Supporting Information for

Synthesis and Characterization of Metallodendritic Palladium-Biscarbene Complexes Derived from 1,1'-Methylenebis(1,2,4-triazole).

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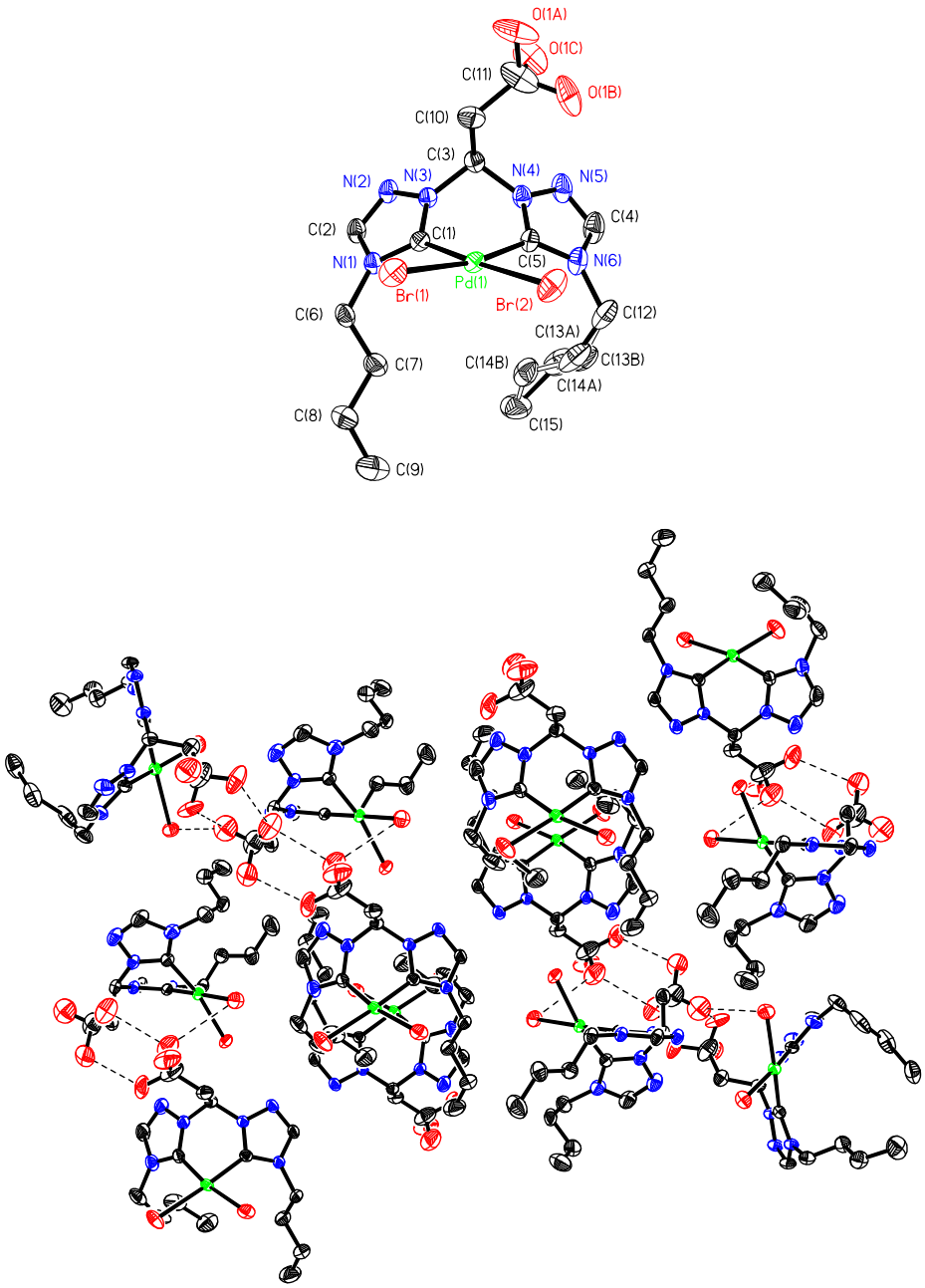
X-ray Diffraction Study of 1,1'-(3-Hydroxypropane-1,1-diyl)bis(4-butyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene)palladium(II) dibromide (4).



Crystallographic Studies: Suitable single crystals of the title compound for X-ray study were grown from a solution in dichloromethane/diethyl ether. Crystal data and refinement are summarized in Table S1. A yellow needle (0.55 × 0.18 × 0.17 mm) of compound **4** was selected

and mounted on a Bruker SMART-CCD area diffractometer. Unit-cell parameters were determined from 1271 frames of intensity data covering 0.3º in ω over a hemisphere of the reciprocal space by combination of three exposure sets, and refined by the least-squares method. Intensities were collected with graphite monochromatized Mo-$K\alpha$ radiation (λ = 0.71073 Å), using the ω/2θ scan-technique. A total of 14026 reflections for **4** were measured in the range $2.05 \leq \theta \leq 28.28$. Lorentz-polarization and absorption corrections were made.

The structures were solved by direct methods using the SHELXS computer program[1] and refined by the full-matrix least-squares method with the SHELX97 computer program,[1] using 5576 reflections. The function minimized was $\Sigma w| |Fo|^2 - |Fc|^2|^2$, where $w = [\sigma^2(I) + (0.052P)^2 + 5.101P]^{-1}$, and $P = (|Fo|^2 + 2|Fc|^2) / 3$, f, f' and f'' were taken from International Tables of X-ray Crystallography.[2] All hydrogen atoms were computed and refined using a riding model. For complex **4**, the final R (on F) factor was 0.0365, wR (on $|F|^2$) = 0.071 and goodness of fit = 1.043 for all observed reflections. The number of refined parameters was 2764. Max. shift/esd = 0.001, Mean shift/esd = 0.00. Max. and min. peaks in final difference synthesis was 1.128 and –1.033 $eÅ^{-3}$, respectively.

Table S1. X-ray Crystallography Data for 4.

Empirical formula	C15 H26 Br2 N6 O Pd	
Formula weight	572.64	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral	
Space group	R-3	
Unit cell dimensions	a = 20.1373(7) Å	α= 117.27°.
	b = 20.1373(7) Å	β= 117.27°.
	c = 20.1373(7) Å	γ = 117.27°.
Volume	3442.3(2) $Å^3$	
Z	6	
Density (calculated)	1.657 Mg/m^3	
Absorption coefficient	4.304 mm^{-1}	
F(000)	1692	
Crystal size	0.55 x 0.18 x 0.17 mm^3	
Theta range for data collection	2.05 to 28.28°.	
Index ranges	-26<=h<=26, -26<=k<=25, -18<=l<=26	
Reflections collected	22268	
Independent reflections	5576 [R(int) = 0.0358]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5281 and 0.2001	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5576 / 0 / 264	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0365, wR2 = 0.0973	
R indices (all data)	R1 = 0.0710, wR2 = 0.1147	
Largest diff. peak and hole	1.128 and -1.083 $e.Å^{-3}$	

TableS2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	3112(1)	5497(1)	1370(1)	38(1)
Br(1)	4765(1)	6654(1)	1747(1)	59(1)
Br(2)	2120(1)	3385(1)	-170(1)	72(1)
O(1A)	5050(20)	7220(20)	5610(20)	136(8)
O(1B)	4120(20)	5670(20)	4030(20)	110(6)
O(1C)	6200(20)	7410(20)	5838(19)	124(7)
N(1)	4234(4)	8031(4)	2790(4)	41(1)
N(2)	4894(4)	8948(4)	4519(4)	46(1)
N(3)	4326(4)	7755(4)	3707(4)	38(1)
N(4)	2716(4)	5688(4)	2628(4)	46(1)
N(5)	1879(6)	5069(5)	2514(6)	68(1)
N(6)	760(5)	3602(5)	480(5)	60(1)
C(1)	3936(5)	7191(5)	2667(5)	39(1)
C(2)	4818(5)	9074(5)	3919(5)	49(1)
C(3)	4152(5)	7189(5)	3984(5)	45(1)
C(4)	685(7)	3792(7)	1171(8)	76(2)
C(5)	2083(5)	4840(5)	1436(5)	43(1)
C(6)	3948(5)	7864(5)	1861(5)	50(1)
C(7)	2452(6)	6681(6)	468(6)	63(1)
C(8)	2227(7)	6586(7)	-411(7)	74(2)
C(9)	728(9)	5425(10)	-1831(8)	114(3)
C(10)	5269(6)	7537(6)	4732(6)	62(1)
C(11)	5149(13)	6983(13)	5045(12)	111(3)
C(12)	-467(6)	2300(6)	-1077(7)	79(2)
C(13A)	-1340(19)	2310(20)	-1735(19)	73(6)
C(14A)	-584(14)	3426(14)	-1357(14)	67(5)
C(13B)	-841(17)	2422(15)	-1698(13)	86(7)
C(14B)	-1290(20)	2820(20)	-1500(20)	96(8)
C(15)	-1457(8)	3293(9)	-2009(8)	105(3)

Table S3. Bond lengths [Å] and angles [°] for **4**.

