109.77(19)
C(28)-Pd(2)-I(1)	93.43(6)	C(23)-C(22)-C(24)	109.0(2)
I(4)-Pd(2)-I(1)	174.534(8)	C(21)-C(25)-C(27)	110.5(2)
C(28)-Pd(2)-I(2)	177.70(6)	C(21)-C(25)-C(26)	111.9(2)
I(4)-Pd(2)-I(2)	90.134(7)	C(27)-C(25)-C(26)	110.5(2)
I(1)-Pd(2)-I(2)	84.496(6)	N(3)-C(28)-N(4)	104.48(17)
C(1)-N(1)-C(3)	110.45(17)	N(3)-C(28)-Pd(2)	128.88(15)
C(1)-N(1)-C(4)	126.35(17)	N(4)-C(28)-Pd(2)	126.60(15)
C(3)-N(1)-C(4)	122.96(17)	C(30)-C(29)-N(4)	106.50(19)
C(1)-N(2)-C(2)	110.88(17)	C(29)-C(30)-N(3)	107.27(19)
C(1)-N(2)-C(16)	124.70(17)	C(36)-C(31)-C(32)	123.1(2)
C(2)-N(2)-C(16)	123.11(17)	C(36)-C(31)-N(3)	118.26(19)
C(28)-N(3)-C(30)	110.68(18)	C(32)-C(31)-N(3)	118.6(2)
C(28)-N(3)-C(31)	126.97(18)	C(33)-C(32)-C(31)	117.0(2)
C(30)-N(3)-C(31)	122.34(18)	C(33)-C(32)-C(37)	119.9(2)
C(28)-N(4)-C(29)	111.06(18)	C(31)-C(32)-C(37)	123.1(2)
C(28)-N(4)-C(43)	126.89(18)	C(34)-C(33)-C(32)	121.0(2)
C(29)-N(4)-C(43)	121.94(18)	C(33)-C(34)-C(35)	120.6(2)
N(2)-C(1)-N(1)	104.72(17)	C(34)-C(35)-C(36)	120.9(2)
N(2)-C(1)-Pd(1)	125.08(14)	C(35)-C(36)-C(31)	117.3(2)
N(1)-C(1)-Pd(1)	129.57(14)	C(35)-C(36)-C(40)	121.2(2)

C(3)-C(2)-N(2)	106.53(18)	C(31)-C(36)-C(40)	121.35(19)
C(2)-C(3)-N(1)	107.37(18)	C(32)-C(37)-C(38)	112.3(3)
C(9)-C(4)-C(5)	122.88(19)	C(32)-C(37)-C(39)	110.4(2)
C(9)-C(4)-N(1)	119.1(2)	C(38)-C(37)-C(39)	110.0(3)
C(5)-C(4)-N(1)	117.81(18)	C(36)-C(40)-C(41)	113.87(19)
C(6)-C(5)-C(4)	117.0(2)	C(36)-C(40)-C(42)	108.87(18)
C(6)-C(5)-C(10)	119.9(2)	C(41)-C(40)-C(42)	110.6(2)
C(4)-C(5)-C(10)	122.99(19)	C(44)-C(43)-C(48)	123.5(2)
C(7)-C(6)-C(5)	121.4(2)	C(44)-C(43)-N(4)	118.2(2)
C(6)-C(7)-C(8)	120.4(2)	C(48)-C(43)-N(4)	118.1(2)
C(7)-C(8)-C(9)	121.4(2)	C(43)-C(44)-C(45)	116.9(2)
C(8)-C(9)-C(4)	116.8(2)	C(43)-C(44)-C(49)	122.6(2)
C(8)-C(9)-C(13)	119.0(2)	C(45)-C(44)-C(49)	120.3(2)
C(4)-C(9)-C(13)	124.0(2)	C(46)-C(45)-C(44)	121.2(3)
C(5)-C(10)-C(11)	113.4(2)	C(45)-C(46)-C(47)	120.7(3)
C(5)-C(10)-C(12)	109.8(2)	C(46)-C(47)-C(48)	121.1(3)
C(11)-C(10)-C(12)	110.7(2)	C(47)-C(48)-C(43)	116.5(3)
C(9)-C(13)-C(14)	112.7(2)	C(47)-C(48)-C(52)	119.6(3)
C(9)-C(13)-C(15)	109.0(2)	C(43)-C(48)-C(52)	123.7(2)
C(14)-C(13)-C(15)	109.2(2)	C(44)-C(49)-C(50)	111.9(3)
C(21)-C(16)-C(17)	122.96(19)	C(44)-C(49)-C(51)	109.0(2)
C(21)-C(16)-N(2)	119.82(19)	C(50)-C(49)-C(51)	111.2(3)
C(17)-C(16)-N(2)	117.23(19)	C(48)-C(52)-C(53)	114.0(3)
C(18)-C(17)-C(16)	117.0(2)	C(48)-C(52)-C(54)	109.3(3)
C(18)-C(17)-C(22)	119.5(2)	C(53)-C(52)-C(54)	108.6(3)

Table S10. Torsion angles for **2c** (°).

Atoms	Angle	Atoms	Angle
C(2)-N(2)-C(1)-N(1)	-2.3(2)	C(30)-N(3)-C(28)-N(4)	0.1(2)
C(16)-N(2)-C(1)-N(1)	164.91(19)	C(31)-N(3)-C(28)-N(4)	178.84(19)
C(2)-N(2)-C(1)-Pd(1)	169.33(15)	C(30)-N(3)-C(28)-Pd(2)	177.92(17)
C(16)-N(2)-C(1)-Pd(1)	-23.4(3)	C(31)-N(3)-C(28)-Pd(2)	-3.4(3)
C(3)-N(1)-C(1)-N(2)	2.0(2)	C(29)-N(4)-C(28)-N(3)	-0.7(2)
C(4)-N(1)-C(1)-N(2)	-172.53(19)	C(43)-N(4)-C(28)-N(3)	-176.8(2)
C(3)-N(1)-C(1)-Pd(1)	-169.14(16)	C(29)-N(4)-C(28)-Pd(2)	-178.55(16)
C(4)-N(1)-C(1)-Pd(1)	16.3(3)	C(43)-N(4)-C(28)-Pd(2)	5.3(3)
C(1)-N(2)-C(2)-C(3)	1.8(2)	C(28)-N(4)-C(29)-C(30)	1.0(3)
C(16)-N(2)-C(2)-C(3)	-165.7(2)	C(43)-N(4)-C(29)-C(30)	177.3(2)
N(2)-C(2)-C(3)-N(1)	-0.5(2)	N(4)-C(29)-C(30)-N(3)	-0.9(3)

C(1)-N(1)-C(3)-C(2)	-1.0(2)	C(28)-N(3)-C(30)-C(29)	0.5(3)
C(4)-N(1)-C(3)-C(2)	173.79(19)	C(31)-N(3)-C(30)-C(29)	-178.3(2)
C(1)-N(1)-C(4)-C(9)	-117.0(2)	C(28)-N(3)-C(31)-C(36)	73.2(3)
C(3)-N(1)-C(4)-C(9)	69.1(3)	C(30)-N(3)-C(31)-C(36)	-108.2(3)
C(1)-N(1)-C(4)-C(5)	67.5(3)	C(28)-N(3)-C(31)-C(32)	-109.6(3)
C(3)-N(1)-C(4)-C(5)	-106.4(2)	C(30)-N(3)-C(31)-C(32)	69.0(3)
C(9)-C(4)-C(5)-C(6)	3.4(3)	C(36)-C(31)-C(32)-C(33)	-1.8(4)
N(1)-C(4)-C(5)-C(6)	178.73(19)	N(3)-C(31)-C(32)-C(33)	-178.9(2)
C(9)-C(4)-C(5)-C(10)	-172.7(2)	C(36)-C(31)-C(32)-C(37)	177.1(2)
N(1)-C(4)-C(5)-C(10)	2.7(3)	N(3)-C(31)-C(32)-C(37)	0.0(4)
C(4)-C(5)-C(6)-C(7)	0.1(3)	C(31)-C(32)-C(33)-C(34)	-1.0(4)
C(10)-C(5)-C(6)-C(7)	176.3(2)	C(37)-C(32)-C(33)-C(34)	-179.9(3)
C(5)-C(6)-C(7)-C(8)	-2.7(4)	C(32)-C(33)-C(34)-C(35)	2.0(4)
C(6)-C(7)-C(8)-C(9)	1.9(4)	C(33)-C(34)-C(35)-C(36)	-0.3(4)
C(7)-C(8)-C(9)-C(4)	1.3(3)	C(34)-C(35)-C(36)-C(31)	-2.3(3)
C(7)-C(8)-C(9)-C(13)	-174.3(2)	C(34)-C(35)-C(36)-C(40)	172.5(2)
C(5)-C(4)-C(9)-C(8)	-4.1(3)	C(32)-C(31)-C(36)-C(35)	3.4(3)
N(1)-C(4)-C(9)-C(8)	-179.35(19)	N(3)-C(31)-C(36)-C(35)	-179.55(19)
C(5)-C(4)-C(9)-C(13)	171.4(2)	C(32)-C(31)-C(36)-C(40)	-171.4(2)
N(1)-C(4)-C(9)-C(13)	-3.9(3)	N(3)-C(31)-C(36)-C(40)	5.7(3)
C(6)-C(5)-C(10)-C(11)	33.7(3)	C(33)-C(32)-C(37)-C(38)	-42.9(4)
C(4)-C(5)-C(10)-C(11)	-150.4(2)	C(31)-C(32)-C(37)-C(38)	138.3(3)
C(6)-C(5)-C(10)-C(12)	-90.7(3)	C(33)-C(32)-C(37)-C(39)	80.3(3)
C(4)-C(5)-C(10)-C(12)	85.3(3)	C(31)-C(32)-C(37)-C(39)	-98.5(3)
C(8)-C(9)-C(13)-C(14)	-48.9(3)	C(35)-C(36)-C(40)-C(41)	36.2(3)
C(4)-C(9)-C(13)-C(14)	135.8(2)	C(31)-C(36)-C(40)-C(41)	-149.3(2)
C(8)-C(9)-C(13)-C(15)	72.6(3)	C(35)-C(36)-C(40)-C(42)	-87.7(3)
C(4)-C(9)-C(13)-C(15)	-102.7(2)	C(31)-C(36)-C(40)-C(42)	86.9(3)
C(1)-N(2)-C(16)-C(21)	82.7(3)	C(28)-N(4)-C(43)-C(44)	73.6(3)
C(2)-N(2)-C(16)-C(21)	-111.5(2)	C(29)-N(4)-C(43)-C(44)	-102.1(3)
C(1)-N(2)-C(16)-C(17)	-97.0(2)	C(28)-N(4)-C(43)-C(48)	-111.4(3)
C(2)-N(2)-C(16)-C(17)	68.7(3)	C(29)-N(4)-C(43)-C(48)	72.9(3)
C(21)-C(16)-C(17)-C(18)	-1.7(3)	C(48)-C(43)-C(44)-C(45)	2.9(4)
N(2)-C(16)-C(17)-C(18)	178.05(19)	N(4)-C(43)-C(44)-C(45)	177.6(2)
C(21)-C(16)-C(17)-C(22)	175.6(2)	C(48)-C(43)-C(44)-C(49)	-171.4(2)
N(2)-C(16)-C(17)-C(22)	-4.6(3)	N(4)-C(43)-C(44)-C(49)	3.4(3)
C(16)-C(17)-C(18)-C(19)	0.8(3)	C(43)-C(44)-C(45)-C(46)	-1.4(4)
C(22)-C(17)-C(18)-C(19)	-176.6(2)	C(49)-C(44)-C(45)-C(46)	172.9(3)
C(17)-C(18)-C(19)-C(20)	0.7(4)	C(44)-C(45)-C(46)-C(47)	-0.1(5)
C(18)-C(19)-C(20)-C(21)	-1.4(4)	C(45)-C(46)-C(47)-C(48)	0.3(5)

C(19)-C(20)-C(21)-C(16)	0.5(3)	C(46)-C(47)-C(48)-C(43)	1.0(4)
C(19)-C(20)-C(21)-C(25)	178.5(2)	C(46)-C(47)-C(48)-C(52)	-174.9(3)
C(17)-C(16)-C(21)-C(20)	1.0(3)	C(44)-C(43)-C(48)-C(47)	-2.7(4)
N(2)-C(16)-C(21)-C(20)	-178.68(19)	N(4)-C(43)-C(48)-C(47)	-177.4(2)
C(17)-C(16)-C(21)-C(25)	-176.8(2)	C(44)-C(43)-C(48)-C(52)	173.0(2)
N(2)-C(16)-C(21)-C(25)	3.4(3)	N(4)-C(43)-C(48)-C(52)	-1.7(3)
C(18)-C(17)-C(22)-C(23)	-46.7(3)	C(43)-C(44)-C(49)-C(50)	-139.6(3)
C(16)-C(17)-C(22)-C(23)	136.0(2)	C(45)-C(44)-C(49)-C(50)	46.4(3)
C(18)-C(17)-C(22)-C(24)	75.6(3)	C(43)-C(44)-C(49)-C(51)	97.0(3)
C(16)-C(17)-C(22)-C(24)	-101.6(2)	C(45)-C(44)-C(49)-C(51)	-77.1(4)
C(20)-C(21)-C(25)-C(27)	-76.2(3)	C(47)-C(48)-C(52)-C(53)	-43.8(4)
C(16)-C(21)-C(25)-C(27)	101.7(3)	C(43)-C(48)-C(52)-C(53)	140.7(3)
C(20)-C(21)-C(25)-C(26)	47.4(3)	C(47)-C(48)-C(52)-C(54)	78.0(4)
C(16)-C(21)-C(25)-C(26)	-134.7(2)	C(43)-C(48)-C(52)-C(54)	-97.6(3)

The structure of 3a

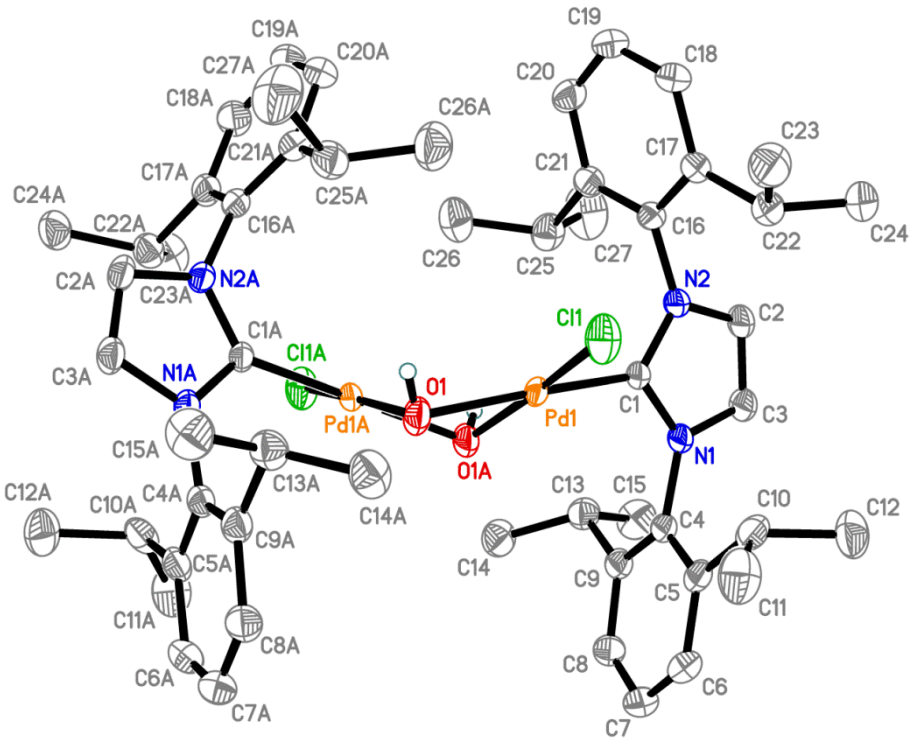


Figure S37. The molecular structure of one crystallographically unique molecule in **3a**. Hydrogen atoms (but hydroxy) are omitted. Thermal ellipsoids are set to a 50% probability level. Symmetry transformations to generate equivalent atoms: (A) -x+1, y, -z+1/2.