Pd(1)-C(1)	1.971(4)	C(9)-H(9A)	0.9600
Pd(1)-C(5)	1.989(5)	C(9)-H(9B)	0.9600
Pd(1)-Br(1)	2.4571(6)	C(9)-H(9C)	0.9600
Pd(1)-Br(2)	2.4788(6)	C(10)-C(11)	1.496(10)
O(1A)-C(11)	1.17(2)	C(10)-H(10A)	0.9700
O(1B)-C(11)	1.267(18)	C(10)-H(10B)	0.9700
O(1C)-C(11)	1.320(17)	C(12)-C(13B)	1.334(19)
N(1)-C(1)	1.353(6)	C(12)-C(13A)	1.66(2)
N(1)-C(2)	1.369(6)	C(13A)-C(14A)	1.48(3)
N(1)-C(6)	1.484(6)	C(14A)-C(15)	1.420(17)
N(2)-C(2)	1.302(6)	C(13B)-C(14B)	1.51(3)
N(2)-N(3)	1.386(5)	C(14B)-C(15)	1.72(3)
N(3)-C(1)	1.338(5)		
N(3)-C(3)	1.459(6)	C(1)-Pd(1)-C(5)	84.25(18)
N(4)-C(5)	1.322(6)	C(1)-Pd(1)-Br(1)	90.64(12)
N(4)-N(5)	1.381(6)	C(5)-Pd(1)-Br(1)	169.60(14)
N(4)-C(3)	1.464(6)	C(1)-Pd(1)-Br(2)	176.83(13)
N(5)-C(4)	1.308(8)	C(5)-Pd(1)-Br(2)	93.93(13)
N(6)-C(5)	1.355(6)	Br(1)-Pd(1)-Br(2)	90.74(2)
N(6)-C(4)	1.365(7)	C(1)-N(1)-C(2)	108.1(4)
N(6)-C(12)	1.496(8)	C(1)-N(1)-C(6)	127.7(4)
C(2)-H(2A)	0.9300	C(2)-N(1)-C(6)	124.1(4)
C(3)-C(10)	1.519(7)	C(2)-N(2)-N(3)	102.3(4)
C(3)-H(3A)	0.9800	C(1)-N(3)-N(2)	113.8(4)
C(4)-H(4A)	0.9300	C(1)-N(3)-C(3)	125.4(4)
C(6)-C(7)	1.474(8)	N(2)-N(3)-C(3)	120.7(3)
C(6)-H(6A)	0.9700	C(5)-N(4)-N(5)	114.6(4)
C(6)-H(6B)	0.9700	C(5)-N(4)-C(3)	126.0(4)
C(7)-C(8)	1.500(8)	N(5)-N(4)-C(3)	119.3(4)
C(7)-H(7A)	0.9700	C(4)-N(5)-N(4)	101.6(4)
C(7)-H(7B)	0.9700	C(5)-N(6)-C(4)	107.5(5)
C(8)-C(9)	1.500(10)	C(5)-N(6)-C(12)	127.4(5)
C(8)-H(8A)	0.9700	C(4)-N(6)-C(12)	124.7(5)
C(8)-H(8B)	0.9700	N(3)-C(1)-N(1)	103.6(4)

N(3)-C(1)-Pd(1)	121.9(3)	C(9)-C(8)-H(8A)	108.6
N(1)-C(1)-Pd(1)	134.5(3)	C(7)-C(8)-H(8B)	108.6
N(2)-C(2)-N(1)	112.1(4)	C(9)-C(8)-H(8B)	108.6
N(2)-C(2)-H(2A)	123.9	H(8A)-C(8)-H(8B)	107.6
N(1)-C(2)-H(2A)	123.9	C(8)-C(9)-H(9A)	109.5
N(3)-C(3)-N(4)	105.9(4)	C(8)-C(9)-H(9B)	109.5
N(3)-C(3)-C(10)	111.5(4)	H(9A)-C(9)-H(9B)	109.5
N(4)-C(3)-C(10)	114.3(4)	C(8)-C(9)-H(9C)	109.5
N(3)-C(3)-H(3A)	108.3	H(9A)-C(9)-H(9C)	109.5
N(4)-C(3)-H(3A)	108.3	H(9B)-C(9)-H(9C)	109.5
C(10)-C(3)-H(3A)	108.3	C(11)-C(10)-C(3)	114.3(6)
N(5)-C(4)-N(6)	112.5(5)	C(11)-C(10)-H(10A)	108.7
N(5)-C(4)-H(4A)	123.8	C(3)-C(10)-H(10A)	108.7
N(6)-C(4)-H(4A)	123.8	C(11)-C(10)-H(10B)	108.7
N(4)-C(5)-N(6)	103.9(4)	C(3)-C(10)-H(10B)	108.7
N(4)-C(5)-Pd(1)	121.3(3)	H(10A)-C(10)-H(10B)	107.6
N(6)-C(5)-Pd(1)	134.8(4)	O(1A)-C(11)-O(1B)	99.8(17)
C(7)-C(6)-N(1)	114.2(4)	O(1A)-C(11)-O(1C)	102.3(15)
C(7)-C(6)-H(6A)	108.7	O(1B)-C(11)-O(1C)	100.3(14)
N(1)-C(6)-H(6A)	108.7	O(1A)-C(11)-C(10)	117.8(13)
C(7)-C(6)-H(6B)	108.7	O(1B)-C(11)-C(10)	118.3(11)
N(1)-C(6)-H(6B)	108.7	O(1C)-C(11)-C(10)	115.4(12)
H(6A)-C(6)-H(6B)	107.6	C(13B)-C(12)-N(6)	115.6(8)
C(6)-C(7)-C(8)	111.9(5)	C(13B)-C(12)-C(13A)	31.9(8)
C(6)-C(7)-H(7A)	109.2	N(6)-C(12)-C(13A)	108.0(8)
C(8)-C(7)-H(7A)	109.2	C(14A)-C(13A)-C(12)	115.3(14)
C(6)-C(7)-H(7B)	109.2	C(15)-C(14A)-C(13A)	109.5(13)
C(8)-C(7)-H(7B)	109.2	C(12)-C(13B)-C(14B)	113.1(15)
H(7A)-C(7)-H(7B)	107.9	C(13B)-C(14B)-C(15)	113.3(16)
C(7)-C(8)-C(9)	114.6(6)	C(14A)-C(15)-C(14B)	41.1(8)
C(7)-C(8)-H(8A)	108.6		

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	38(1)	35(1)	35(1)	27(1)	31(1)	31(1)
Br(1)	58(1)	63(1)	59(1)	49(1)	53(1)	51(1)
Br(2)	65(1)	49(1)	62(1)	38(1)	51(1)	50(1)
O(1A)	163(19)	157(18)	156(18)	143(17)	138(17)	138(17)
O(1B)	178(17)	122(13)	172(16)	136(14)	160(16)	138(14)
O(1C)	171(17)	203(19)	133(14)	153(16)	133(14)	176(17)
N(1)	46(2)	37(2)	44(2)	34(2)	40(2)	34(2)
N(2)	52(2)	36(2)	47(2)	33(2)	43(2)	36(2)
N(3)	44(2)	35(2)	39(2)	31(2)	36(2)	33(2)
N(4)	53(2)	45(2)	53(2)	42(2)	48(2)	42(2)
N(5)	80(3)	65(3)	84(4)	65(3)	76(3)	59(3)
N(6)	54(3)	45(2)	65(3)	44(2)	52(3)	40(2)
C(1)	37(2)	37(2)	36(2)	29(2)	31(2)	30(2)
C(2)	59(3)	38(2)	54(3)	38(2)	50(3)	40(3)
C(3)	56(3)	46(3)	48(3)	41(2)	47(3)	44(3)
C(4)	74(4)	59(4)	90(5)	62(4)	74(4)	53(4)
C(5)	42(2)	36(2)	46(3)	33(2)	37(2)	32(2)
C(6)	59(3)	52(3)	57(3)	48(3)	52(3)	46(3)
C(7)	62(3)	71(4)	64(3)	59(3)	55(3)	55(3)
C(8)	83(4)	79(4)	69(4)	66(4)	65(4)	67(4)
C(9)	106(6)	120(7)	84(5)	89(6)	78(5)	89(6)
C(10)	70(4)	70(4)	56(3)	54(3)	54(3)	61(3)
C(11)	169(9)	174(10)	148(9)	151(9)	144(9)	158(9)
C(12)	45(3)	35(3)	51(4)	24(3)	36(3)	25(3)
C(13A)	46(8)	71(11)	62(9)	51(10)	48(8)	44(9)
C(14A)	48(7)	58(8)	65(8)	49(7)	48(7)	40(7)
C(13B)	56(9)	64(9)	43(7)	35(7)	41(7)	39(8)
C(14B)	72(11)	103(16)	72(11)	67(12)	59(10)	73(13)
C(15)	64(4)	109(6)	80(5)	79(5)	55(4)	64(5)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **4**.

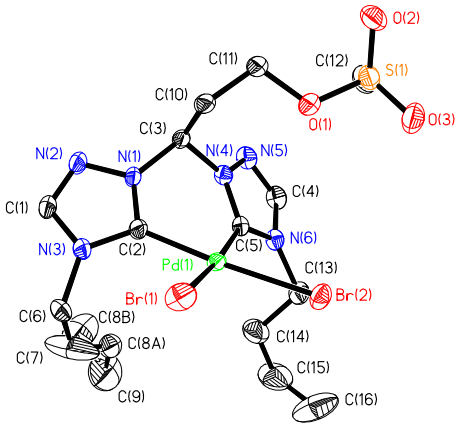
	x	y	z	U(eq)
H(2A)	5125	9791	4222	58
H(3A)	4237	7612	4589	54
H(4A)	-125	3092	735	91
H(6A)	4449	8721	2317	60
H(6B)	4312	7736	1743	60
H(7A)	2075	6793	578	76
H(7B)	1948	5816	-8	76
H(8A)	2592	6457	-530	88
H(8B)	2764	7468	89	88
H(9A)	674	5438	-2324	171
H(9B)	361	5554	-1728	171
H(9C)	190	4543	-2349	171
H(10A)	5219	7160	4158	74
H(10B)	6182	8546	5605	74

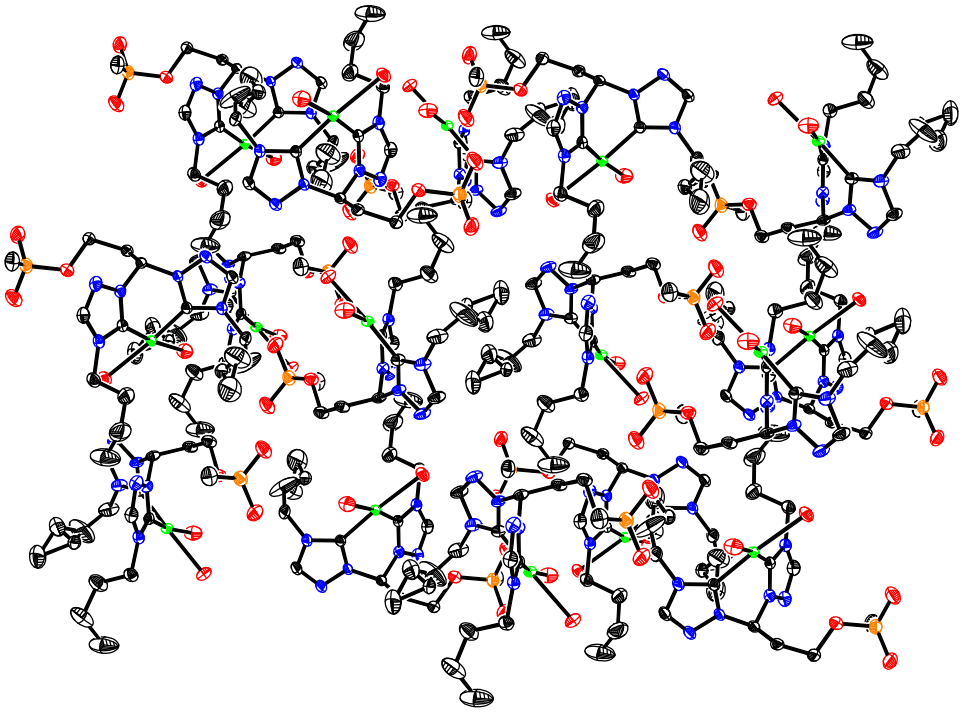
Table S6. Torsion angles [°] for **4.**

C(2)-N(2)-N(3)-C(1)	0.7(5)	N(5)-N(4)-C(5)-Pd(1)	-177.9(3)
C(2)-N(2)-N(3)-C(3)	-177.3(4)	C(3)-N(4)-C(5)-Pd(1)	6.0(7)
C(5)-N(4)-N(5)-C(4)	-0.9(6)	C(4)-N(6)-C(5)-N(4)	0.1(6)
C(3)-N(4)-N(5)-C(4)	175.5(5)	C(12)-N(6)-C(5)-N(4)	172.6(6)
N(2)-N(3)-C(1)-N(1)	-1.3(5)	C(4)-N(6)-C(5)-Pd(1)	178.2(4)
C(3)-N(3)-C(1)-N(1)	176.5(4)	C(12)-N(6)-C(5)-Pd(1)	-9.4(9)
N(2)-N(3)-C(1)-Pd(1)	179.6(3)	C(1)-Pd(1)-C(5)-N(4)	-42.4(4)
C(3)-N(3)-C(1)-Pd(1)	-2.6(6)	Br(1)-Pd(1)-C(5)-N(4)	18.5(10)
C(2)-N(1)-C(1)-N(3)	1.4(5)	Br(2)-Pd(1)-C(5)-N(4)	135.0(4)
C(6)-N(1)-C(1)-N(3)	-176.3(4)	C(1)-Pd(1)-C(5)-N(6)	139.8(5)
C(2)-N(1)-C(1)-Pd(1)	-179.6(4)	Br(1)-Pd(1)-C(5)-N(6)	-159.3(5)
C(6)-N(1)-C(1)-Pd(1)	2.6(7)	Br(2)-Pd(1)-C(5)-N(6)	-42.8(5)
C(5)-Pd(1)-C(1)-N(3)	40.8(4)	C(1)-N(1)-C(6)-C(7)	70.4(6)
Br(1)-Pd(1)-C(1)-N(3)	-130.1(3)	C(2)-N(1)-C(6)-C(7)	-107.1(6)
Br(2)-Pd(1)-C(1)-N(3)	-14(3)	N(1)-C(6)-C(7)-C(8)	178.5(5)
C(5)-Pd(1)-C(1)-N(1)	-138.0(5)	C(6)-C(7)-C(8)-C(9)	-178.4(6)
Br(1)-Pd(1)-C(1)-N(1)	51.1(4)	N(3)-C(3)-C(10)-C(11)	-179.8(6)
Br(2)-Pd(1)-C(1)-N(1)	166.8(19)	N(4)-C(3)-C(10)-C(11)	-59.7(7)
N(3)-N(2)-C(2)-N(1)	0.3(5)	C(3)-C(10)-C(11)-O(1A)	-51.1(19)
C(1)-N(1)-C(2)-N(2)	-1.1(6)	C(3)-C(10)-C(11)-O(1B)	69.0(13)
C(6)-N(1)-C(2)-N(2)	176.7(4)	C(3)-C(10)-C(11)-O(1C)	-172.3(11)
C(1)-N(3)-C(3)-N(4)	-46.1(6)	C(5)-N(6)-C(12)-C(13B)	-60.5(13)
N(2)-N(3)-C(3)-N(4)	131.6(4)	C(4)-N(6)-C(12)-C(13B)	110.7(12)
C(1)-N(3)-C(3)-C(10)	78.9(6)	C(5)-N(6)-C(12)-C(13A)	-94.0(9)
N(2)-N(3)-C(3)-C(10)	-103.4(5)	C(4)-N(6)-C(12)-C(13A)	77.3(11)
C(5)-N(4)-C(3)-N(3)	44.2(6)	C(13B)-C(12)-C(13A)-C(14A)	-43.5(16)
N(5)-N(4)-C(3)-N(3)	-131.8(4)	N(6)-C(12)-C(13A)-C(14A)	66.3(16)
C(5)-N(4)-C(3)-C(10)	-79.1(6)	C(12)-C(13A)-C(14A)-C(15)	178.8(11)
N(5)-N(4)-C(3)-C(10)	105.0(5)	N(6)-C(12)-C(13B)-C(14B)	-61.6(17)
N(4)-N(5)-C(4)-N(6)	1.0(7)	C(13A)-C(12)-C(13B)-C(14B)	21.3(18)
C(5)-N(6)-C(4)-N(5)	-0.8(8)	C(12)-C(13B)-C(14B)-C(15)	168.7(11)
C(12)-N(6)-C(4)-N(5)	-173.5(6)	C(13A)-C(14A)-C(15)-C(14B)	22.7(14)
N(5)-N(4)-C(5)-N(6)	0.5(6)	C(13B)-C(14B)-C(15)-C(14A)	-36.5(13)
C(3)-N(4)-C(5)-N(6)	-175.7(4)		