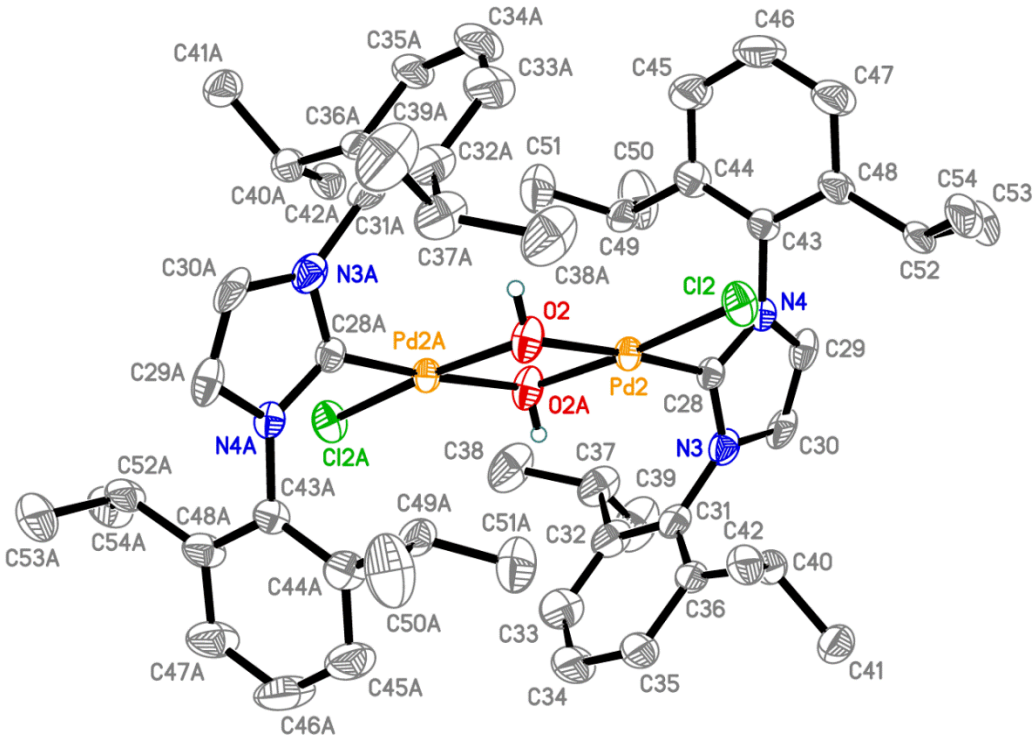


Figure S38. The molecular structure of the second crystallographically unique molecule in **3a**. The disorder of the whole complex is not shown. Hydrogen atoms (but hydroxy) are omitted. Thermal ellipsoids are set to a 50% probability level. Symmetry transformation to generate equivalent atoms: (A) -x+3/2, -y+1/2, -z+1.

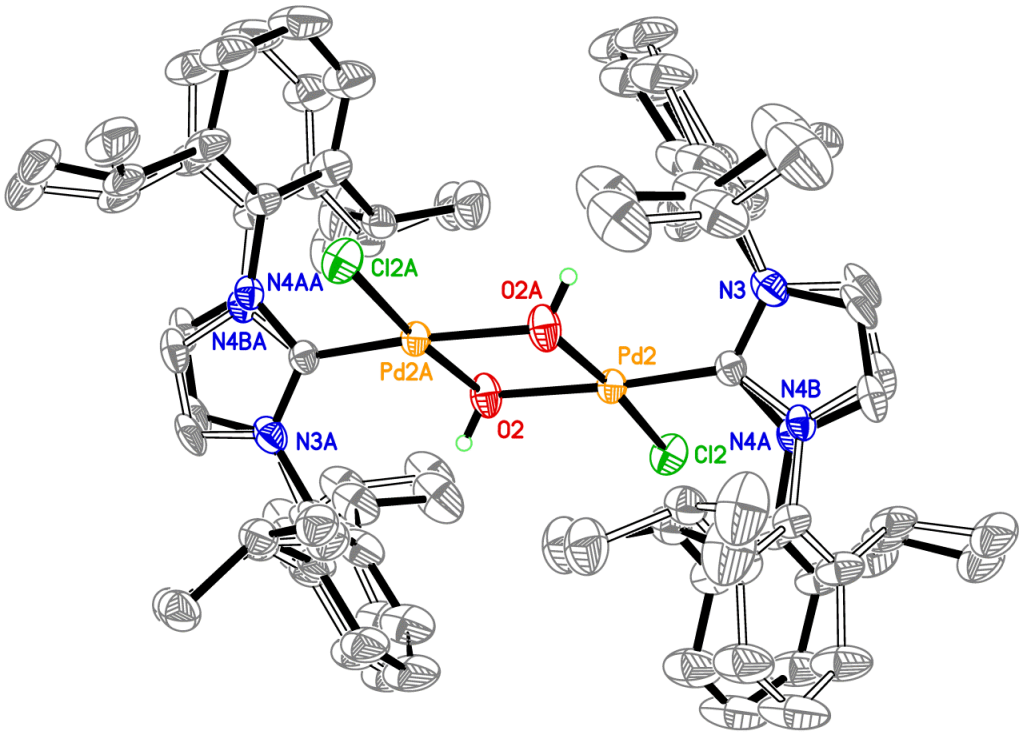


Figure S39. Disorder 0.649(3):0.351(3) of the second crystallographically unique molecule in **3a**. A minor component of the disorder is shown with open lines. Hydrogen atoms are omitted.

Table S11. Selected bond distances for **3a** (Å).

Atoms	Distance	Atoms	Distance	Atoms	Distance
Pd(1)-C(1)	1.9505(14)	C(4)-C(9)	1.399(2)	C(16)-C(17)	1.403(2)
Pd(1)-O(1)#1	2.0162(13)	C(4)-C(5)	1.406(3)	C(16)-C(21)	1.403(2)
Pd(1)-O(1)	2.0698(11)	C(5)-C(6)	1.400(3)	C(17)-C(18)	1.396(2)
Pd(1)-Cl(1)	2.2698(5)	C(5)-C(10)	1.514(3)	C(17)-C(22)	1.525(3)
O(1)-H(1O)	0.8400	C(6)-C(7)	1.383(3)	C(18)-C(19)	1.383(3)
N(1)-C(1)	1.3571(19)	C(7)-C(8)	1.384(3)	C(19)-C(20)	1.386(3)
N(1)-C(3)	1.389(2)	C(8)-C(9)	1.401(2)	C(20)-C(21)	1.398(3)
N(1)-C(4)	1.442(2)	C(9)-C(13)	1.519(3)	C(21)-C(25)	1.516(3)
N(2)-C(1)	1.348(2)	C(10)-C(11)	1.524(3)	C(22)-C(23)	1.529(3)
N(2)-C(2)	1.392(2)	C(10)-C(12)	1.525(3)	C(22)-C(24)	1.534(3)
N(2)-C(16)	1.444(2)	C(13)-C(15)	1.531(3)	C(25)-C(26)	1.527(3)
C(2)-C(3)	1.343(2)	C(13)-C(14)	1.533(3)	C(25)-C(27)	1.534(3)
Pd(2)-C(28)	1.9491(16)	C(36A)-C(40A)	1.525(3)	C(32B)-C(33B)	1.402(5)
Pd(2)-O(2)#2	2.0182(13)	C(37A)-C(39A)	1.522(5)	C(32B)-C(37B)	1.516(5)
Pd(2)-O(2)	2.0884(13)	C(37A)-C(38A)	1.546(4)	C(33B)-C(34B)	1.367(7)
Pd(2)-Cl(2)	2.2747(4)	C(40A)-C(42A)	1.524(4)	C(34B)-C(35B)	1.386(5)
O(2)-H(2O)	0.8400	C(40A)-C(41A)	1.539(3)	C(35B)-C(36B)	1.394(4)
N(3)-C(28)	1.354(2)	C(43A)-C(48A)	1.397(3)	C(36B)-C(40B)	1.524(4)

N(3)-C(30B)	1.401(4)	C(43A)-C(44A)	1.403(3)	C(37B)-C(39B)	1.522(5)
N(3)-C(30A)	1.403(3)	C(44A)-C(45A)	1.396(4)	C(37B)-C(38B)	1.546(5)
N(3)-C(31B)	1.450(4)	C(44A)-C(49A)	1.520(4)	C(40B)-C(42B)	1.524(4)
N(3)-C(31A)	1.452(3)	C(45A)-C(46A)	1.386(5)	C(40B)-C(41B)	1.539(4)
C(28)-N(4B)	1.359(3)	C(46A)-C(47A)	1.390(5)	C(43B)-C(48B)	1.396(4)
C(28)-N(4A)	1.361(2)	C(47A)-C(48A)	1.400(4)	C(43B)-C(44B)	1.403(4)
N(4A)-C(29A)	1.386(3)	C(48A)-C(52A)	1.519(3)	C(44B)-C(45B)	1.395(5)
N(4A)-C(43A)	1.442(3)	C(49A)-C(51A)	1.507(4)	C(44B)-C(49B)	1.520(4)
C(29A)-C(30A)	1.331(4)	C(49A)-C(50A)	1.518(5)	C(45B)-C(46B)	1.385(5)
C(31A)-C(36A)	1.396(4)	C(52A)-C(54A)	1.524(4)	C(46B)-C(47B)	1.388(5)
C(31A)-C(32A)	1.409(3)	C(52A)-C(53A)	1.533(4)	C(47B)-C(48B)	1.399(5)
C(32A)-C(33A)	1.403(5)	N(4B)-C(29B)	1.384(4)	C(48B)-C(52B)	1.519(4)
C(32A)-C(37A)	1.517(5)	N(4B)-C(43B)	1.440(3)	C(49B)-C(51B)	1.507(5)
C(33A)-C(34A)	1.369(6)	C(29B)-C(30B)	1.329(5)	C(49B)-C(50B)	1.517(5)
C(34A)-C(35A)	1.386(5)	C(31B)-C(36B)	1.394(4)	C(52B)-C(54B)	1.523(5)
C(35A)-C(36A)	1.395(4)	C(31B)-C(32B)	1.407(4)	C(52B)-C(53B)	1.533(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, y, -z+1/2 #2 -x+3/2, -y+1/2, -z+1

Table S12. Selected bond angles for **3a** (°).

Atoms	Angle	Atoms	Angle
C(1)-Pd(1)-O(1)#1	94.33(6)	C(7)-C(6)-C(5)	121.05(18)
C(1)-Pd(1)-O(1)	174.57(6)	C(6)-C(7)-C(8)	120.44(17)
O(1)#1-Pd(1)-O(1)	80.27(6)	C(7)-C(8)-C(9)	121.30(17)
C(1)-Pd(1)-Cl(1)	95.25(5)	C(4)-C(9)-C(8)	116.73(17)
O(1)#1-Pd(1)-Cl(1)	170.30(4)	C(4)-C(9)-C(13)	122.76(16)
O(1)-Pd(1)-Cl(1)	90.13(4)	C(8)-C(9)-C(13)	120.51(16)
C(1)-Pd(1)-Pd(1)#1	132.26(5)	C(5)-C(10)-C(11)	113.54(18)
O(1)#1-Pd(1)-Pd(1)#1	44.70(3)	C(5)-C(10)-C(12)	110.11(16)
O(1)-Pd(1)-Pd(1)#1	43.25(4)	C(11)-C(10)-C(12)	110.04(18)
Cl(1)-Pd(1)-Pd(1)#1	127.288(13)	C(9)-C(13)-C(15)	111.08(16)
Pd(1)#1-O(1)-Pd(1)	92.05(5)	C(9)-C(13)-C(14)	112.53(17)
Pd(1)#1-O(1)-H(1O)	109.5	C(15)-C(13)-C(14)	110.08(17)
Pd(1)-O(1)-H(1O)	106.3	C(17)-C(16)-C(21)	123.42(16)
C(1)-N(1)-C(3)	110.67(14)	C(17)-C(16)-N(2)	118.60(15)
C(1)-N(1)-C(4)	125.64(13)	C(21)-C(16)-N(2)	117.87(15)
C(3)-N(1)-C(4)	123.66(13)	C(18)-C(17)-C(16)	116.67(17)
C(1)-N(2)-C(2)	110.76(13)	C(18)-C(17)-C(22)	120.71(17)
C(1)-N(2)-C(16)	126.58(13)	C(16)-C(17)-C(22)	122.62(15)
C(2)-N(2)-C(16)	122.45(13)	C(19)-C(18)-C(17)	121.31(19)

N(2)-C(1)-N(1)	105.00(12)	C(18)-C(19)-C(20)	120.80(18)
N(2)-C(1)-Pd(1)	129.63(11)	C(19)-C(20)-C(21)	120.46(18)
N(1)-C(1)-Pd(1)	125.32(11)	C(20)-C(21)-C(16)	117.32(18)
C(3)-C(2)-N(2)	106.81(14)	C(20)-C(21)-C(25)	120.28(17)
C(2)-C(3)-N(1)	106.75(14)	C(16)-C(21)-C(25)	122.38(16)
C(9)-C(4)-C(5)	123.50(16)	C(17)-C(22)-C(23)	111.59(16)
C(9)-C(4)-N(1)	118.45(16)	C(17)-C(22)-C(24)	112.49(17)
C(5)-C(4)-N(1)	118.01(15)	C(23)-C(22)-C(24)	110.52(17)
C(6)-C(5)-C(4)	116.92(16)	C(21)-C(25)-C(26)	112.38(18)
C(6)-C(5)-C(10)	121.18(17)	C(21)-C(25)-C(27)	110.19(19)
C(4)-C(5)-C(10)	121.87(16)	C(26)-C(25)-C(27)	110.90(19)
C(28)-Pd(2)-O(2)#2	93.91(6)	C(46A)-C(45A)-C(44A)	120.4(3)
C(28)-Pd(2)-O(2)	175.24(6)	C(45A)-C(46A)-C(47A)	120.6(4)
O(2)#2-Pd(2)-O(2)	81.97(6)	C(46A)-C(47A)-C(48A)	121.0(4)
C(28)-Pd(2)-Cl(2)	91.24(5)	C(43A)-C(48A)-C(47A)	116.9(4)
O(2)#2-Pd(2)-Cl(2)	174.20(4)	C(43A)-C(48A)-C(52A)	123.2(3)
O(2)-Pd(2)-Cl(2)	92.99(4)	C(47A)-C(48A)-C(52A)	119.9(4)
C(28)-Pd(2)-Pd(2)#2	135.70(5)	C(51A)-C(49A)-C(50A)	112.2(5)
O(2)#2-Pd(2)-Pd(2)#2	41.84(4)	C(51A)-C(49A)-C(44A)	113.6(5)
O(2)-Pd(2)-Pd(2)#2	40.13(4)	C(50A)-C(49A)-C(44A)	110.1(3)
Cl(2)-Pd(2)-Pd(2)#2	133.060(14)	C(48A)-C(52A)-C(54A)	113.3(7)
Pd(2)#2-O(2)-Pd(2)	98.03(6)	C(48A)-C(52A)-C(53A)	110.1(6)
Pd(2)#2-O(2)-H(2O)	109.5	C(54A)-C(52A)-C(53A)	110.8(9)
Pd(2)-O(2)-H(2O)	121.8	C(28)-N(4B)-C(29B)	114.2(8)
C(28)-N(3)-C(30B)	118.7(6)	C(28)-N(4B)-C(43B)	121.4(7)
C(28)-N(3)-C(30A)	106.1(3)	C(29B)-N(4B)-C(43B)	124.4(6)
C(28)-N(3)-C(31B)	131.0(6)	C(30B)-C(29B)-N(4B)	108.7(10)
C(30B)-N(3)-C(31B)	109.6(8)	C(29B)-C(30B)-N(3)	100.8(9)
C(28)-N(3)-C(31A)	120.6(3)	C(36B)-C(31B)-C(32B)	128.3(6)
C(30A)-N(3)-C(31A)	132.9(3)	C(36B)-C(31B)-N(3)	114.8(6)
N(3)-C(28)-N(4B)	97.3(3)	C(32B)-C(31B)-N(3)	116.6(6)
N(3)-C(28)-N(4A)	108.45(19)	C(33B)-C(32B)-C(31B)	112.7(6)
N(3)-C(28)-Pd(2)	126.46(13)	C(33B)-C(32B)-C(37B)	121.1(9)
N(4B)-C(28)-Pd(2)	136.2(3)	C(31B)-C(32B)-C(37B)	126.2(9)
N(4A)-C(28)-Pd(2)	125.10(17)	C(34B)-C(33B)-C(32B)	121.5(8)
C(28)-N(4A)-C(29A)	108.9(3)	C(33B)-C(34B)-C(35B)	122.9(9)
C(28)-N(4A)-C(43A)	127.1(3)	C(34B)-C(35B)-C(36B)	119.6(10)
C(29A)-N(4A)-C(43A)	123.3(3)	C(35B)-C(36B)-C(31B)	114.7(8)
C(30A)-C(29A)-N(4A)	106.4(5)	C(35B)-C(36B)-C(40B)	121.9(11)
C(29A)-C(30A)-N(3)	110.0(4)	C(31B)-C(36B)-C(40B)	123.4(11)