Symmetry transformations used to generate equivalent atoms:

X-ray Diffraction Study of 1,1'-(3-Methanesulphonyloxypropane-1,1-diyl)bis(4-butyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene)palladium(II) dibromide (7):





Crystallographic Studies: Suitable single crystals for X-ray of the title compound were grown from a solution in dichloromethane/diethyl ether. Crystal data and refinement are summarized in Table S2. A colourless prismatic crystal (0.50 × 0.48 × 0.30 mm) of compound **7** was selected and mounted on a Bruker SMART-CCD area

diffractometer. Unit-cell parameters were determined from 1271 frames of intensity data covering 0.3º in ω over a hemisphere of the reciprocal space by combination of three exposure sets, and refined by the least-squares method. Intensities were collected with graphite monochromatized Mo-$K\alpha$ radiation (λ = 0.71073 Å), using the ω/2θ scan-technique. A total of 14026 reflections for **7** were measured in the range $1.92 \leq \theta \leq 26.37$. Lorentz-polarization and absorption corrections were made.

The structures were solved by direct methods using the SHELXS computer program[1] and refined by the full-matrix least-squares method with the SHELX97 computer program,[1] using 4836 reflections. The function minimized was $\Sigma w| |Fo|^2 - |Fc|^2|^2$, where $w = [\sigma^2(I) + (0.0523P)^2 + 2.1157P]^{-1}$, and $P = (|Fo|^2 + 2|Fc|^2) / 3$, f, f' and f'' were taken from International Tables of X-ray Crystallography.[2] All hydrogen atoms were computed and refined using a riding model. For complex **7**, the final R (on F) factor was 0.0337, wR (on $|F|^2$) = 0.0466 and goodness of fit = 1.054 for all observed reflections. The number of refined parameters was 272. Max. shift/esd = 0.001, Mean shift/esd = 0.00. Max. and min. peaks in final difference synthesis was 0.625 and –0.943 eÅ^{-3}, respectively.

Table S7. X-ray Crystallography Data for 7

Empirical formula	$C_{16}H_{28}Br_2N_6O_3Pd\ S$	
Formula weight	650.72	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.4862(6) Å	α = 90°
	b = 15.5606(9) Å	β = 100.5700(10)°
	c = 14.7375(8) Å	γ = 90°
Volume	2363.9(2) $Å^3$	
Z	4	
Density (calculated)	1.828 Mg/m^3	
Absorption coefficient	4.282 mm^{-1}	
F(000)	1288	
Crystal size	0.50 × 0.48 × 0.30 mm^3	
Theta range for data collection	1.92 to 26.37°.	
Index ranges	$-12\le h\le 13$, $-19\le k\le 11$, $-18\le l\le 15$	
Reflections collected	14026	
Independent reflections	4836 [R(int) = 0.0233]	
Completeness to theta = 26.37°	100.0%	
Absorption correction	Multiscan	
Max. and min. transmission	0.3598 and 0.2233	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4836 / 0 / 272	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0337, wR2 = 0.0885	
R indices (all data)	R1 = 0.0466, wR2 = 0.0945	
Largest diff. peak and hole	0.625 and –0.943 $e.Å^{-3}$	

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **7**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	1272(1)	2327(1)	7972(1)	31(1)
Br(1)	2063(1)	2239(1)	6499(1)	61(1)
Br(2)	-169(1)	3528(1)	7356(1)	49(1)
S(1)	2382(1)	5117(1)	10340(1)	53(1)
O(1)	2682(3)	4250(2)	9904(2)	50(1)
O(2)	3549(3)	5573(2)	10646(3)	71(1)
O(3)	1390(3)	5505(2)	9671(3)	75(1)
N(1)	3212(3)	1511(2)	9378(2)	38(1)
N(2)	3955(4)	811(2)	9679(2)	52(1)
N(3)	2771(3)	622(2)	8300(2)	48(1)
N(4)	1825(3)	2459(2)	9969(2)	34(1)
N(5)	1416(4)	2641(2)	10778(2)	43(1)
N(6)	-193(3)	2637(2)	9594(2)	37(1)
C(1)	3666(4)	278(3)	9005(3)	58(1)
C(2)	2473(4)	1419(3)	8543(3)	37(1)
C(3)	3192(4)	2259(3)	9987(3)	37(1)
C(4)	185(4)	2741(3)	10516(3)	44(1)
C(5)	877(4)	2463(2)	9230(3)	32(1)
C(6)	2106(5)	119(3)	7487(4)	72(2)
C(7)	891(11)	-269(9)	7629(7)	165(5)
C(8A)	85(18)	-30(13)	8099(16)	62(8)
C(8B)	475(15)	-483(13)	8471(15)	134(7)
C(9)	-939(10)	-639(5)	8459(8)	143(4)
C(10)	3958(4)	3004(3)	9708(3)	43(1)
C(11)	3901(4)	3804(3)	10283(3)	49(1)
C(12)	1724(5)	4817(4)	11294(4)	69(1)
C(13)	-1560(4)	2596(3)	9126(3)	49(1)
C(14)	-1969(5)	1680(4)	8916(5)	82(2)
C(15)	-3374(7)	1531(6)	8708(7)	116(3)
C(16)	-4061(8)	2048(8)	8031(5)	142(4)

Table S9. Bond lengths [Å] and angles [°] for **7**.

Pd(1)-C(2)	1.975(4)	C(8A)-C(9)	1.59(2)
Pd(1)-C(5)	1.983(4)	C(8B)-C(9)	1.499(16)
Pd(1)-Br(1)	2.4663(5)	C(10)-C(11)	1.513(6)
Pd(1)-Br(2)	2.4686(5)	C(10)-H(10A)	0.9700
S(1)-O(2)	1.415(3)	C(10)-H(10B)	0.9700
S(1)-O(3)	1.429(4)	C(11)-H(11A)	0.9700
S(1)-O(1)	1.552(3)	C(11)-H(11B)	0.9700
S(1)-C(12)	1.740(5)	C(12)-H(12A)	0.9600
O(1)-C(11)	1.471(5)	C(12)-H(12B)	0.9600
N(1)-C(2)	1.336(5)	C(12)-H(12C)	0.9600
N(1)-N(2)	1.365(4)	C(13)-C(14)	1.504(7)
N(1)-C(3)	1.472(5)	C(13)-H(13A)	0.9700
N(2)-C(1)	1.287(6)	C(13)-H(13B)	0.9700
N(2)-H(2B)	0.8600	C(14)-C(15)	1.467(8)
N(3)-C(2)	1.344(5)	C(14)-H(14A)	0.9700
N(3)-C(1)	1.375(5)	C(14)-H(14B)	0.9700
N(3)-C(6)	1.492(5)	C(15)-C(16)	1.377(11)
N(4)-C(5)	1.333(5)	C(15)-H(15A)	0.9700
N(4)-N(5)	1.369(4)	C(15)-H(15B)	0.9700
N(4)-C(3)	1.462(5)	C(16)-H(16A)	0.9600
N(5)-C(4)	1.288(6)	C(16)-H(16B)	0.9600
N(5)-H(5A)	0.8600	C(16)-H(16C)	0.9600
N(6)-C(4)	1.354(5)		
N(6)-C(5)	1.357(5)	C(2)-Pd(1)-C(5)	84.52(15)
N(6)-C(13)	1.474(5)	C(2)-Pd(1)-Br(1)	92.53(11)
C(1)-H(1A)	0.9300	C(5)-Pd(1)-Br(1)	172.06(11)
C(3)-C(10)	1.510(6)	C(2)-Pd(1)-Br(2)	175.87(11)
C(3)-H(3B)	0.9800	C(5)-Pd(1)-Br(2)	92.53(10)
C(4)-H(4A)	0.9300	Br(1)-Pd(1)-Br(2)	90.025(18)
C(6)-C(7)	1.459(12)	O(2)-S(1)-O(3)	119.1(2)
C(6)-H(6A)	0.9700	O(2)-S(1)-O(1)	109.79(19)
C(6)-H(6B)	0.9700	O(3)-S(1)-O(1)	105.0(2)
C(7)-C(8A)	1.24(2)	O(2)-S(1)-C(12)	108.9(3)