C(36A)-C(31A)-C(32A)	120.8(3)	C(32B)-C(37B)-C(39B)	108.9(11)
C(36A)-C(31A)-N(3)	121.8(3)	C(32B)-C(37B)-C(38B)	109.2(16)
C(32A)-C(31A)-N(3)	117.3(4)	C(39B)-C(37B)-C(38B)	112.1(19)
C(33A)-C(32A)-C(31A)	118.5(4)	C(42B)-C(40B)-C(36B)	111.6(7)
C(33A)-C(32A)-C(37A)	119.8(4)	C(42B)-C(40B)-C(41B)	114.1(16)
C(31A)-C(32A)-C(37A)	121.8(5)	C(36B)-C(40B)-C(41B)	108.0(16)
C(34A)-C(33A)-C(32A)	121.2(4)	C(48B)-C(43B)-C(44B)	123.0(7)
C(33A)-C(34A)-C(35A)	119.6(5)	C(48B)-C(43B)-N(4B)	118.4(8)
C(34A)-C(35A)-C(36A)	121.6(5)	C(44B)-C(43B)-N(4B)	118.3(9)
C(35A)-C(36A)-C(31A)	118.3(4)	C(45B)-C(44B)-C(43B)	115.3(6)
C(35A)-C(36A)-C(40A)	118.0(5)	C(45B)-C(44B)-C(49B)	124.5(6)
C(31A)-C(36A)-C(40A)	123.6(5)	C(43B)-C(44B)-C(49B)	120.0(6)
C(32A)-C(37A)-C(39A)	110.8(5)	C(46B)-C(45B)-C(44B)	123.7(6)
C(32A)-C(37A)-C(38A)	113.7(8)	C(45B)-C(46B)-C(47B)	119.2(6)
C(39A)-C(37A)-C(38A)	109.6(9)	C(46B)-C(47B)-C(48B)	119.9(7)
C(42A)-C(40A)-C(36A)	113.1(4)	C(43B)-C(48B)-C(47B)	118.9(7)
C(42A)-C(40A)-C(41A)	109.1(7)	C(43B)-C(48B)-C(52B)	122.0(8)
C(36A)-C(40A)-C(41A)	109.7(8)	C(47B)-C(48B)-C(52B)	119.0(8)
C(48A)-C(43A)-C(44A)	123.3(3)	C(51B)-C(49B)-C(50B)	107.6(10)
C(48A)-C(43A)-N(4A)	119.2(4)	C(51B)-C(49B)-C(44B)	110.3(12)
C(44A)-C(43A)-N(4A)	117.5(5)	C(50B)-C(49B)-C(44B)	108.8(7)
C(45A)-C(44A)-C(43A)	117.6(3)	C(48B)-C(52B)-C(54B)	110.7(15)
C(45A)-C(44A)-C(49A)	118.6(3)	C(48B)-C(52B)-C(53B)	109.9(12)
C(43A)-C(44A)-C(49A)	123.7(3)	C(54B)-C(52B)-C(53B)	109(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, y, -z+1/2 #2 -x+3/2, -y+1/2, -z+1

Table S13. Torsion angles for **3a** (°).

Atoms	Angle	Atoms	Angle
C(2)-N(2)-C(1)-N(1)	0.19(18)	C(32A)-C(31A)-C(36A)-C(40A)	173.5(6)
C(16)-N(2)-C(1)-N(1)	175.01(15)	N(3)-C(31A)-C(36A)-C(40A)	-4.3(9)
C(2)-N(2)-C(1)-Pd(1)	-177.35(12)	C(33A)-C(32A)-C(37A)-C(39A)	-78.9(9)
C(16)-N(2)-C(1)-Pd(1)	-2.5(2)	C(31A)-C(32A)-C(37A)-C(39A)	100.2(9)
C(3)-N(1)-C(1)-N(2)	0.15(18)	C(33A)-C(32A)-C(37A)-C(38A)	45.1(10)
C(4)-N(1)-C(1)-N(2)	178.30(15)	C(31A)-C(32A)-C(37A)-C(38A)	-135.8(8)
C(3)-N(1)-C(1)-Pd(1)	177.83(12)	C(35A)-C(36A)-C(40A)-C(42A)	-59.0(10)
C(4)-N(1)-C(1)-Pd(1)	-4.0(2)	C(31A)-C(36A)-C(40A)-C(42A)	125.6(7)
C(1)-N(2)-C(2)-C(3)	-0.5(2)	C(35A)-C(36A)-C(40A)-C(41A)	63.0(9)
C(16)-N(2)-C(2)-C(3)	-175.53(16)	C(31A)-C(36A)-C(40A)-C(41A)	-112.4(10)

N(2)-C(2)-C(3)-N(1)	0.5(2)	C(28)-N(4A)-C(43A)-C(48A)	113.4(7)
C(1)-N(1)-C(3)-C(2)	-0.4(2)	C(29A)-N(4A)-C(43A)-C(48A)	-76.5(9)
C(4)-N(1)-C(3)-C(2)	-178.63(16)	C(28)-N(4A)-C(43A)-C(44A)	-66.3(8)
C(1)-N(1)-C(4)-C(9)	102.39(19)	C(29A)-N(4A)-C(43A)-C(44A)	103.8(8)
C(3)-N(1)-C(4)-C(9)	-79.7(2)	C(48A)-C(43A)-C(44A)-C(45A)	-4.3(6)
C(1)-N(1)-C(4)-C(5)	-79.6(2)	N(4A)-C(43A)-C(44A)-C(45A)	175.4(4)
C(3)-N(1)-C(4)-C(5)	98.4(2)	C(48A)-C(43A)-C(44A)-C(49A)	172.0(4)
C(9)-C(4)-C(5)-C(6)	1.5(2)	N(4A)-C(43A)-C(44A)-C(49A)	-8.3(6)
N(1)-C(4)-C(5)-C(6)	-176.45(15)	C(43A)-C(44A)-C(45A)-C(46A)	1.5(7)
C(9)-C(4)-C(5)-C(10)	179.42(16)	C(49A)-C(44A)-C(45A)-C(46A)	-175.0(5)
N(1)-C(4)-C(5)-C(10)	1.5(2)	C(44A)-C(45A)-C(46A)-C(47A)	1.9(9)
C(4)-C(5)-C(6)-C(7)	0.5(3)	C(45A)-C(46A)-C(47A)-C(48A)	-2.7(9)
C(10)-C(5)-C(6)-C(7)	-177.45(17)	C(44A)-C(43A)-C(48A)-C(47A)	3.5(6)
C(5)-C(6)-C(7)-C(8)	-1.4(3)	N(4A)-C(43A)-C(48A)-C(47A)	-176.2(4)
C(6)-C(7)-C(8)-C(9)	0.4(3)	C(44A)-C(43A)-C(48A)-C(52A)	-175.9(5)
C(5)-C(4)-C(9)-C(8)	-2.4(2)	N(4A)-C(43A)-C(48A)-C(52A)	4.4(7)
N(1)-C(4)-C(9)-C(8)	175.51(15)	C(46A)-C(47A)-C(48A)-C(43A)	0.1(7)
C(5)-C(4)-C(9)-C(13)	177.67(15)	C(46A)-C(47A)-C(48A)-C(52A)	179.5(6)
N(1)-C(4)-C(9)-C(13)	-4.4(2)	C(45A)-C(44A)-C(49A)-C(51A)	-45.6(7)
C(7)-C(8)-C(9)-C(4)	1.4(3)	C(43A)-C(44A)-C(49A)-C(51A)	138.2(6)
C(7)-C(8)-C(9)-C(13)	-178.66(17)	C(45A)-C(44A)-C(49A)-C(50A)	81.2(5)
C(6)-C(5)-C(10)-C(11)	-37.4(2)	C(43A)-C(44A)-C(49A)-C(50A)	-95.0(5)
C(4)-C(5)-C(10)-C(11)	144.79(18)	C(43A)-C(48A)-C(52A)-C(54A)	-136.0(9)
C(6)-C(5)-C(10)-C(12)	86.5(2)	C(47A)-C(48A)-C(52A)-C(54A)	44.7(11)
C(4)-C(5)-C(10)-C(12)	-91.3(2)	C(43A)-C(48A)-C(52A)-C(53A)	99.3(6)
C(4)-C(9)-C(13)-C(15)	101.2(2)	C(47A)-C(48A)-C(52A)-C(53A)	-80.1(6)
C(8)-C(9)-C(13)-C(15)	-78.7(2)	N(3)-C(28)-N(4B)-C(29B)	-5.9(15)
C(4)-C(9)-C(13)-C(14)	-134.86(17)	Pd(2)-C(28)-N(4B)-C(29B)	176.8(9)
C(8)-C(9)-C(13)-C(14)	45.2(2)	N(3)-C(28)-N(4B)-C(43B)	173.0(12)
C(1)-N(2)-C(16)-C(17)	99.0(2)	Pd(2)-C(28)-N(4B)-C(43B)	-4(2)
C(2)-N(2)-C(16)-C(17)	-86.8(2)	C(28)-N(4B)-C(29B)-C(30B)	5(2)
C(1)-N(2)-C(16)-C(21)	-84.6(2)	C(43B)-N(4B)-C(29B)-C(30B)	-173.7(16)
C(2)-N(2)-C(16)-C(21)	89.63(19)	N(4B)-C(29B)-C(30B)-N(3)	-2(2)
C(21)-C(16)-C(17)-C(18)	-1.2(3)	C(28)-N(3)-C(30B)-C(29B)	-2.4(18)
N(2)-C(16)-C(17)-C(18)	174.97(16)	C(31B)-N(3)-C(30B)-C(29B)	169.1(12)
C(21)-C(16)-C(17)-C(22)	178.33(16)	C(28)-N(3)-C(31B)-C(36B)	-82.0(12)
N(2)-C(16)-C(17)-C(22)	-5.5(2)	C(30B)-N(3)-C(31B)-C(36B)	107.9(14)
C(16)-C(17)-C(18)-C(19)	0.2(3)	C(28)-N(3)-C(31B)-C(32B)	92.7(12)
C(22)-C(17)-C(18)-C(19)	-179.38(19)	C(30B)-N(3)-C(31B)-C(32B)	-77.4(15)
C(17)-C(18)-C(19)-C(20)	1.0(3)	C(36B)-C(31B)-C(32B)-C(33B)	-4(2)

C(18)-C(19)-C(20)-C(21)	-1.2(3)	N(3)-C(31B)-C(32B)-C(33B)	-177.6(11)
C(19)-C(20)-C(21)-C(16)	0.2(3)	C(36B)-C(31B)-C(32B)-C(37B)	179.6(15)
C(19)-C(20)-C(21)-C(25)	-178.11(19)	N(3)-C(31B)-C(32B)-C(37B)	6(2)
C(17)-C(16)-C(21)-C(20)	1.1(3)	C(31B)-C(32B)-C(33B)-C(34B)	5.5(19)
N(2)-C(16)-C(21)-C(20)	-175.17(15)	C(37B)-C(32B)-C(33B)-C(34B)	-177.7(13)
C(17)-C(16)-C(21)-C(25)	179.30(16)	C(32B)-C(33B)-C(34B)-C(35B)	-3(2)
N(2)-C(16)-C(21)-C(25)	3.1(2)	C(33B)-C(34B)-C(35B)-C(36B)	-3(2)
C(18)-C(17)-C(22)-C(23)	34.4(3)	C(34B)-C(35B)-C(36B)-C(31B)	4.3(18)
C(16)-C(17)-C(22)-C(23)	-145.13(18)	C(34B)-C(35B)-C(36B)-C(40B)	-176.0(13)
C(18)-C(17)-C(22)-C(24)	-90.5(2)	C(32B)-C(31B)-C(36B)-C(35B)	-1(2)
C(16)-C(17)-C(22)-C(24)	90.0(2)	N(3)-C(31B)-C(36B)-C(35B)	172.9(11)
C(20)-C(21)-C(25)-C(26)	-47.2(2)	C(32B)-C(31B)-C(36B)-C(40B)	179.3(14)
C(16)-C(21)-C(25)-C(26)	134.56(19)	N(3)-C(31B)-C(36B)-C(40B)	-6.7(19)
C(20)-C(21)-C(25)-C(27)	77.0(2)	C(33B)-C(32B)-C(37B)-C(39B)	-67(2)
C(16)-C(21)-C(25)-C(27)	-101.2(2)	C(31B)-C(32B)-C(37B)-C(39B)	109.0(19)
C(30B)-N(3)-C(28)-N(4B)	5.1(13)	C(33B)-C(32B)-C(37B)-C(38B)	55(2)
C(31B)-N(3)-C(28)-N(4B)	-164.2(9)	C(31B)-C(32B)-C(37B)-C(38B)	-128(2)
C(30A)-N(3)-C(28)-N(4A)	-2.3(6)	C(35B)-C(36B)-C(40B)-C(42B)	-56(2)
C(31A)-N(3)-C(28)-N(4A)	-176.5(5)	C(31B)-C(36B)-C(40B)-C(42B)	123.6(17)
C(30B)-N(3)-C(28)-Pd(2)	-177.2(10)	C(35B)-C(36B)-C(40B)-C(41B)	70.2(19)
C(30A)-N(3)-C(28)-Pd(2)	178.0(4)	C(31B)-C(36B)-C(40B)-C(41B)	-110(2)
C(31B)-N(3)-C(28)-Pd(2)	13.4(5)	C(28)-N(4B)-C(43B)-C(48B)	112.1(14)
C(31A)-N(3)-C(28)-Pd(2)	3.8(3)	C(29B)-N(4B)-C(43B)-C(48B)	-69.1(19)
N(3)-C(28)-N(4A)-C(29A)	3.1(7)	C(28)-N(4B)-C(43B)-C(44B)	-73.8(16)
Pd(2)-C(28)-N(4A)-C(29A)	-177.2(4)	C(29B)-N(4B)-C(43B)-C(44B)	105.0(18)
N(3)-C(28)-N(4A)-C(43A)	174.4(6)	C(48B)-C(43B)-C(44B)-C(45B)	2.5(13)
Pd(2)-C(28)-N(4A)-C(43A)	-5.9(10)	N(4B)-C(43B)-C(44B)-C(45B)	-171.4(8)
C(28)-N(4A)-C(29A)-C(30A)	-2.6(9)	C(48B)-C(43B)-C(44B)-C(49B)	177.7(8)
C(43A)-N(4A)-C(29A)-C(30A)	-174.3(7)	N(4B)-C(43B)-C(44B)-C(49B)	3.8(12)
N(4A)-C(29A)-C(30A)-N(3)	1.2(10)	C(43B)-C(44B)-C(45B)-C(46B)	-1.6(15)
C(28)-N(3)-C(30A)-C(29A)	0.7(8)	C(49B)-C(44B)-C(45B)-C(46B)	-176.6(10)
C(31A)-N(3)-C(30A)-C(29A)	173.9(5)	C(44B)-C(45B)-C(46B)-C(47B)	0.4(18)
C(28)-N(3)-C(31A)-C(36A)	-80.3(6)	C(45B)-C(46B)-C(47B)-C(48B)	0.1(17)
C(30A)-N(3)-C(31A)-C(36A)	107.4(7)	C(44B)-C(43B)-C(48B)-C(47B)	-2.2(14)
C(28)-N(3)-C(31A)-C(32A)	101.9(5)	N(4B)-C(43B)-C(48B)-C(47B)	171.7(9)
C(30A)-N(3)-C(31A)-C(32A)	-70.5(8)	C(44B)-C(43B)-C(48B)-C(52B)	-178.0(11)
C(36A)-C(31A)-C(32A)-C(33A)	3.3(9)	N(4B)-C(43B)-C(48B)-C(52B)	-4.1(14)
N(3)-C(31A)-C(32A)-C(33A)	-178.8(5)	C(46B)-C(47B)-C(48B)-C(43B)	0.8(15)
C(36A)-C(31A)-C(32A)-C(37A)	-175.8(6)	C(46B)-C(47B)-C(48B)-C(52B)	176.7(12)
N(3)-C(31A)-C(32A)-C(37A)	2.1(8)	C(45B)-C(44B)-C(49B)-C(51B)	-46.0(14)

C(31A)-C(32A)-C(33A)-C(34A)	-2.1(9)	C(43B)-C(44B)-C(49B)-C(51B)	139.3(11)
C(37A)-C(32A)-C(33A)-C(34A)	177.0(6)	C(45B)-C(44B)-C(49B)-C(50B)	71.8(12)
C(32A)-C(33A)-C(34A)-C(35A)	-0.4(9)	C(43B)-C(44B)-C(49B)-C(50B)	-102.9(10)
C(33A)-C(34A)-C(35A)-C(36A)	2.0(9)	C(43B)-C(48B)-C(52B)-C(54B)	-132.1(19)
C(34A)-C(35A)-C(36A)-C(31A)	-0.8(8)	C(47B)-C(48B)-C(52B)-C(54B)	52(2)
C(34A)-C(35A)-C(36A)-C(40A)	-176.4(6)	C(43B)-C(48B)-C(52B)-C(53B)	108.0(13)
C(32A)-C(31A)-C(36A)-C(35A)	-1.9(8)	C(47B)-C(48B)-C(52B)-C(53B)	-67.8(14)
N(3)-C(31A)-C(36A)-C(35A)	-179.7(5)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1, y, -z+1/2; #2 -x+3/2, -y+1/2, -z+1.

The structure of 3b

Crystals of **3b** easily lose non-coordinating solvent molecules, when they are taken out of the mother liquor. A crystal that was kept without solvent for a while and presumably lost most lattice solvent molecules displayed a fast decay of reflection intensities while going from small to high θ angles. Its structure was solved in the $P2_1/n$ space group (Fig. S40). The presence of non-coordinating solvent molecules was not detected in the crystalline lattice. The structure was publishable, although it exhibited rather high thermal motions and, therefore, a low bond precision on C-C bonds = 0.0125 Å. Some parameters are provided in Table S14.

Table S14. Some crystal data, data collection and structure refinement details for a first crystal **3b** with poor-quality X-ray data.

Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 12.6643(8) Å b = 14.4378(9) Å c = 15.6924(11) Å β= 91.580(2)°
Volume	2868.2(3) $Å^3$
Z	2
Density (calculated)	1.371 g/cm^3
Absorption coefficient	2.059 mm^{-1}
F(000)	1208
Crystal size	0.21 x 0.14 x 0.10 mm
Theta range for data collection	1.917 to 29.000°.
Index ranges	-17<=h<=17, -19<=k<=19, -21<=l<=21
Reflections collected	76772
Independent reflections	7617 [R(int) = 0.0753]
Observed reflections	5111
Max. and min. transmission	0.1076 and 0.0652
Data / restraints / parameters	7617 / 43 / 340
Goodness-of-fit on F^2	1.145

Final R indices [I>2σ(I)]	R1 = 0.0745, wR2 = 0.1809
R indices (all data)	R1 = 0.1160, wR2 = 0.2234
Largest diff. peak and hole	1.740 and -1.344 e·Å^{-3}

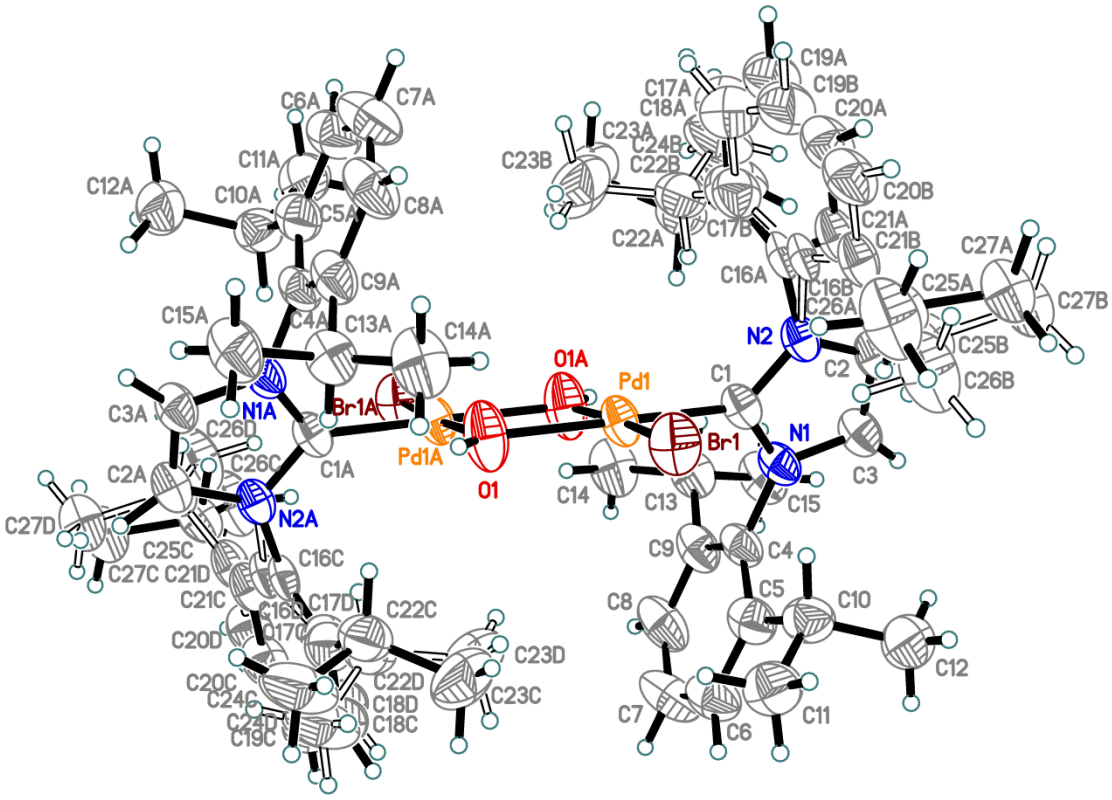


Figure S40. The structure of **3b** solved in the $P2_1/n$ space group. The disorder is shown with solid and open lines. Thermal ellipsoids are set to a 50% probability level. Symmetry transformation to generate equivalent atoms: -x+1,-y+1,-z+1.

A better specimen was obtained from a mother liquor. Its structure was solved in a chiral space group – $P2_1$ – providing much better geometrical parameters (Tables S1, S15-S17, Figs. S41-S43). The entire molecule in monocrystal **3b** is disordered. The disorder is modeled over two positions **A** and **B** with the 0.7274(11):0.2726(11) ratio (Fig. S41). Disordered unresolved non-coordinating molecules located in crystal voids of **3b** were removed by the SQUEEZE method.

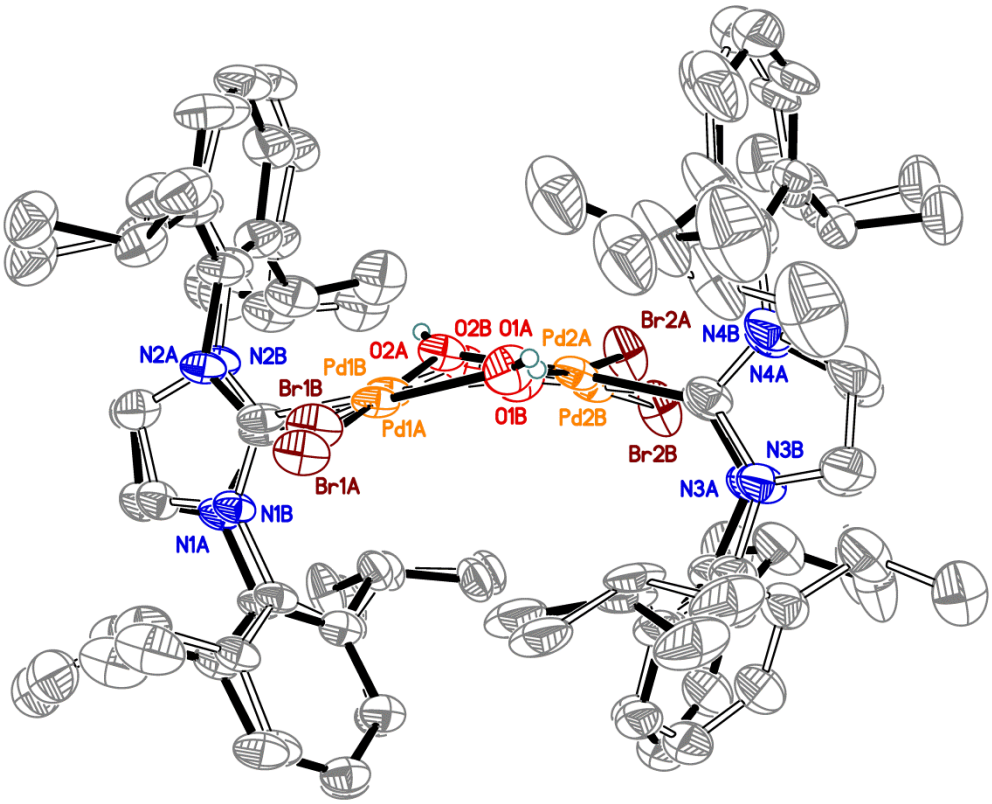


Figure S41. The structure of **3b**. The disorder is shown with solid and open lines. Hydrogen atoms (but hydroxy) are omitted. Thermal ellipsoids are set to a 50% probability level.

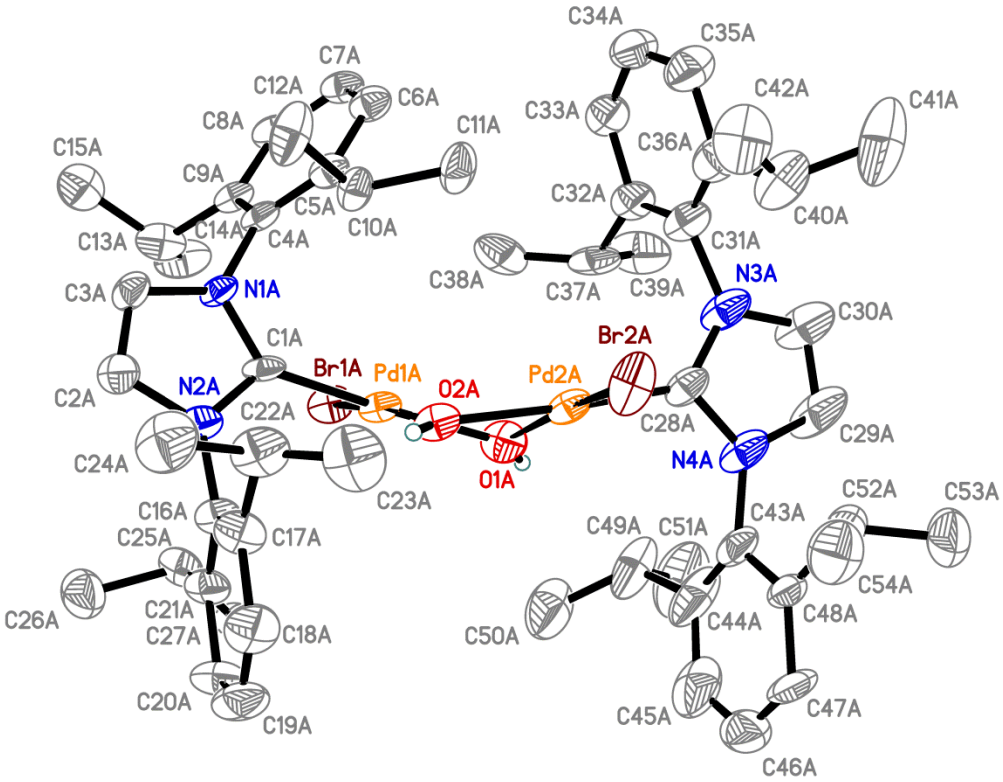


Figure S42. The structure of the major component of disorder **A**. Hydrogen atoms (but hydroxy) are omitted. Thermal ellipsoids are set to a 50% probability level.