C(7)-C(8B)	1.43(2)	O(3)-S(1)-C(12)	109.0(3)
O(1)-S(1)-C(12)	104.0(2)	N(4)-C(5)-Pd(1)	120.7(3)
C(11)-O(1)-S(1)	118.8(3)	N(6)-C(5)-Pd(1)	136.1(3)
C(2)-N(1)-N(2)	114.4(3)	C(7)-C(6)-N(3)	113.2(5)
C(2)-N(1)-C(3)	125.1(3)	C(7)-C(6)-H(6A)	108.9
N(2)-N(1)-C(3)	120.3(3)	N(3)-C(6)-H(6A)	108.9
C(1)-N(2)-N(1)	103.0(3)	C(7)-C(6)-H(6B)	108.9
C(1)-N(2)-H(2B)	128.5	N(3)-C(6)-H(6B)	108.9
N(1)-N(2)-H(2B)	128.5	H(6A)-C(6)-H(6B)	107.7
C(2)-N(3)-C(1)	108.5(3)	C(8A)-C(7)-C(8B)	40.4(9)
C(2)-N(3)-C(6)	127.0(3)	C(8A)-C(7)-C(6)	131.0(12)
C(1)-N(3)-C(6)	123.8(4)	C(8B)-C(7)-C(6)	129.4(9)
C(5)-N(4)-N(5)	113.9(3)	C(7)-C(8A)-C(9)	125.2(15)
C(5)-N(4)-C(3)	126.7(3)	C(7)-C(8B)-C(9)	119.1(15)
N(5)-N(4)-C(3)	119.4(3)	C(8B)-C(9)-C(8A)	35.2(7)
C(4)-N(5)-N(4)	102.8(3)	C(3)-C(10)-C(11)	113.7(3)
C(4)-N(5)-H(5A)	128.6	C(3)-C(10)-H(10A)	108.8
N(4)-N(5)-H(5A)	128.6	C(11)-C(10)-H(10A)	108.8
C(4)-N(6)-C(5)	108.1(3)	C(3)-C(10)-H(10B)	108.8
C(4)-N(6)-C(13)	123.7(3)	C(11)-C(10)-H(10B)	108.8
C(5)-N(6)-C(13)	127.6(3)	H(10A)-C(10)-H(10B)	107.7
N(2)-C(1)-N(3)	111.3(4)	O(1)-C(11)-C(10)	107.2(3)
N(2)-C(1)-H(1A)	124.3	O(1)-C(11)-H(11A)	110.3
N(3)-C(1)-H(1A)	124.3	C(10)-C(11)-H(11A)	110.3
N(1)-C(2)-N(3)	102.8(3)	O(1)-C(11)-H(11B)	110.3
N(1)-C(2)-Pd(1)	122.2(3)	C(10)-C(11)-H(11B)	110.3
N(3)-C(2)-Pd(1)	135.0(3)	H(11A)-C(11)-H(11B)	108.5
N(4)-C(3)-N(1)	106.3(3)	S(1)-C(12)-H(12A)	109.5
N(4)-C(3)-C(10)	113.6(3)	S(1)-C(12)-H(12B)	109.5
N(1)-C(3)-C(10)	112.0(3)	H(12A)-C(12)-H(12B)	109.5
N(4)-C(3)-H(3B)	108.3	S(1)-C(12)-H(12C)	109.5
N(1)-C(3)-H(3B)	108.3	H(12A)-C(12)-H(12C)	109.5
C(10)-C(3)-H(3B)	108.3	H(12B)-C(12)-H(12C)	109.5
N(5)-C(4)-N(6)	112.3(3)	N(6)-C(13)-C(14)	110.7(4)
N(5)-C(4)-H(4A)	123.9	N(6)-C(13)-H(13A)	109.5

N(6)-C(4)-H(4A)	123.9	C(14)-C(13)-H(13A)	109.5
N(4)-C(5)-N(6)	103.0(3)	N(6)-C(13)-H(13B)	109.5
C(14)-C(13)-H(13B)	109.5	C(14)-C(15)-H(15A)	108.4
H(13A)-C(13)-H(13B)	108.1	C(16)-C(15)-H(15B)	108.4
C(15)-C(14)-C(13)	115.5(5)	C(14)-C(15)-H(15B)	108.4
C(15)-C(14)-H(14A)	108.4	H(15A)-C(15)-H(15B)	107.5
C(13)-C(14)-H(14A)	108.4	C(15)-C(16)-H(16A)	109.5
C(15)-C(14)-H(14B)	108.4	C(15)-C(16)-H(16B)	109.5
C(13)-C(14)-H(14B)	108.4	H(16A)-C(16)-H(16B)	109.5
H(14A)-C(14)-H(14B)	107.5	C(15)-C(16)-H(16C)	109.5
C(16)-C(15)-C(14)	115.5(8)	H(16A)-C(16)-H(16C)	109.5
C(16)-C(15)-H(15A)	108.4	H(16B)-C(16)-H(16C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	28(1)	38(1)	26(1)	-3(1)	4(1)	4(1)
Br(1)	54(1)	97(1)	36(1)	-7(1)	17(1)	9(1)
Br(2)	56(1)	52(1)	39(1)	8(1)	5(1)	18(1)
S(1)	49(1)	40(1)	70(1)	-5(1)	14(1)	1(1)
O(1)	37(2)	52(2)	58(2)	-4(1)	4(1)	6(1)
O(2)	57(2)	51(2)	104(3)	-19(2)	18(2)	-11(2)
O(3)	67(2)	57(2)	97(3)	16(2)	9(2)	16(2)
N(1)	38(2)	37(2)	35(2)	-7(1)	0(1)	14(1)
N(2)	52(2)	50(2)	46(2)	-8(2)	-10(2)	24(2)
N(3)	48(2)	48(2)	45(2)	-16(2)	-2(2)	17(2)
N(4)	39(2)	36(2)	28(2)	-2(1)	10(1)	4(1)
N(5)	59(2)	47(2)	26(2)	-1(1)	15(2)	5(2)
N(6)	33(2)	35(2)	45(2)	0(1)	18(1)	1(1)
C(1)	56(3)	52(3)	59(3)	-13(2)	-10(2)	27(2)
C(2)	35(2)	42(2)	34(2)	-7(2)	6(2)	8(2)
C(3)	37(2)	42(2)	28(2)	-7(2)	-1(2)	12(2)
C(4)	53(3)	46(2)	39(2)	0(2)	24(2)	2(2)
C(5)	33(2)	27(2)	36(2)	1(1)	11(2)	2(1)
C(6)	79(4)	66(3)	61(3)	-36(3)	-15(3)	27(3)
C(7)	148(9)	220(13)	118(8)	-69(9)	5(7)	-104(9)
C(8A)	60(10)	35(11)	85(15)	8(8)	-5(9)	-3(7)
C(8B)	85(9)	101(12)	209(17)	55(12)	7(10)	-20(9)
C(9)	138(7)	68(5)	217(11)	27(6)	17(7)	-21(5)
C(10)	30(2)	51(2)	47(2)	-12(2)	5(2)	4(2)
C(11)	36(2)	48(2)	59(3)	-12(2)	3(2)	3(2)
C(12)	79(4)	59(3)	76(4)	-10(3)	29(3)	2(3)
C(13)	35(2)	50(3)	65(3)	-3(2)	17(2)	3(2)
C(14)	61(3)	70(4)	114(5)	-27(4)	10(3)	-10(3)
C(15)	67(4)	125(7)	155(8)	-46(6)	23(5)	-32(4)
C(16)	82(5)	276(14)	64(5)	4(6)	1(4)	12(7)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **7**.

	x	y	z	U(eq)
H(2B)	4486	743	10192	62
H(5A)	1869	2680	11325	52
H(1A)	4018	-270	8995	70
H(3B)	3584	2089	10617	44
H(4A)	-381	2870	10915	53
H(6A)	1930	496	6954	87
H(6B)	2684	-331	7353	87
H(10A)	3630	3140	9065	51
H(10B)	4857	2830	9760	51
H(11A)	3920	3651	10923	58
H(11B)	4637	4173	10251	58
H(12A)	1508	5322	11607	104
H(12B)	2347	4482	11706	104
H(12C)	956	4481	11094	104
H(13A)	-1671	2922	8556	59
H(13B)	-2107	2851	9517	59
H(14A)	-1601	1487	8393	99
H(14B)	-1599	1326	9441	99
H(15A)	-3525	936	8522	139
H(15B)	-3716	1612	9270	139
H(16A)	-4966	1908	7948	213
H(16B)	-3758	1956	7462	213
H(16C)	-3936	2639	8211	213

Table S12. Torsion angles [°] for **7**.

O(2)-S(1)-O(1)-C(11)	33.4(4)	C(13)-N(6)-C(4)-N(5)	171.2(4)
O(3)-S(1)-O(1)-C(11)	162.6(3)	N(5)-N(4)-C(5)-N(6)	-1.5(4)
C(12)-S(1)-O(1)-C(11)	-83.0(4)	C(3)-N(4)-C(5)-N(6)	176.5(3)
C(2)-N(1)-N(2)-C(1)	0.3(5)	N(5)-N(4)-C(5)-Pd(1)	174.1(2)
C(3)-N(1)-N(2)-C(1)	175.9(4)	C(3)-N(4)-C(5)-Pd(1)	-7.9(5)
C(5)-N(4)-N(5)-C(4)	1.2(4)	C(4)-N(6)-C(5)-N(4)	1.2(4)
C(3)-N(4)-N(5)-C(4)	-177.0(3)	C(13)-N(6)-C(5)-N(4)	-170.2(4)
N(1)-N(2)-C(1)-N(3)	-0.1(6)	C(4)-N(6)-C(5)-Pd(1)	-173.3(3)
C(2)-N(3)-C(1)-N(2)	-0.2(6)	C(13)-N(6)-C(5)-Pd(1)	15.3(6)
C(6)-N(3)-C(1)-N(2)	-170.9(5)	C(2)-Pd(1)-C(5)-N(4)	43.2(3)
N(2)-N(1)-C(2)-N(3)	-0.4(5)	Br(1)-Pd(1)-C(5)-N(4)	-25.3(10)
C(3)-N(1)-C(2)-N(3)	-175.7(4)	Br(2)-Pd(1)-C(5)-N(4)	-133.9(3)
N(2)-N(1)-C(2)-Pd(1)	178.1(3)	C(2)-Pd(1)-C(5)-N(6)	-143.0(4)
C(3)-N(1)-C(2)-Pd(1)	2.8(5)	Br(1)-Pd(1)-C(5)-N(6)	148.5(5)
C(1)-N(3)-C(2)-N(1)	0.4(5)	Br(2)-Pd(1)-C(5)-N(6)	39.9(4)
C(6)-N(3)-C(2)-N(1)	170.7(5)	C(2)-N(3)-C(6)-C(7)	-78.6(9)
C(1)-N(3)-C(2)-Pd(1)	-177.9(4)	C(1)-N(3)-C(6)-C(7)	90.3(8)
C(6)-N(3)-C(2)-Pd(1)	-7.6(7)	N(3)-C(6)-C(7)-C(8A)	31(2)
C(5)-Pd(1)-C(2)-N(1)	-41.0(3)	N(3)-C(6)-C(7)-C(8B)	-23(2)
Br(1)-Pd(1)-C(2)-N(1)	131.6(3)	C(8B)-C(7)-C(8A)-C(9)	-52.7(19)
Br(2)-Pd(1)-C(2)-N(1)	3.5(19)	C(6)-C(7)-C(8A)-C(9)	-158.7(13)
C(5)-Pd(1)-C(2)-N(3)	137.0(4)	C(8A)-C(7)-C(8B)-C(9)	52.3(17)
Br(1)-Pd(1)-C(2)-N(3)	-50.4(4)	C(6)-C(7)-C(8B)-C(9)	162.5(13)
Br(2)-Pd(1)-C(2)-N(3)	-178.5(13)	C(7)-C(8B)-C(9)-C(8A)	-44.0(16)
C(5)-N(4)-C(3)-N(1)	-42.2(5)	C(7)-C(8A)-C(9)-C(8B)	59(2)
N(5)-N(4)-C(3)-N(1)	135.7(3)	N(4)-C(3)-C(10)-C(11)	56.3(4)
C(5)-N(4)-C(3)-C(10)	81.4(5)	N(1)-C(3)-C(10)-C(11)	176.7(3)
N(5)-N(4)-C(3)-C(10)	-100.8(4)	S(1)-O(1)-C(11)-C(10)	-177.9(3)
C(2)-N(1)-C(3)-N(4)	44.9(5)	C(3)-C(10)-C(11)-O(1)	-82.0(4)
N(2)-N(1)-C(3)-N(4)	-130.1(4)	C(4)-N(6)-C(13)-C(14)	-100.7(5)
C(2)-N(1)-C(3)-C(10)	-79.7(5)	C(5)-N(6)-C(13)-C(14)	69.5(6)
N(2)-N(1)-C(3)-C(10)	105.3(4)	N(6)-C(13)-C(14)-C(15)	162.6(6)
N(4)-N(5)-C(4)-N(6)	-0.3(4)	C(13)-C(14)-C(15)-C(16)	52.3(10)
C(5)-N(6)-C(4)-N(5)	-0.6(5)		

Symmetry transformations used to generate equivalent atoms:

Theoretical calculation

Table S13. Total electronic energies[a] (E, in a.u.), zero point corrections to energies[b] (ZPCE, in a.u.), energies[b] (ΔE, in a. u.) and number of imaginary frequencies (NIMAG) of all stationary points discussed in the main text.

Structure	E	ZPCE	ΔE	NIMAG(ν)
4a	**–6260.6004732**	**0.423187**	**–6260.177286**	**0**
4b	**–6260.5964972**	**0.423421**	**–6260.173076**	**0**
4'a	**–6024.7134259**	**0.251400**	**–6024.462026**	**0**
4'b	**–6024.7105554**	**0.251561**	**–6024.458994**	**0**
5'a	**–904.6741907**	**0.250569**	**–904.423622**	**0**
5'b	**–904.6724811**	**0.251004**	**–904.421477**	**0**
6'a	**–8520.3120369**	**0.237375**	**–8520.074662**	**0**
6'b	**–8520.3095561**	**0.237650**	**–8520.071906**	**0**
7'a	**–6612.6059518**	**0.290078**	**–6612.315873**	**0**
7'b	**–6612.6018401**	**0.290328**	**–6612.311513**	**0**

[a]Computed at the B3LYP/6-31+G*& LANL2DZ level of theory. [b]Computed at 298 K at the B3LYP/6-31G*& LANL2DZ level of theory.

Cartesian coordinates (optimized at the B3LYP/6-31G*& LANL2DZ level) of all the stationary points discussed in the main text.