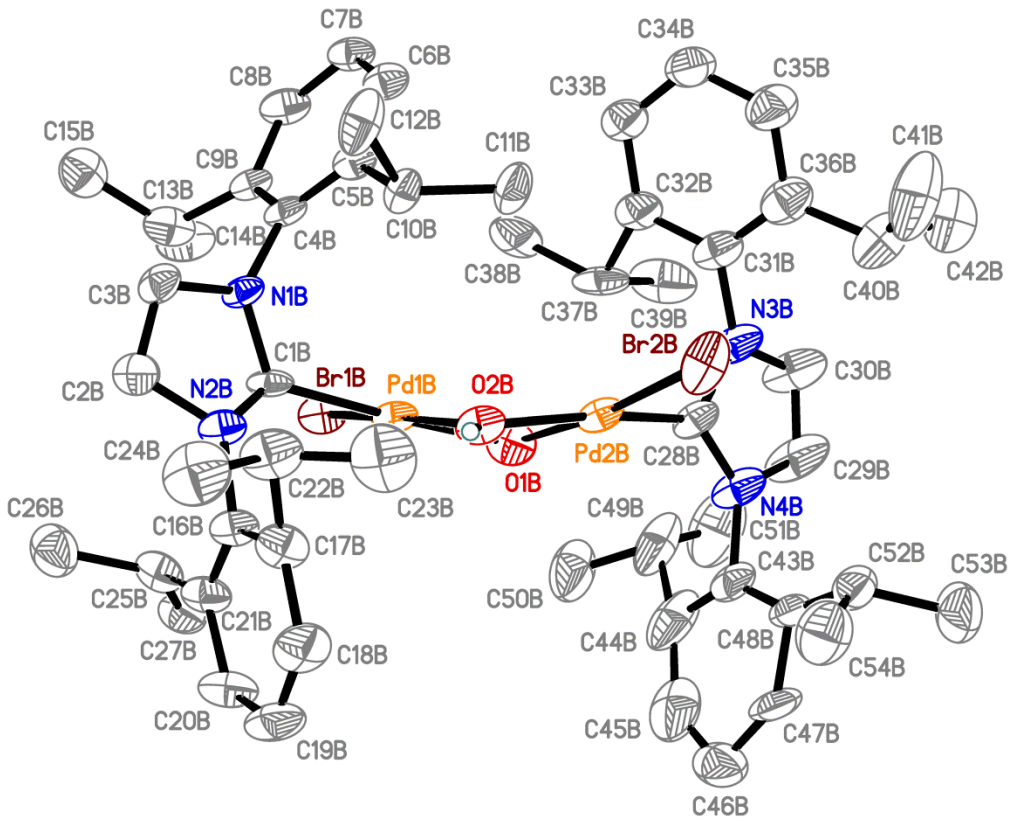


Figure S43. The structure of the minor component of disorder **B**. Hydrogen atoms (but hydroxy) are omitted. Thermal ellipsoids are set to a 50% probability level.

Table S15. Selected bond distances for **3b** (Å).

Atoms	Distance	Atoms	Distance	Atoms	Distance
Pd(1A)-C(1A)	1.956(4)	C(9A)-C(13A)	1.535(7)	C(31A)-C(36A)	1.390(4)
Pd(1A)-O(2A)	2.035(4)	C(10A)-C(11A)	1.528(5)	C(31A)-C(32A)	1.393(4)
Pd(1A)-O(1A)	2.045(5)	C(10A)-C(12A)	1.529(5)	C(32A)-C(33A)	1.391(4)
Pd(1A)-Br(1A)	2.4022(8)	C(13A)-C(15A)	1.520(6)	C(32A)-C(37A)	1.526(8)
Pd(2A)-C(28A)	1.951(6)	C(13A)-C(14A)	1.521(6)	C(33A)-C(34A)	1.389(4)
Pd(2A)-O(1A)	2.038(5)	C(16A)-C(21A)	1.393(3)	C(34A)-C(35A)	1.390(4)
Pd(2A)-O(2A)	2.059(4)	C(16A)-C(17A)	1.394(3)	C(35A)-C(36A)	1.390(4)
Pd(2A)-Br(2A)	2.3926(14)	C(17A)-C(18A)	1.395(3)	C(36A)-C(40A)	1.527(10)
O(1A)-H(1C)	0.8500	C(17A)-C(22A)	1.538(9)	C(37A)-C(38A)	1.532(7)
O(2A)-H(2C)	0.8500	C(18A)-C(19A)	1.392(4)	C(37A)-C(39A)	1.532(6)
N(1A)-C(1A)	1.363(6)	C(19A)-C(20A)	1.391(4)	C(40A)-C(41A)	1.541(11)
N(1A)-C(3A)	1.385(6)	C(20A)-C(21A)	1.394(3)	C(40A)-C(42A)	1.542(10)
N(1A)-C(4A)	1.448(5)	C(21A)-C(25A)	1.510(7)	C(43A)-C(44A)	1.388(4)
C(1A)-N(2A)	1.369(6)	C(22A)-C(23A)	1.523(8)	C(43A)-C(48A)	1.388(4)
N(2A)-C(2A)	1.402(8)	C(22A)-C(24A)	1.525(8)	C(44A)-C(45A)	1.387(4)
N(2A)-C(16A)	1.446(5)	C(25A)-C(26A)	1.540(6)	C(44A)-C(49A)	1.580(12)

C(2A)-C(3A)	1.362(7)	C(25A)-C(27A)	1.541(6)	C(45A)-C(46A)	1.386(4)
C(4A)-C(5A)	1.396(3)	N(3A)-C(28A)	1.336(9)	C(46A)-C(47A)	1.386(4)
C(4A)-C(9A)	1.398(3)	N(3A)-C(30A)	1.374(9)	C(47A)-C(48A)	1.387(4)
C(5A)-C(6A)	1.397(3)	N(3A)-C(31A)	1.462(7)	C(48A)-C(52A)	1.540(9)
C(5A)-C(10A)	1.528(6)	C(28A)-N(4A)	1.359(7)	C(49A)-C(51A)	1.507(10)
C(6A)-C(7A)	1.393(3)	N(4A)-C(29A)	1.396(9)	C(49A)-C(50A)	1.507(10)
C(7A)-C(8A)	1.392(3)	N(4A)-C(43A)	1.448(7)	C(52A)-C(54A)	1.520(7)
C(8A)-C(9A)	1.396(3)	C(29A)-C(30A)	1.345(11)	C(52A)-C(53A)	1.521(7)
Pd(1B)-C(1B)	1.956(6)	C(9B)-C(13B)	1.535(8)	C(31B)-C(36B)	1.390(4)
Pd(1B)-O(2B)	2.035(5)	C(10B)-C(11B)	1.529(6)	C(31B)-C(32B)	1.391(4)
Pd(1B)-O(1B)	2.045(6)	C(10B)-C(12B)	1.529(6)	C(32B)-C(33B)	1.390(4)
Pd(1B)-Br(1B)	2.393(3)	C(13B)-C(14B)	1.520(7)	C(32B)-C(37B)	1.525(9)
Pd(2B)-C(28B)	1.952(7)	C(13B)-C(15B)	1.520(7)	C(33B)-C(34B)	1.390(4)
Pd(2B)-O(1B)	2.037(5)	C(16B)-C(17B)	1.392(4)	C(34B)-C(35B)	1.390(4)
Pd(2B)-O(2B)	2.060(5)	C(16B)-C(21B)	1.393(4)	C(35B)-C(36B)	1.390(4)
Pd(2B)-Br(2B)	2.358(3)	C(17B)-C(18B)	1.393(4)	C(36B)-C(40B)	1.528(11)
O(1B)-H(1D)	0.8500	C(17B)-C(22B)	1.537(10)	C(37B)-C(38B)	1.531(7)
O(2B)-H(2D)	0.8500	C(18B)-C(19B)	1.392(4)	C(37B)-C(39B)	1.532(7)
N(1B)-C(1B)	1.363(7)	C(19B)-C(20B)	1.392(4)	C(40B)-C(41B)	1.542(11)
N(1B)-C(3B)	1.385(7)	C(20B)-C(21B)	1.393(4)	C(40B)-C(42B)	1.542(11)
N(1B)-C(4B)	1.448(6)	C(21B)-C(25B)	1.511(8)	C(43B)-C(44B)	1.387(4)
C(1B)-N(2B)	1.368(7)	C(22B)-C(23B)	1.523(8)	C(43B)-C(48B)	1.388(4)
N(2B)-C(2B)	1.402(8)	C(22B)-C(24B)	1.524(8)	C(44B)-C(45B)	1.387(4)
N(2B)-C(16B)	1.445(6)	C(25B)-C(27B)	1.541(7)	C(44B)-C(49B)	1.580(12)
C(2B)-C(3B)	1.362(8)	C(25B)-C(26B)	1.542(7)	C(45B)-C(46B)	1.387(4)
C(4B)-C(5B)	1.395(4)	C(28B)-N(4B)	1.359(8)	C(46B)-C(47B)	1.387(4)
C(4B)-C(9B)	1.396(4)	C(28B)-N(3B)	1.42(2)	C(47B)-C(48B)	1.387(4)
C(5B)-C(6B)	1.396(4)	N(3B)-C(30B)	1.374(9)	C(48B)-C(52B)	1.540(9)
C(5B)-C(10B)	1.528(7)	N(3B)-C(31B)	1.463(8)	C(49B)-C(51B)	1.507(11)
C(6B)-C(7B)	1.394(4)	N(4B)-C(29B)	1.396(10)	C(49B)-C(50B)	1.508(11)
C(7B)-C(8B)	1.394(4)	N(4B)-C(43B)	1.447(8)	C(52B)-C(54B)	1.521(8)
C(8B)-C(9B)	1.395(4)	C(29B)-C(30B)	1.345(11)	C(52B)-C(53B)	1.521(8)

Table S16. Selected bond angles for **3b** (°).

Atoms	Angle	Atoms	Angle
C(1A)-Pd(1A)-O(2A)	93.0(4)	C(20A)-C(19A)-C(18A)	120.9(6)
C(1A)-Pd(1A)-O(1A)	171.8(4)	C(19A)-C(20A)-C(21A)	119.6(6)
O(2A)-Pd(1A)-O(1A)	79.3(4)	C(16A)-C(21A)-C(20A)	118.9(5)
C(1A)-Pd(1A)-Br(1A)	93.2(4)	C(16A)-C(21A)-C(25A)	121.4(6)
O(2A)-Pd(1A)-Br(1A)	172.93(16)	C(20A)-C(21A)-C(25A)	119.6(6)
O(1A)-Pd(1A)-Br(1A)	94.7(3)	C(23A)-C(22A)-C(24A)	108.2(8)
C(1A)-Pd(1A)-Pd(2A)	130.5(4)	C(23A)-C(22A)-C(17A)	119.6(8)
O(2A)-Pd(1A)-Pd(2A)	41.94(11)	C(24A)-C(22A)-C(17A)	108.2(12)
O(1A)-Pd(1A)-Pd(2A)	41.36(12)	C(21A)-C(25A)-C(26A)	106.5(6)
Br(1A)-Pd(1A)-Pd(2A)	133.49(5)	C(21A)-C(25A)-C(27A)	109.2(8)
C(28A)-Pd(2A)-O(1A)	99.5(4)	C(26A)-C(25A)-C(27A)	110.3(6)
C(28A)-Pd(2A)-O(2A)	176.3(3)	C(28A)-N(3A)-C(30A)	110.7(6)
O(1A)-Pd(2A)-O(2A)	78.9(3)	C(28A)-N(3A)-C(31A)	127.2(5)
C(28A)-Pd(2A)-Br(2A)	90.45(19)	C(30A)-N(3A)-C(31A)	121.6(5)
O(1A)-Pd(2A)-Br(2A)	168.2(7)	N(3A)-C(28A)-N(4A)	106.1(5)
O(2A)-Pd(2A)-Br(2A)	91.51(11)	N(3A)-C(28A)-Pd(2A)	129.0(5)
C(28A)-Pd(2A)-Pd(1A)	135.9(2)	N(4A)-C(28A)-Pd(2A)	125.0(5)
O(1A)-Pd(2A)-Pd(1A)	41.55(14)	C(28A)-N(4A)-C(29A)	109.3(6)
O(2A)-Pd(2A)-Pd(1A)	41.34(11)	C(28A)-N(4A)-C(43A)	128.8(7)
Br(2A)-Pd(2A)-Pd(1A)	131.23(6)	C(29A)-N(4A)-C(43A)	121.9(7)
Pd(2A)-O(1A)-Pd(1A)	97.09(15)	C(30A)-C(29A)-N(4A)	106.6(6)
Pd(1A)-O(2A)-Pd(2A)	96.72(15)	C(29A)-C(30A)-N(3A)	107.3(6)
C(1A)-N(1A)-C(3A)	111.5(10)	C(36A)-C(31A)-C(32A)	123.8(6)
C(1A)-N(1A)-C(4A)	122.8(7)	C(36A)-C(31A)-N(3A)	118.4(5)
C(3A)-N(1A)-C(4A)	125.4(10)	C(32A)-C(31A)-N(3A)	117.2(6)
N(1A)-C(1A)-N(2A)	103.8(6)	C(33A)-C(32A)-C(31A)	116.8(7)
N(1A)-C(1A)-Pd(1A)	129.7(6)	C(33A)-C(32A)-C(37A)	114.7(6)
N(2A)-C(1A)-Pd(1A)	125.7(6)	C(31A)-C(32A)-C(37A)	128.4(7)
C(1A)-N(2A)-C(2A)	111.3(10)	C(34A)-C(33A)-C(32A)	121.1(8)
C(1A)-N(2A)-C(16A)	124.5(9)	C(33A)-C(34A)-C(35A)	120.3(7)
C(2A)-N(2A)-C(16A)	123.4(11)	C(34A)-C(35A)-C(36A)	120.4(6)
C(3A)-C(2A)-N(2A)	105.6(13)	C(35A)-C(36A)-C(31A)	117.6(6)
C(2A)-C(3A)-N(1A)	107.2(13)	C(35A)-C(36A)-C(40A)	118.4(6)
C(5A)-C(4A)-C(9A)	122.7(9)	C(31A)-C(36A)-C(40A)	124.1(6)
C(5A)-C(4A)-N(1A)	117.9(10)	C(32A)-C(37A)-C(38A)	116.5(7)
C(9A)-C(4A)-N(1A)	119.3(10)	C(32A)-C(37A)-C(39A)	111.6(7)
C(4A)-C(5A)-C(6A)	118.4(9)	C(38A)-C(37A)-C(39A)	109.9(8)
C(4A)-C(5A)-C(10A)	120.9(10)	C(36A)-C(40A)-C(41A)	110.5(16)