4a

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	2.433868	1.572810	-2.450984
2	7	0	1.963177	0.645215	-1.553711
3	6	0	0.985680	1.099810	-0.741984
4	7	0	0.824681	2.389264	-1.154794
5	6	0	1.715605	2.624986	-2.173324
6	6	0	2.483638	-0.725303	-1.585250
7	6	0	3.452567	-1.034638	-0.440941
8	6	0	4.682951	-0.128951	-0.440880
9	8	0	5.581928	-0.677080	0.508953
10	46	0	0.136583	-0.121202	0.637995
11	35	0	-0.715598	-1.779959	2.323518

12	6	0	-0.178854	3.352540	-0.664933
13	6	0	0.258990	-1.558080	-0.791942
14	7	0	-0.531067	-2.572279	-1.244610
15	6	0	0.125277	-3.193941	-2.279128
16	7	0	1.279889	-2.642866	-2.530043
17	7	0	1.337051	-1.634862	-1.600039
18	6	0	-1.887843	-2.908280	-0.773711
19	35	0	0.237149	1.684035	2.387632
20	1	0	-0.276445	-4.041065	-2.815432
21	1	0	1.804212	3.575528	-2.678712
22	1	0	2.970917	-0.836045	-2.554378
23	1	0	3.781087	-2.073695	-0.558576
24	1	0	2.930041	-0.956280	0.518171
25	1	0	4.391860	0.898694	-0.177932
26	1	0	5.132533	-0.096954	-1.448502
27	1	0	0.182610	4.347481	-0.945476
28	6	0	-1.571878	3.086399	-1.241115
29	1	0	-0.181850	3.269659	0.424570
30	1	0	-1.846953	-2.909526	0.318091
31	6	0	-2.940426	-1.919238	-1.281026
32	1	0	-2.095887	-3.924527	-1.124477
33	1	0	6.281905	-0.028603	0.675845
34	6	0	-4.337345	-2.256577	-0.743218
35	1	0	-2.656033	-0.911308	-0.953174
36	1	0	-2.949042	-1.911835	-2.380634
37	6	0	-5.407581	-1.270529	-1.222449
38	1	0	-4.613665	-3.275788	-1.049465
39	1	0	-4.303654	-2.259523	0.353860
40	1	0	-6.393000	-1.531618	-0.821605
41	1	0	-5.176006	-0.249134	-0.896709
42	1	0	-5.482910	-1.263393	-2.316953
43	6	0	-2.602922	4.090753	-0.708893
44	1	0	-1.537835	3.126217	-2.339547
45	1	0	-1.874532	2.068484	-0.964368
46	6	0	-4.011262	3.836372	-1.255718
47	1	0	-2.617852	4.038293	0.387433
48	1	0	-2.287860	5.112014	-0.967171
49	1	0	-4.726698	4.564189	-0.857838
50	1	0	-4.033888	3.909123	-2.350171
51	1	0	-4.366361	2.835968	-0.980139

4b

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-3.018450	1.610451	1.292079
2	7	0	-2.301407	0.748147	0.501253
3	6	0	-1.050344	1.169494	0.217071
4	7	0	-0.976423	2.369626	0.854668
5	6	0	-2.179686	2.590267	1.480854
6	6	0	-2.813617	-0.570461	0.086679
7	6	0	-4.243431	-0.842393	0.534384
8	6	0	-5.275731	-0.036628	-0.254257
9	8	0	-6.546746	-0.524073	0.150440
10	46	0	0.225338	-0.017769	-0.815286
11	35	0	1.639241	-1.632754	-2.126166
12	6	0	0.198470	3.258454	0.918109
13	6	0	-0.533359	-1.520628	0.320463
14	7	0	-0.038455	-2.579489	1.017361
15	6	0	-1.089542	-3.196155	1.654007
16	7	0	-2.224481	-2.600868	1.416821
17	7	0	-1.856425	-1.570425	0.589961

18	6	0	1.378466	-2.966530	1.135881
19	35	0	0.908178	1.916879	-2.269692
20	1	0	-0.980174	-4.077000	2.269662
21	1	0	-2.399285	3.479161	2.054029
22	1	0	-2.738889	-0.598146	-1.003947
23	1	0	-4.354329	-0.648054	1.603879
24	1	0	-4.441701	-1.905513	0.373556
25	1	0	-5.115801	-0.185664	-1.335882
26	1	0	-5.167522	1.034983	-0.040593
27	1	0	-0.174714	4.248965	1.198667
28	6	0	1.253200	2.761987	1.910547
29	1	0	0.605330	3.304846	-0.095170
30	1	0	1.836897	-2.722052	0.175947
31	6	0	2.075510	-2.265871	2.307631
32	1	0	1.401017	-4.054288	1.262427
33	1	0	-7.226806	0.019361	-0.274824
34	6	0	3.574822	-2.605817	2.380319
35	1	0	1.949553	-1.180785	2.196543
36	1	0	1.581184	-2.550702	3.246842
37	1	0	3.953030	-2.282254	3.358510
38	1	0	3.700698	-3.697989	2.355471
39	6	0	4.416750	-1.956527	1.273931
40	1	0	5.470030	-2.242620	1.370590
41	1	0	4.083595	-2.240536	0.270237
42	1	0	4.361237	-0.862793	1.333260
43	6	0	2.474980	3.689793	1.946491
44	1	0	0.812521	2.677844	2.914521
45	1	0	1.566566	1.754307	1.609127
46	6	0	3.558183	3.200986	2.913542
47	1	0	2.893006	3.767217	0.934552
48	1	0	2.158408	4.703451	2.231342
49	1	0	4.417971	3.879666	2.919104
50	1	0	3.177145	3.135781	3.940321
51	1	0	3.921247	2.206491	2.627615

4'a

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.811502	2.787080	-1.005073
2	6	0	0.182697	1.674392	-0.531763
3	7	0	-1.067709	2.120145	-0.287994
4	7	0	-1.261585	3.450390	-0.564791
5	6	0	-0.090680	3.823852	-0.998413
6	46	0	0.672705	-0.263633	-0.182558
7	35	0	1.043646	-2.677594	0.416567
8	6	0	-2.186776	1.308825	0.194875
9	6	0	-2.101876	1.051991	1.701535
10	6	0	-3.273345	0.228304	2.234509
11	8	0	-3.203368	0.304126	3.648732
12	6	0	2.183312	2.865556	-1.517179
13	7	0	-2.225811	0.082043	-0.608174
14	6	0	-1.165803	-0.694670	-0.913868
15	7	0	-1.710207	-1.641310	-1.729611
16	6	0	-3.053850	-1.380967	-1.849663
17	7	0	-3.409497	-0.323617	-1.175415
18	6	0	-0.988744	-2.706980	-2.432929
19	35	0	2.835142	0.415816	0.900739
20	1	0	0.151369	4.826936	-1.317757
21	1	0	-3.728213	-1.986322	-2.437521
22	1	0	-3.093151	1.858929	-0.059908
23	1	0	-2.104472	2.027733	2.200948

24	1	0	-1.154199	0.557837	1.939998
25	1	0	-3.193633	-0.809776	1.879773
26	1	0	-4.227922	0.633961	1.856637
27	1	0	-1.697611	-3.501326	-2.675816
28	1	0	-0.547898	-2.310691	-3.351839
29	1	0	-0.207519	-3.082992	-1.769319
30	1	0	2.806019	2.193093	-0.924026
31	1	0	2.202000	2.572724	-2.570735
32	1	0	2.532435	3.895059	-1.413485
33	1	0	-3.798762	-0.363762	4.019942

4'b

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.086462	-1.390301	-3.283945
2	6	0	-0.089630	-0.831474	-2.043196
3	7	0	-1.261653	-1.256117	-1.522382
4	7	0	-1.998742	-2.048338	-2.364913
5	6	0	-1.252115	-2.104875	-3.431177
6	46	0	1.181505	0.282847	-0.923743
7	35	0	2.561930	1.671750	0.651125
8	6	0	-1.687278	-0.939991	-0.147592
9	6	0	-3.041735	-1.540801	0.203846
10	6	0	-3.649642	-0.936471	1.469676
11	8	0	-4.963913	-1.465879	1.564510
12	6	0	0.988573	-1.303865	-4.277189
13	7	0	-0.595149	-1.375175	0.742841
14	6	0	0.684752	-0.974747	0.582292
15	7	0	1.347543	-1.671606	1.545160
16	6	0	0.429970	-2.440858	2.220449
17	7	0	-0.775677	-2.289859	1.749677
18	6	0	2.793677	-1.662305	1.787412
19	35	0	1.547389	1.870064	-2.834942
20	1	0	-1.512789	-2.642557	-4.331056
21	1	0	0.686050	-3.087551	3.046960
22	1	0	-1.719606	0.151089	-0.082295
23	1	0	-2.965409	-2.626022	0.306411
24	1	0	-3.717787	-1.339002	-0.631375
25	1	0	-3.665906	0.163570	1.384806
26	1	0	-3.043774	-1.199352	2.346875
27	1	0	2.972194	-1.932800	2.830272
28	1	0	3.284561	-2.383995	1.128587
29	1	0	3.163043	-0.654210	1.587987
30	1	0	1.441797	-0.313501	-4.200116
31	1	0	1.734985	-2.079546	-4.084375
32	1	0	0.555501	-1.446676	-5.269472
33	1	0	-5.352208	-1.160147	2.397900