C(6A)-C(5A)-C(10A)	120.5(11)	C(36A)-C(40A)-C(42A)	110.7(7)
C(7A)-C(6A)-C(5A)	119.8(9)	C(41A)-C(40A)-C(42A)	111.1(10)
C(8A)-C(7A)-C(6A)	120.7(10)	C(44A)-C(43A)-C(48A)	117.8(7)
C(7A)-C(8A)-C(9A)	120.7(9)	C(44A)-C(43A)-N(4A)	123.3(8)
C(8A)-C(9A)-C(4A)	117.6(9)	C(48A)-C(43A)-N(4A)	118.4(8)
C(8A)-C(9A)-C(13A)	119.3(8)	C(45A)-C(44A)-C(43A)	122.9(8)
C(4A)-C(9A)-C(13A)	123.1(9)	C(45A)-C(44A)-C(49A)	107.3(9)
C(5A)-C(10A)-C(11A)	111.7(13)	C(43A)-C(44A)-C(49A)	129.6(9)
C(5A)-C(10A)-C(12A)	111.5(11)	C(46A)-C(45A)-C(44A)	116.3(9)
C(11A)-C(10A)-C(12A)	110.9(8)	C(45A)-C(46A)-C(47A)	123.6(9)
C(15A)-C(13A)-C(14A)	110.6(7)	C(46A)-C(47A)-C(48A)	117.3(8)
C(15A)-C(13A)-C(9A)	108.9(8)	C(47A)-C(48A)-C(43A)	121.9(7)
C(14A)-C(13A)-C(9A)	112.0(9)	C(47A)-C(48A)-C(52A)	122.5(8)
C(21A)-C(16A)-C(17A)	122.2(5)	C(43A)-C(48A)-C(52A)	115.3(7)
C(21A)-C(16A)-N(2A)	119.4(5)	C(51A)-C(49A)-C(50A)	109.9(11)
C(17A)-C(16A)-N(2A)	118.3(5)	C(51A)-C(49A)-C(44A)	107.5(8)
C(16A)-C(17A)-C(18A)	118.0(6)	C(50A)-C(49A)-C(44A)	117.8(9)
C(16A)-C(17A)-C(22A)	125.5(6)	C(54A)-C(52A)-C(53A)	109.5(8)
C(18A)-C(17A)-C(22A)	116.4(5)	C(54A)-C(52A)-C(48A)	111.4(8)
C(19A)-C(18A)-C(17A)	120.4(6)	C(53A)-C(52A)-C(48A)	109.2(8)
C(1B)-Pd(1B)-O(2B)	106.4(13)	C(20B)-C(19B)-C(18B)	116.4(19)
C(1B)-Pd(1B)-O(1B)	170.2(18)	C(19B)-C(20B)-C(21B)	125.5(18)
O(2B)-Pd(1B)-O(1B)	82.9(7)	C(16B)-C(21B)-C(20B)	112.7(16)
C(1B)-Pd(1B)-Br(1B)	82.7(13)	C(16B)-C(21B)-C(25B)	126.0(19)
O(2B)-Pd(1B)-Br(1B)	170.9(3)	C(20B)-C(21B)-C(25B)	121.3(19)
O(1B)-Pd(1B)-Br(1B)	88.0(6)	C(23B)-C(22B)-C(24B)	108(2)
C(1B)-Pd(1B)-Pd(2B)	145.8(13)	C(23B)-C(22B)-C(17B)	95(3)
O(2B)-Pd(1B)-Pd(2B)	42.78(16)	C(24B)-C(22B)-C(17B)	113(4)
O(1B)-Pd(1B)-Pd(2B)	42.18(16)	C(21B)-C(25B)-C(27B)	126(3)
Br(1B)-Pd(1B)-Pd(2B)	128.49(16)	C(21B)-C(25B)-C(26B)	119(2)
C(28B)-Pd(2B)-O(1B)	88.1(9)	C(27B)-C(25B)-C(26B)	107.0(16)
C(28B)-Pd(2B)-O(2B)	169.8(8)	N(4B)-C(28B)-N(3B)	102.1(10)
O(1B)-Pd(2B)-O(2B)	82.5(8)	N(4B)-C(28B)-Pd(2B)	132.4(12)
C(28B)-Pd(2B)-Br(2B)	94.3(7)	N(3B)-C(28B)-Pd(2B)	125.5(12)
O(1B)-Pd(2B)-Br(2B)	174(2)	C(30B)-N(3B)-C(28B)	111.2(9)
O(2B)-Pd(2B)-Br(2B)	95.4(3)	C(30B)-N(3B)-C(31B)	123.7(12)
C(28B)-Pd(2B)-Pd(1B)	129.6(7)	C(28B)-N(3B)-C(31B)	125.1(11)
O(1B)-Pd(2B)-Pd(1B)	42.38(18)	C(28B)-N(4B)-C(29B)	112.3(11)
O(2B)-Pd(2B)-Pd(1B)	42.14(16)	C(28B)-N(4B)-C(43B)	125.3(18)
Br(2B)-Pd(2B)-Pd(1B)	133.90(19)	C(29B)-N(4B)-C(43B)	121.9(18)

Pd(2B)-O(1B)-Pd(1B)	95.4(2)	C(30B)-C(29B)-N(4B)	107.1(11)
Pd(1B)-O(2B)-Pd(2B)	95.1(2)	C(29B)-C(30B)-N(3B)	107.3(7)
C(1B)-N(1B)-C(3B)	107(3)	C(36B)-C(31B)-C(32B)	121.5(14)
C(1B)-N(1B)-C(4B)	132(2)	C(36B)-C(31B)-N(3B)	117.1(14)
C(3B)-N(1B)-C(4B)	121(3)	C(32B)-C(31B)-N(3B)	121.3(16)
N(1B)-C(1B)-N(2B)	107.2(19)	C(33B)-C(32B)-C(31B)	119.8(18)
N(1B)-C(1B)-Pd(1B)	120.1(18)	C(33B)-C(32B)-C(37B)	136.5(16)
N(2B)-C(1B)-Pd(1B)	124(2)	C(31B)-C(32B)-C(37B)	101.9(18)
C(1B)-N(2B)-C(2B)	104(3)	C(34B)-C(33B)-C(32B)	120(2)
C(1B)-N(2B)-C(16B)	126(3)	C(33B)-C(34B)-C(35B)	120(2)
C(2B)-N(2B)-C(16B)	125(3)	C(36B)-C(35B)-C(34B)	121.7(16)
C(3B)-C(2B)-N(2B)	106(4)	C(35B)-C(36B)-C(31B)	117.7(13)
C(2B)-C(3B)-N(1B)	107(4)	C(35B)-C(36B)-C(40B)	118.1(15)
C(5B)-C(4B)-C(9B)	123(2)	C(31B)-C(36B)-C(40B)	124.2(15)
C(5B)-C(4B)-N(1B)	119(3)	C(32B)-C(37B)-C(38B)	98(2)
C(9B)-C(4B)-N(1B)	118(3)	C(32B)-C(37B)-C(39B)	104(2)
C(4B)-C(5B)-C(6B)	117(3)	C(38B)-C(37B)-C(39B)	113.7(19)
C(4B)-C(5B)-C(10B)	125(3)	C(36B)-C(40B)-C(41B)	109(5)
C(6B)-C(5B)-C(10B)	118(3)	C(36B)-C(40B)-C(42B)	110.9(17)
C(7B)-C(6B)-C(5B)	123(3)	C(41B)-C(40B)-C(42B)	110(2)
C(8B)-C(7B)-C(6B)	117(3)	C(44B)-C(43B)-C(48B)	138.0(17)
C(7B)-C(8B)-C(9B)	123(3)	C(44B)-C(43B)-N(4B)	107(2)
C(8B)-C(9B)-C(4B)	117(3)	C(48B)-C(43B)-N(4B)	115(2)
C(8B)-C(9B)-C(13B)	119(3)	C(45B)-C(44B)-C(43B)	102.3(19)
C(4B)-C(9B)-C(13B)	123(3)	C(45B)-C(44B)-C(49B)	152(2)
C(5B)-C(10B)-C(11B)	115(4)	C(43B)-C(44B)-C(49B)	104(2)
C(5B)-C(10B)-C(12B)	106(3)	C(46B)-C(45B)-C(44B)	137(2)
C(11B)-C(10B)-C(12B)	111(2)	C(47B)-C(46B)-C(45B)	104(2)
C(14B)-C(13B)-C(15B)	110.8(18)	C(46B)-C(47B)-C(48B)	136(2)
C(14B)-C(13B)-C(9B)	112(3)	C(47B)-C(48B)-C(43B)	102.9(18)
C(15B)-C(13B)-C(9B)	113(3)	C(47B)-C(48B)-C(52B)	107(2)
C(17B)-C(16B)-C(21B)	127.3(16)	C(43B)-C(48B)-C(52B)	149(2)
C(17B)-C(16B)-N(2B)	115.8(18)	C(51B)-C(49B)-C(50B)	110(2)
C(21B)-C(16B)-N(2B)	116.7(19)	C(51B)-C(49B)-C(44B)	122(3)
C(16B)-C(17B)-C(18B)	114.8(17)	C(50B)-C(49B)-C(44B)	100(2)
C(16B)-C(17B)-C(22B)	110.6(18)	C(54B)-C(52B)-C(53B)	109(2)
C(18B)-C(17B)-C(22B)	131.1(18)	C(54B)-C(52B)-C(48B)	114(2)
C(19B)-C(18B)-C(17B)	123.4(19)	C(53B)-C(52B)-C(48B)	112(2)

Table S17. Torsion angles for **3b** (°).

Atoms	Angle	Atoms	Angle
C(3A)-N(1A)-C(1A)-N(2A)	4.8(19)	C(30A)-N(3A)-C(28A)-N(4A)	1.4(9)
C(4A)-N(1A)-C(1A)-N(2A)	179.0(13)	C(31A)-N(3A)-C(28A)-N(4A)	173.7(7)
C(3A)-N(1A)-C(1A)-Pd(1A)	174.7(14)	C(30A)-N(3A)-C(28A)-Pd(2A)	-179.1(6)
C(4A)-N(1A)-C(1A)-Pd(1A)	-11(2)	C(31A)-N(3A)-C(28A)-Pd(2A)	-6.8(11)
N(1A)-C(1A)-N(2A)-C(2A)	-7.8(18)	N(3A)-C(28A)-N(4A)-C(29A)	0.0(9)
Pd(1A)-C(1A)-N(2A)-C(2A)	-178.2(15)	Pd(2A)-C(28A)-N(4A)-C(29A)	-179.6(7)
N(1A)-C(1A)-N(2A)-C(16A)	-177.9(10)	N(3A)-C(28A)-N(4A)-C(43A)	176.5(8)
Pd(1A)-C(1A)-N(2A)-C(16A)	11.7(15)	Pd(2A)-C(28A)-N(4A)-C(43A)	-3.0(12)
C(1A)-N(2A)-C(2A)-C(3A)	8(2)	C(28A)-N(4A)-C(29A)-C(30A)	-1.4(11)
C(16A)-N(2A)-C(2A)-C(3A)	178.1(14)	C(43A)-N(4A)-C(29A)-C(30A)	-178.2(9)
N(2A)-C(2A)-C(3A)-N(1A)	-5(3)	N(4A)-C(29A)-C(30A)-N(3A)	2.2(12)
C(1A)-N(1A)-C(3A)-C(2A)	0(3)	C(28A)-N(3A)-C(30A)-C(29A)	-2.3(12)
C(4A)-N(1A)-C(3A)-C(2A)	-174.1(19)	C(31A)-N(3A)-C(30A)-C(29A)	-175.1(8)
C(1A)-N(1A)-C(4A)-C(5A)	-65.5(17)	C(28A)-N(3A)-C(31A)-C(36A)	107.6(8)
C(3A)-N(1A)-C(4A)-C(5A)	107.8(18)	C(30A)-N(3A)-C(31A)-C(36A)	-80.9(9)
C(1A)-N(1A)-C(4A)-C(9A)	111.9(15)	C(28A)-N(3A)-C(31A)-C(32A)	-80.3(8)
C(3A)-N(1A)-C(4A)-C(9A)	-75(2)	C(30A)-N(3A)-C(31A)-C(32A)	91.2(9)
C(9A)-C(4A)-C(5A)-C(6A)	-0.2(3)	C(36A)-C(31A)-C(32A)-C(33A)	0.3(3)
N(1A)-C(4A)-C(5A)-C(6A)	177.1(8)	N(3A)-C(31A)-C(32A)-C(33A)	-171.3(5)
C(9A)-C(4A)-C(5A)-C(10A)	174.7(10)	C(36A)-C(31A)-C(32A)-C(37A)	-174.8(8)
N(1A)-C(4A)-C(5A)-C(10A)	-8.0(9)	N(3A)-C(31A)-C(32A)-C(37A)	13.6(9)
C(4A)-C(5A)-C(6A)-C(7A)	-0.3(3)	C(31A)-C(32A)-C(33A)-C(34A)	0.1(3)
C(10A)-C(5A)-C(6A)-C(7A)	-175.3(10)	C(37A)-C(32A)-C(33A)-C(34A)	175.9(8)
C(5A)-C(6A)-C(7A)-C(8A)	0.9(5)	C(32A)-C(33A)-C(34A)-C(35A)	-0.2(6)
C(6A)-C(7A)-C(8A)-C(9A)	-0.9(7)	C(33A)-C(34A)-C(35A)-C(36A)	-0.1(8)
C(7A)-C(8A)-C(9A)-C(4A)	0.3(7)	C(34A)-C(35A)-C(36A)-C(31A)	0.5(7)
C(7A)-C(8A)-C(9A)-C(13A)	178.1(7)	C(34A)-C(35A)-C(36A)-C(40A)	-179.1(7)
C(5A)-C(4A)-C(9A)-C(8A)	0.2(5)	C(32A)-C(31A)-C(36A)-C(35A)	-0.6(6)
N(1A)-C(4A)-C(9A)-C(8A)	-177.1(8)	N(3A)-C(31A)-C(36A)-C(35A)	170.9(5)
C(5A)-C(4A)-C(9A)-C(13A)	-177.4(6)	C(32A)-C(31A)-C(36A)-C(40A)	179.0(7)
N(1A)-C(4A)-C(9A)-C(13A)	5.3(9)	N(3A)-C(31A)-C(36A)-C(40A)	-9.5(8)
C(4A)-C(5A)-C(10A)-C(11A)	152.9(9)	C(33A)-C(32A)-C(37A)-C(38A)	-48.1(6)
C(6A)-C(5A)-C(10A)-C(11A)	-32.3(14)	C(31A)-C(32A)-C(37A)-C(38A)	127.1(7)
C(4A)-C(5A)-C(10A)-C(12A)	-82.3(14)	C(33A)-C(32A)-C(37A)-C(39A)	79.2(7)
C(6A)-C(5A)-C(10A)-C(12A)	92.5(13)	C(31A)-C(32A)-C(37A)-C(39A)	-105.7(9)
C(8A)-C(9A)-C(13A)-C(15A)	-79.6(10)	C(35A)-C(36A)-C(40A)-C(41A)	-73.1(14)
C(4A)-C(9A)-C(13A)-C(15A)	98.0(9)	C(31A)-C(36A)-C(40A)-C(41A)	107.3(14)
C(8A)-C(9A)-C(13A)-C(14A)	43.1(9)	C(35A)-C(36A)-C(40A)-C(42A)	50.4(10)

C(4A)-C(9A)-C(13A)-C(14A)	-139.3(7)	C(31A)-C(36A)-C(40A)-C(42A)	-129.3(8)
C(1A)-N(2A)-C(16A)-C(21A)	-88.4(11)	C(28A)-N(4A)-C(43A)-C(44A)	87.6(10)
C(2A)-N(2A)-C(16A)-C(21A)	102.7(16)	C(29A)-N(4A)-C(43A)-C(44A)	-96.3(11)
C(1A)-N(2A)-C(16A)-C(17A)	95.5(9)	C(28A)-N(4A)-C(43A)-C(48A)	-100.8(10)
C(2A)-N(2A)-C(16A)-C(17A)	-73.4(16)	C(29A)-N(4A)-C(43A)-C(48A)	75.3(10)
C(21A)-C(16A)-C(17A)-C(18A)	0.0(3)	C(48A)-C(43A)-C(44A)-C(45A)	-0.06(19)
N(2A)-C(16A)-C(17A)-C(18A)	176.0(8)	N(4A)-C(43A)-C(44A)-C(45A)	171.6(10)
C(21A)-C(16A)-C(17A)-C(22A)	176.3(9)	C(48A)-C(43A)-C(44A)-C(49A)	174.8(11)
N(2A)-C(16A)-C(17A)-C(22A)	-7.7(10)	N(4A)-C(43A)-C(44A)-C(49A)	-13.5(11)
C(16A)-C(17A)-C(18A)-C(19A)	0.0(3)	C(43A)-C(44A)-C(45A)-C(46A)	-0.2(2)
C(22A)-C(17A)-C(18A)-C(19A)	-176.7(8)	C(49A)-C(44A)-C(45A)-C(46A)	-176.1(9)
C(17A)-C(18A)-C(19A)-C(20A)	0.1(6)	C(44A)-C(45A)-C(46A)-C(47A)	0.6(5)
C(18A)-C(19A)-C(20A)-C(21A)	0.0(8)	C(45A)-C(46A)-C(47A)-C(48A)	-0.6(6)
C(17A)-C(16A)-C(21A)-C(20A)	0.1(6)	C(46A)-C(47A)-C(48A)-C(43A)	0.3(6)
N(2A)-C(16A)-C(21A)-C(20A)	-175.9(9)	C(46A)-C(47A)-C(48A)-C(52A)	-173.1(10)
C(17A)-C(16A)-C(21A)-C(25A)	176.6(8)	C(44A)-C(43A)-C(48A)-C(47A)	0.0(4)
N(2A)-C(16A)-C(21A)-C(25A)	0.6(10)	N(4A)-C(43A)-C(48A)-C(47A)	-172.1(10)
C(19A)-C(20A)-C(21A)-C(16A)	-0.1(7)	C(44A)-C(43A)-C(48A)-C(52A)	173.9(9)
C(19A)-C(20A)-C(21A)-C(25A)	-176.6(8)	N(4A)-C(43A)-C(48A)-C(52A)	1.8(9)
C(16A)-C(17A)-C(22A)-C(23A)	-131.7(9)	C(45A)-C(44A)-C(49A)-C(51A)	-75.4(12)
C(18A)-C(17A)-C(22A)-C(23A)	44.7(10)	C(43A)-C(44A)-C(49A)-C(51A)	109.1(12)
C(16A)-C(17A)-C(22A)-C(24A)	104.0(11)	C(45A)-C(44A)-C(49A)-C(50A)	49.4(10)
C(18A)-C(17A)-C(22A)-C(24A)	-79.7(10)	C(43A)-C(44A)-C(49A)-C(50A)	-126.1(10)
C(16A)-C(21A)-C(25A)-C(26A)	-103.8(8)	C(47A)-C(48A)-C(52A)-C(54A)	-53.7(10)
C(20A)-C(21A)-C(25A)-C(26A)	72.6(9)	C(43A)-C(48A)-C(52A)-C(54A)	132.4(8)
C(16A)-C(21A)-C(25A)-C(27A)	137.1(7)	C(47A)-C(48A)-C(52A)-C(53A)	67.3(10)
C(20A)-C(21A)-C(25A)-C(27A)	-46.5(9)	C(43A)-C(48A)-C(52A)-C(53A)	-106.5(8)
C(3B)-N(1B)-C(1B)-N(2B)	-17(6)	N(4B)-C(28B)-N(3B)-C(30B)	2(3)
C(4B)-N(1B)-C(1B)-N(2B)	161(5)	Pd(2B)-C(28B)-N(3B)-C(30B)	-179.8(19)
C(3B)-N(1B)-C(1B)-Pd(1B)	-165(4)	N(4B)-C(28B)-N(3B)-C(31B)	-176(2)
C(4B)-N(1B)-C(1B)-Pd(1B)	13(8)	Pd(2B)-C(28B)-N(3B)-C(31B)	3(3)
N(1B)-C(1B)-N(2B)-C(2B)	28(5)	N(3B)-C(28B)-N(4B)-C(29B)	-2(3)
Pd(1B)-C(1B)-N(2B)-C(2B)	175(4)	Pd(2B)-C(28B)-N(4B)-C(29B)	180(2)
N(1B)-C(1B)-N(2B)-C(16B)	-176(3)	N(3B)-C(28B)-N(4B)-C(43B)	170(3)
Pd(1B)-C(1B)-N(2B)-C(16B)	-29(5)	Pd(2B)-C(28B)-N(4B)-C(43B)	-9(4)
C(1B)-N(2B)-C(2B)-C(3B)	-29(7)	C(28B)-N(4B)-C(29B)-C(30B)	1(4)
C(16B)-N(2B)-C(2B)-C(3B)	174(4)	C(43B)-N(4B)-C(29B)-C(30B)	-171(3)
N(2B)-C(2B)-C(3B)-N(1B)	19(8)	N(4B)-C(29B)-C(30B)-N(3B)	0(4)
C(1B)-N(1B)-C(3B)-C(2B)	-2(8)	C(28B)-N(3B)-C(30B)-C(29B)	-1(3)
C(4B)-N(1B)-C(3B)-C(2B)	-179(6)	C(31B)-N(3B)-C(30B)-C(29B)	176(2)

C(1B)-N(1B)-C(4B)-C(5B)	-85(6)	C(30B)-N(3B)-C(31B)-C(36B)	-69(2)
C(3B)-N(1B)-C(4B)-C(5B)	92(5)	C(28B)-N(3B)-C(31B)-C(36B)	107(2)
C(1B)-N(1B)-C(4B)-C(9B)	100(6)	C(30B)-N(3B)-C(31B)-C(32B)	109(2)
C(3B)-N(1B)-C(4B)-C(9B)	-83(6)	C(28B)-N(3B)-C(31B)-C(32B)	-74(2)
C(9B)-C(4B)-C(5B)-C(6B)	0.0(3)	C(36B)-C(31B)-C(32B)-C(33B)	0.0(3)
N(1B)-C(4B)-C(5B)-C(6B)	-174(2)	N(3B)-C(31B)-C(32B)-C(33B)	-178.5(14)
C(9B)-C(4B)-C(5B)-C(10B)	-177(3)	C(36B)-C(31B)-C(32B)-C(37B)	167.3(16)
N(1B)-C(4B)-C(5B)-C(10B)	8(3)	N(3B)-C(31B)-C(32B)-C(37B)	-11.1(19)
C(4B)-C(5B)-C(6B)-C(7B)	0.0(3)	C(31B)-C(32B)-C(33B)-C(34B)	0.1(3)
C(10B)-C(5B)-C(6B)-C(7B)	178(3)	C(37B)-C(32B)-C(33B)-C(34B)	-162(2)
C(5B)-C(6B)-C(7B)-C(8B)	0.0(7)	C(32B)-C(33B)-C(34B)-C(35B)	-0.1(7)
C(6B)-C(7B)-C(8B)-C(9B)	0.0(9)	C(33B)-C(34B)-C(35B)-C(36B)	0.2(10)
C(7B)-C(8B)-C(9B)-C(4B)	0.0(9)	C(34B)-C(35B)-C(36B)-C(31B)	-0.2(9)
C(7B)-C(8B)-C(9B)-C(13B)	170(2)	C(34B)-C(35B)-C(36B)-C(40B)	178.2(18)
C(5B)-C(4B)-C(9B)-C(8B)	0.0(7)	C(32B)-C(31B)-C(36B)-C(35B)	0.1(7)
N(1B)-C(4B)-C(9B)-C(8B)	174(2)	N(3B)-C(31B)-C(36B)-C(35B)	178.6(13)
C(5B)-C(4B)-C(9B)-C(13B)	-169(2)	C(32B)-C(31B)-C(36B)-C(40B)	-178.2(19)
N(1B)-C(4B)-C(9B)-C(13B)	5(3)	N(3B)-C(31B)-C(36B)-C(40B)	0.4(18)
C(4B)-C(5B)-C(10B)-C(11B)	131(3)	C(33B)-C(32B)-C(37B)-C(38B)	-21(2)
C(6B)-C(5B)-C(10B)-C(11B)	-46(4)	C(31B)-C(32B)-C(37B)-C(38B)	175.1(15)
C(4B)-C(5B)-C(10B)-C(12B)	-105(4)	C(33B)-C(32B)-C(37B)-C(39B)	96(2)
C(6B)-C(5B)-C(10B)-C(12B)	77(4)	C(31B)-C(32B)-C(37B)-C(39B)	-68(2)
C(8B)-C(9B)-C(13B)-C(14B)	54(3)	C(35B)-C(36B)-C(40B)-C(41B)	40(4)
C(4B)-C(9B)-C(13B)-C(14B)	-137(2)	C(31B)-C(36B)-C(40B)-C(41B)	-142(4)
C(8B)-C(9B)-C(13B)-C(15B)	-72(3)	C(35B)-C(36B)-C(40B)-C(42B)	-81(2)
C(4B)-C(9B)-C(13B)-C(15B)	97(3)	C(31B)-C(36B)-C(40B)-C(42B)	97(2)
C(1B)-N(2B)-C(16B)-C(17B)	108(3)	C(28B)-N(4B)-C(43B)-C(44B)	100(3)
C(2B)-N(2B)-C(16B)-C(17B)	-100(5)	C(29B)-N(4B)-C(43B)-C(44B)	-89(3)
C(1B)-N(2B)-C(16B)-C(21B)	-67(4)	C(28B)-N(4B)-C(43B)-C(48B)	-81(3)
C(2B)-N(2B)-C(16B)-C(21B)	85(5)	C(29B)-N(4B)-C(43B)-C(48B)	90(3)
C(21B)-C(16B)-C(17B)-C(18B)	0.0(3)	C(48B)-C(43B)-C(44B)-C(45B)	0.0(2)
N(2B)-C(16B)-C(17B)-C(18B)	-174(3)	N(4B)-C(43B)-C(44B)-C(45B)	178(2)
C(21B)-C(16B)-C(17B)-C(22B)	-161(2)	C(48B)-C(43B)-C(44B)-C(49B)	-169(2)
N(2B)-C(16B)-C(17B)-C(22B)	24(3)	N(4B)-C(43B)-C(44B)-C(49B)	9.3(19)
C(16B)-C(17B)-C(18B)-C(19B)	0.0(3)	C(43B)-C(44B)-C(45B)-C(46B)	0.0(2)
C(22B)-C(17B)-C(18B)-C(19B)	156(3)	C(49B)-C(44B)-C(45B)-C(46B)	157(5)
C(17B)-C(18B)-C(19B)-C(20B)	-0.1(7)	C(44B)-C(45B)-C(46B)-C(47B)	0.1(4)
C(18B)-C(19B)-C(20B)-C(21B)	0.1(9)	C(45B)-C(46B)-C(47B)-C(48B)	-0.1(6)
C(17B)-C(16B)-C(21B)-C(20B)	0.1(7)	C(46B)-C(47B)-C(48B)-C(43B)	0.0(6)
N(2B)-C(16B)-C(21B)-C(20B)	174(3)	C(46B)-C(47B)-C(48B)-C(52B)	171(2)

C(17B)-C(16B)-C(21B)-C(25B)	180(3)	C(44B)-C(43B)-C(48B)-C(47B)	0.0(4)
N(2B)-C(16B)-C(21B)-C(25B)	-6(3)	N(4B)-C(43B)-C(48B)-C(47B)	-178(3)
C(19B)-C(20B)-C(21B)-C(16B)	-0.2(9)	C(44B)-C(43B)-C(48B)-C(52B)	-164(5)
C(19B)-C(20B)-C(21B)-C(25B)	180(3)	N(4B)-C(43B)-C(48B)-C(52B)	18(4)
C(16B)-C(17B)-C(22B)-C(23B)	-139(2)	C(45B)-C(44B)-C(49B)-C(51B)	-74(5)
C(18B)-C(17B)-C(22B)-C(23B)	64(3)	C(43B)-C(44B)-C(49B)-C(51B)	83(3)
C(16B)-C(17B)-C(22B)-C(24B)	108(3)	C(45B)-C(44B)-C(49B)-C(50B)	47(5)
C(18B)-C(17B)-C(22B)-C(24B)	-49(4)	C(43B)-C(44B)-C(49B)-C(50B)	-156.0(19)
C(16B)-C(21B)-C(25B)-C(27B)	138(3)	C(47B)-C(48B)-C(52B)-C(54B)	-45(3)
C(20B)-C(21B)-C(25B)-C(27B)	-42(3)	C(43B)-C(48B)-C(52B)-C(54B)	118(4)
C(16B)-C(21B)-C(25B)-C(26B)	-78(3)	C(47B)-C(48B)-C(52B)-C(53B)	79(2)
C(20B)-C(21B)-C(25B)-C(26B)	102(3)	C(43B)-C(48B)-C(52B)-C(53B)	-117(4)

The structure of 3c

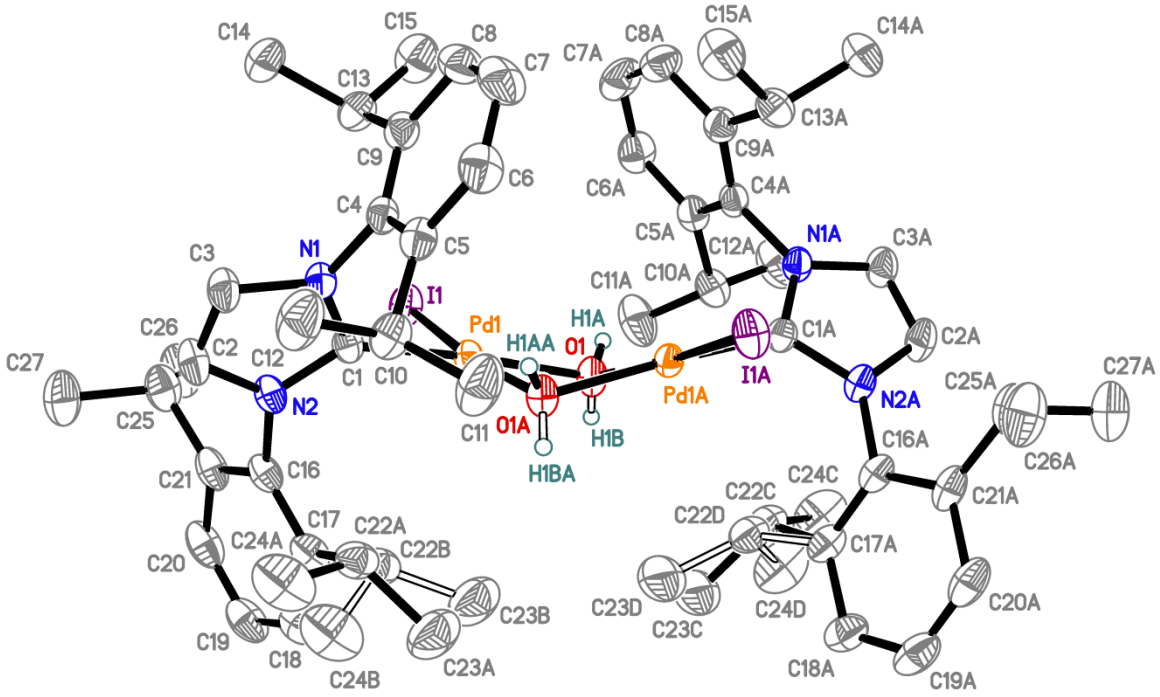


Figure S44. The molecular structure of **3c**. Hydrogen atoms (but hydroxy) are omitted. Atom H1 is disordered over two positions with a ratio of 0.74(5):0.26(5). Thermal ellipsoids are set to a 50% probability level. Symmetry transformation to generate equivalent atoms: -x+1, y, -z+3/2.

Table S18. Selected bond distances for **3c** (Å).

Atoms	Distance	Atoms	Distance	Atoms	Distance
I(1)-Pd(1)	2.5616(2)	C(4)-C(5)	1.406(3)	C(17)-C(18)	1.394(4)
Pd(1)-C(1)	1.960(2)	C(5)-C(6)	1.391(3)	C(17)-C(22A)	1.532(4)
Pd(1)-O(1)#1	2.0561(16)	C(5)-C(10)	1.525(4)	C(17)-C(22B)	1.533(4)
Pd(1)-O(1)	2.0681(16)	C(6)-C(7)	1.378(4)	C(18)-C(19)	1.384(4)
O(1)-H(1A)	0.80(2)	C(7)-C(8)	1.386(4)	C(19)-C(20)	1.375(4)
O(1)-H(1B)	0.82(3)	C(8)-C(9)	1.395(3)	C(20)-C(21)	1.397(4)
N(1)-C(1)	1.359(3)	C(9)-C(13)	1.519(3)	C(21)-C(25)	1.520(4)
N(1)-C(3)	1.392(3)	C(10)-C(11)	1.526(4)	C(22A)-C(24A)	1.529(6)
N(1)-C(4)	1.441(3)	C(10)-C(12)	1.533(4)	C(22A)-C(23A)	1.533(6)
C(1)-N(2)	1.364(3)	C(13)-C(15)	1.518(4)	C(22B)-C(24B)	1.529(6)
N(2)-C(2)	1.392(3)	C(13)-C(14)	1.536(3)	C(22B)-C(23B)	1.532(7)
N(2)-C(16)	1.441(3)	C(16)-C(17)	1.395(4)	C(25)-C(26)	1.533(4)
C(2)-C(3)	1.336(3)	C(16)-C(21)	1.406(3)	C(25)-C(27)	1.543(4)
C(4)-C(9)	1.392(3)				

Table S19. Selected bond angles for **3c** (°).

Atoms	Angle	Atoms	Angle
C(1)-Pd(1)-O(1)#1	97.05(7)	C(7)-C(8)-C(9)	120.7(3)
C(1)-Pd(1)-O(1)	175.65(8)	C(4)-C(9)-C(8)	116.8(2)
O(1)#1-Pd(1)-O(1)	79.55(7)	C(4)-C(9)-C(13)	121.2(2)
C(1)-Pd(1)-I(1)	90.93(6)	C(8)-C(9)-C(13)	121.9(2)
O(1)#1-Pd(1)-I(1)	171.49(5)	C(5)-C(10)-C(11)	113.4(2)
O(1)-Pd(1)-I(1)	92.61(5)	C(5)-C(10)-C(12)	110.8(2)
C(1)-Pd(1)-Pd(1)#1	135.92(6)	C(11)-C(10)-C(12)	108.3(2)
O(1)#1-Pd(1)-Pd(1)#1	42.16(4)	C(15)-C(13)-C(9)	113.6(2)
O(1)-Pd(1)-Pd(1)#1	41.86(4)	C(15)-C(13)-C(14)	110.6(2)
I(1)-Pd(1)-Pd(1)#1	129.334(9)	C(9)-C(13)-C(14)	108.4(2)
Pd(1)#1-O(1)-Pd(1)	95.98(7)	C(17)-C(16)-C(21)	122.9(2)
Pd(1)#1-O(1)-H(1A)	113(3)	C(17)-C(16)-N(2)	118.4(2)
Pd(1)-O(1)-H(1A)	113(3)	C(21)-C(16)-N(2)	118.6(2)
Pd(1)#1-O(1)-H(1B)	130(8)	C(18)-C(17)-C(16)	117.6(2)
Pd(1)-O(1)-H(1B)	113(8)	C(18)-C(17)-C(22A)	121.8(4)
C(1)-N(1)-C(3)	111.21(18)	C(16)-C(17)-C(22A)	119.7(3)
C(1)-N(1)-C(4)	125.79(17)	C(18)-C(17)-C(22B)	114.6(5)
C(3)-N(1)-C(4)	122.86(18)	C(16)-C(17)-C(22B)	127.6(5)
N(1)-C(1)-N(2)	104.31(18)	C(19)-C(18)-C(17)	121.0(3)
N(1)-C(1)-Pd(1)	126.57(15)	C(20)-C(19)-C(18)	119.9(3)
N(2)-C(1)-Pd(1)	129.12(16)	C(19)-C(20)-C(21)	122.0(2)

C(1)-N(2)-C(2)	110.47(19)	C(20)-C(21)-C(16)	116.5(2)
C(1)-N(2)-C(16)	126.73(19)	C(20)-C(21)-C(25)	119.6(2)
C(2)-N(2)-C(16)	122.41(19)	C(16)-C(21)-C(25)	123.9(2)
C(3)-C(2)-N(2)	107.5(2)	C(24A)-C(22A)-C(17)	111.9(4)
C(2)-C(3)-N(1)	106.5(2)	C(24A)-C(22A)-C(23A)	111.2(6)
C(9)-C(4)-C(5)	124.0(2)	C(17)-C(22A)-C(23A)	110.0(5)
C(9)-C(4)-N(1)	118.1(2)	C(24B)-C(22B)-C(23B)	111.4(8)
C(5)-C(4)-N(1)	117.8(2)	C(24B)-C(22B)-C(17)	107.9(6)
C(6)-C(5)-C(4)	116.4(2)	C(23B)-C(22B)-C(17)	116.4(6)
C(6)-C(5)-C(10)	120.7(2)	C(21)-C(25)-C(26)	111.8(2)
C(4)-C(5)-C(10)	122.9(2)	C(21)-C(25)-C(27)	110.9(2)
C(7)-C(6)-C(5)	121.2(2)	C(26)-C(25)-C(27)	108.8(2)
C(6)-C(7)-C(8)	120.8(2)		

Symmetry transformation to generate equivalent atoms: #1 -x+1, y, -z+3/2

Table S20. Torsion angles for **3c** (°).

Atoms	Angle	Atoms	Angle
C(3)-N(1)-C(1)-N(2)	-1.5(2)	C(8)-C(9)-C(13)-C(15)	36.8(3)
C(4)-N(1)-C(1)-N(2)	174.3(2)	C(4)-C(9)-C(13)-C(14)	89.3(3)
C(3)-N(1)-C(1)-Pd(1)	177.75(17)	C(8)-C(9)-C(13)-C(14)	-86.6(3)
C(4)-N(1)-C(1)-Pd(1)	-6.4(3)	C(1)-N(2)-C(16)-C(17)	64.1(3)
N(1)-C(1)-N(2)-C(2)	1.2(2)	C(2)-N(2)-C(16)-C(17)	-107.9(3)
Pd(1)-C(1)-N(2)-C(2)	-178.05(17)	C(1)-N(2)-C(16)-C(21)	-120.7(2)
N(1)-C(1)-N(2)-C(16)	-171.6(2)	C(2)-N(2)-C(16)-C(21)	67.2(3)
Pd(1)-C(1)-N(2)-C(16)	9.1(3)	C(21)-C(16)-C(17)-C(18)	1.7(4)
C(1)-N(2)-C(2)-C(3)	-0.4(3)	N(2)-C(16)-C(17)-C(18)	176.6(2)
C(16)-N(2)-C(2)-C(3)	172.7(2)	C(21)-C(16)-C(17)-C(22A)	-168.1(3)
N(2)-C(2)-C(3)-N(1)	-0.5(3)	N(2)-C(16)-C(17)-C(22A)	6.8(4)
C(1)-N(1)-C(3)-C(2)	1.3(3)	C(21)-C(16)-C(17)-C(22B)	176.6(4)
C(4)-N(1)-C(3)-C(2)	-174.7(2)	N(2)-C(16)-C(17)-C(22B)	-8.5(5)
C(1)-N(1)-C(4)-C(9)	85.9(3)	C(16)-C(17)-C(18)-C(19)	-1.9(4)
C(3)-N(1)-C(4)-C(9)	-98.7(3)	C(22A)-C(17)-C(18)-C(19)	167.7(3)
C(1)-N(1)-C(4)-C(5)	-96.6(3)	C(22B)-C(17)-C(18)-C(19)	-177.5(4)
C(3)-N(1)-C(4)-C(5)	78.8(3)	C(17)-C(18)-C(19)-C(20)	0.7(4)
C(9)-C(4)-C(5)-C(6)	-1.4(3)	C(18)-C(19)-C(20)-C(21)	0.8(4)
N(1)-C(4)-C(5)-C(6)	-178.7(2)	C(19)-C(20)-C(21)-C(16)	-0.9(4)
C(9)-C(4)-C(5)-C(10)	176.4(2)	C(19)-C(20)-C(21)-C(25)	-179.5(2)
N(1)-C(4)-C(5)-C(10)	-1.0(3)	C(17)-C(16)-C(21)-C(20)	-0.3(3)
C(4)-C(5)-C(6)-C(7)	1.1(4)	N(2)-C(16)-C(21)-C(20)	-175.2(2)

C(10)-C(5)-C(6)-C(7)	-176.7(2)	C(17)-C(16)-C(21)-C(25)	178.2(2)
C(5)-C(6)-C(7)-C(8)	-0.3(4)	N(2)-C(16)-C(21)-C(25)	3.3(3)
C(6)-C(7)-C(8)-C(9)	-0.4(4)	C(18)-C(17)-C(22A)-C(24A)	-90.6(6)
C(5)-C(4)-C(9)-C(8)	0.8(3)	C(16)-C(17)-C(22A)-C(24A)	78.8(6)
N(1)-C(4)-C(9)-C(8)	178.1(2)	C(18)-C(17)-C(22A)-C(23A)	33.6(6)
C(5)-C(4)-C(9)-C(13)	-175.3(2)	C(16)-C(17)-C(22A)-C(23A)	-157.1(4)
N(1)-C(4)-C(9)-C(13)	2.0(3)	C(18)-C(17)-C(22B)-C(24B)	-73.8(8)
C(7)-C(8)-C(9)-C(4)	0.1(4)	C(16)-C(17)-C(22B)-C(24B)	111.2(7)
C(7)-C(8)-C(9)-C(13)	176.2(2)	C(18)-C(17)-C(22B)-C(23B)	52.3(10)
C(6)-C(5)-C(10)-C(11)	-39.9(3)	C(16)-C(17)-C(22B)-C(23B)	-122.8(8)
C(4)-C(5)-C(10)-C(11)	142.4(2)	C(20)-C(21)-C(25)-C(26)	-50.2(3)
C(6)-C(5)-C(10)-C(12)	82.1(3)	C(16)-C(21)-C(25)-C(26)	131.3(3)
C(4)-C(5)-C(10)-C(12)	-95.6(3)	C(20)-C(21)-C(25)-C(27)	71.5(3)
C(4)-C(9)-C(13)-C(15)	-147.3(2)	C(16)-C(21)-C(25)-C(27)	-107.0(3)

Symmetry transformation to generate equivalent atoms: #1 -x+1, y, -z+3/2

Table S21. Atom deviations from planes (Å)

Complex	Plane	Atom deviations
2a	$Pd_2C_2Cl_4$	-0.0141(3) Pd1, 0.0141(3) Pd1#1, 0.0140(5) Cl1, -0.0140(5) Cl1#1, 0.0107(2) Cl2, -0.0107(2) Cl2#1, -0.0038(4) C1, 0.0038(4) C1#1
2b	$Pd_2C_2Br_4$	-0.0203(4) Pd1, 0.0203(4) Pd1#1, -0.0185(5) Br1, 0.0185(5) Br1#1, 0.0145(2) Br2, -0.0145(2) Br2#1, -0.0045(4) C1, 0.0045(4) C1#1
2c	$PdCCI_3$	-0.0482(5) Pd1, -0.0106(6) I1, 0.0342(4) I2, 0.0345(4) I3, -0.0099(7) C1,
2c	$PdCCI_3$	0.0176(5) Pd2, -0.0063(4) I1, -0.0018(6) I2, -0.0064(4) I4, -0.0031(7) C28
3a	$PdCClO_2$	-0.0152(6) Pd1, 0.0103(4) Cl1, -0.0027(5) C1, -0.0045(5) O1, 0.0120 (4) O1#2
3a	$Pd_2C_2Cl_2O_2$	0.0048(4) Pd2, -0.0277(5) Cl2, 0.0277(6) C28, 0.0623(12) O2, -0.0623(12) O2#3, -0.0048(4) Pd2#3, 0.0277(5) Cl2#3, -0.0277(6) C28#3
3b	$PdCBrO_2$	-0.048(9) C1A, -0.011(6) Pd1A, 0.048(6) Br1A, -0.05(1) O1A, 0.064(8) O2A
3b	$PdCClO_2$	-0.077(6) C28A, -0.028(7) Pd2A, 0.088(9) Br2A, 0.11(1) O1A, -0.091(8) O2A
3c	$PdCIO_2$	-0.0488(7) C1, -0.0061(9) Pd1, 0.0472(5) I1, -0.0549(7) O1, 0.0626(6) O1#4

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z+1;
#2 -x+1, y, -z+1/2; #3 -x+3/2, -y+1/2, -z+1; #4 -x+1, y, -z+3/2.

Table S22. Dihedral angles (°)

Complex	Plane1	Plane2	Angle
2a	N1, C1, N2, C2, C3	Pd1, Pd1#1, Cl1, Cl1#1, Cl2, Cl2#1, C1, C1#1	61.75(4)
2a	N1, C1, N2, C2, C3	C4 .. C9	76.15(4)
2a	N1, C1, N2, C2, C3	C16 .. C21	70.17(4)
2b	N1, C1, N2, C2, C3	Pd1, Pd1#1, Br1, Br1#1, Br2, Br2#1, C1, C1#1	62.00(5)
2b	N1, C1, N2, C2, C3	C4 .. C9	69.82(5)
2b	N1, C1, N2, C2, C3	C16 .. C21	74.66(6)
2c	Pd1, I1, I2, I3, C1	Pd2, I1, I2, I4, C28	43.18(2)
2c	N1, C1, N2, C2, C3	Pd1, I1, I2, I3, C1	69.83(6)
2c	N3, C28, N4, C29, C30	Pd2, I1, I2, I4, C28	64.67(6)
2c	N1, C1, N2, C2, C3	C4 .. C9	68.66(8)
2c	N1, C1, N2, C2, C3	C16 .. C21	76.46(7)
2c	N3, C28, N4, C29, C30	C31 .. C36	70.51(9)
2c	N3, C28, N4, C29, C30	C43 .. C48	73.41(9)
3a	Pd1, Cl1, C1, O1, O1#2	Pd1#2, Cl1#2, C1#2, O1#2, O1	38.08(3)
3a	N1, C1, N2, C2, C3	Pd1, Cl1, C1, O1, O1#2	64.24(6)
3a	N1, C1, N2, C2, C3	C4 .. C9	79.47(5)
3a	N1, C1, N2, C2, C3	C16 .. C21	86.16(5)
3a	N3, C28, N4A, C29A, C30A	Pd2, Cl2, C28, O2, O2#3, Pd2#3, Cl2#3, C28#3	58.6(2)
3a	N3, C28, N4A, C29A, C30A	C31A .. C36A	76.04(2)
3a	N3, C28, N4A, C29A, C30A	C43A .. C48A	71.35(2)
3b	C1A, Pd1A, Br1A, O1A, O2A	C28A, Pd2A, Br2A, O1A, O2A	26.9(4)
3b	C1A, N1A, N2A, C2A, C3A	C1A, Pd1A, Br1A, O1A, O2A	67.1(6)
3b	C1A, N1A, N2A, C2A, C3A	C4A .. C9A	71.1(7)
3b	C1A, N1A, N2A, C2A, C3A	C16A .. C21A	80.65(6)
3b	C28A, N3A, N4A, C29A, C30A	C28A, Pd2A, Br2A, O1A, O2A	81.8(4)
3b	C28A, N3A, N4A, C29A, C30A	C31A .. C36A	81.6(3)
3b	C28A, N3A, N4A, C29A, C30A	C43A .. C48A	81.1(4)
3c	C1, Pd1, I1, O1, O1#4	C1#4, Pd1#4, I1#4, O1#4, O1	30.80(3)
3c	N1, C1, N2, C2, C3	C1, Pd1, I1, O1, O1#4	66.14(6)
3c	N1, C1, N2, C2, C3	C4 .. C9	82.37(9)
3c	N1, C1, N2, C2, C3	C16 .. C21	66.15(9)

Symmetry transformation used to generate equivalent atoms: #1 -x+1, -y+1, -z+1; #2 -x+1, y, -z+1/2; #3 -x+3/2, -y+1/2, -z+1; #4 -x+1, y, -z+3/2