5'a

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-3.822631	-0.431064	-0.759460
2	7	0	-2.598646	0.024692	-0.332938
3	6	0	-1.543780	-0.605379	-0.890427
4	7	0	-2.136755	-1.506012	-1.724742
5	6	0	-3.499331	-1.369557	-1.603712
6	6	0	-2.524913	1.187007	0.561283
7	6	0	-2.130499	0.835589	1.997547
8	6	0	-3.086488	-0.161126	2.652123
9	8	0	-2.769836	-0.168623	4.034060

10	46	0	0.343325	-0.031545	-0.388371
11	53	0	2.715414	0.900948	0.594542
12	6	0	-1.456128	-2.407367	-2.657945
13	6	0	-0.385117	1.865004	-0.551323
14	7	0	0.005864	3.055546	-1.087662
15	6	0	-0.989042	3.976592	-0.857849
16	7	0	-2.000493	3.454286	-0.224125
17	7	0	-1.604836	2.151536	-0.048664
18	6	0	1.223647	3.306951	-1.862579
19	53	0	1.045040	-2.624949	0.122145
20	1	0	-0.930134	5.008834	-1.170522
21	1	0	-4.210242	-1.971946	-2.150113
22	1	0	-3.512304	1.648030	0.526162
23	1	0	-2.142709	1.765699	2.577393
24	1	0	-1.108539	0.443070	2.019432
25	1	0	-2.955413	-1.155198	2.200539
26	1	0	-4.133671	0.144510	2.482106
27	1	0	-2.177351	-3.148368	-3.008331
28	1	0	-1.069816	-1.837673	-3.506945
29	1	0	-0.632545	-2.896759	-2.135135
30	1	0	2.048529	2.760155	-1.403024
31	1	0	1.081744	2.975377	-2.894820
32	1	0	1.430164	4.378945	-1.844410
33	1	0	-3.173631	-0.951749	4.436313

5'b

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.306592	-1.552486	0.767786
2	7	0	2.275054	-0.789426	0.281403
3	6	0	1.059561	-1.129039	0.763254
4	7	0	1.340605	-2.169422	1.595269
5	6	0	2.697701	-2.389517	1.558633
6	6	0	2.489699	0.386926	-0.583009
7	6	0	3.941048	0.588814	-0.996120
8	6	0	4.418459	-0.442719	-2.018280
9	8	0	5.717144	-0.027297	-2.414527
10	46	0	-0.559465	-0.008176	0.250223
11	53	0	-2.511357	1.646716	-0.697094
12	6	0	0.385477	-2.893890	2.437449
13	6	0	0.667036	1.580573	0.601856
14	7	0	0.623934	2.757514	1.284807
15	6	0	1.859804	3.353453	1.184894
16	7	0	2.695729	2.631508	0.494542
17	7	0	1.936962	1.544723	0.142472
18	6	0	-0.511024	3.281772	2.048532
19	53	0	-1.930167	-2.256762	-0.473087
20	1	0	2.098607	4.309934	1.626436
21	1	0	3.191432	-3.169765	2.119294
22	1	0	1.851296	0.243125	-1.458870
23	1	0	4.594679	0.576777	-0.120662
24	1	0	4.019013	1.581760	-1.447461
25	1	0	3.725302	-0.465216	-2.876271
26	1	0	4.434638	-1.445018	-1.569780
27	1	0	0.850768	-3.826408	2.762988
28	1	0	0.123784	-2.287997	3.308738
29	1	0	-0.509917	-3.103003	1.849342
30	1	0	-1.415618	3.182964	1.446085
31	1	0	-0.623657	2.719369	2.978895
32	1	0	-0.317939	4.332424	2.273976
33	1	0	6.077929	-0.697150	-3.014387

6'a

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.043351	-1.594645	3.318254
2	7	0	-0.036504	-1.783482	2.489461
3	6	0	-0.035131	-0.790425	1.556612
4	7	0	1.046884	-0.059765	1.899960
5	7	0	1.734108	-0.539220	2.989452
6	6	0	1.472030	1.190088	1.266588
7	6	0	2.200358	0.984110	-0.073380
8	6	0	3.468622	0.153284	0.091253
9	35	0	4.475682	0.092842	-1.602912
10	46	0	-1.183052	-0.244699	-0.021215
11	35	0	-2.398339	0.572712	-2.060408
12	6	0	-1.052331	-2.829817	2.647189
13	6	0	-0.905784	1.656237	0.631298
14	7	0	0.293984	2.043509	1.115004
15	7	0	0.351281	3.356734	1.511834
16	6	0	-0.857601	3.778786	1.268956
17	7	0	-1.654545	2.788803	0.745426
18	6	0	-3.083098	2.925456	0.442672
19	35	0	-1.238847	-2.616001	-0.846635
20	1	0	-1.202081	4.785529	1.454856
21	1	0	1.283485	-2.249298	4.143235
22	1	0	2.117496	1.688383	1.990526
23	1	0	2.449684	1.978228	-0.459062
24	1	0	1.518627	0.510210	-0.787113
25	1	0	3.254813	-0.884123	0.346981
26	1	0	4.152071	0.575288	0.829956
27	1	0	-0.604439	-3.667276	3.186027
28	1	0	-1.901677	-2.436862	3.212765
29	1	0	-1.372098	-3.144479	1.651838
30	1	0	-3.302361	2.316283	-0.436403
31	1	0	-3.675865	2.588155	1.297478
32	1	0	-3.293557	3.977322	0.238605

6'b

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.267403	-2.509931	1.939943
2	7	0	-0.054866	-2.282948	1.641109
3	6	0	-0.123197	-1.191261	0.831488
4	7	0	1.171696	-0.830444	0.698469
5	7	0	2.052135	-1.631106	1.383005
6	6	0	1.596358	0.369788	-0.042024
7	6	0	3.108415	0.599625	-0.015091
8	6	0	3.850548	-0.421325	-0.873275
9	35	0	5.777229	0.005478	-0.920009
10	46	0	-1.585432	-0.073503	-0.011925
11	35	0	-3.212971	1.441392	-1.176033
12	6	0	-1.190012	-3.052267	2.161079
13	6	0	-0.500756	1.518843	0.619857
14	7	0	0.846881	1.505887	0.518800
15	7	0	1.462041	2.621187	1.028775
16	6	0	0.456520	3.333980	1.451219
17	7	0	-0.748279	2.708644	1.231854

18	6	0	-2.058995	3.220438	1.645206
19	35	0	-2.694829	-2.142487	-0.903406
20	1	0	0.549376	4.304899	1.915495
21	1	0	1.608518	-3.326405	2.559585
22	1	0	1.241101	0.242699	-1.068492
23	1	0	3.472666	0.573028	1.014181
24	1	0	3.288237	1.606583	-0.398594
25	1	0	3.519161	-0.407419	-1.912821
26	1	0	3.779694	-1.429998	-0.471997
27	1	0	-0.851736	-4.068152	2.375441
28	1	0	-1.565810	-2.585796	3.075910
29	1	0	-1.966883	-3.065001	1.394018
30	1	0	-2.793368	2.911378	0.898716
31	1	0	-2.321546	2.816170	2.626726
32	1	0	-2.004545	4.309841	1.696600

7'a

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	1.070707	0.766898	3.096667
2	7	0	0.423840	0.777188	1.884632
3	6	0	-0.468755	-0.221922	1.718736
4	7	0	-0.388303	-0.896182	2.899736
5	6	0	0.550108	-0.272007	3.686844
6	6	0	0.696591	1.848088	0.923469
7	6	0	1.570129	1.390883	-0.252731
8	6	0	2.952723	0.933729	0.199661
9	8	0	3.627170	0.492217	-1.000423
10	46	0	-1.524201	-0.373244	-0.005734
11	35	0	-2.632153	-0.401132	-2.259694
12	6	0	-1.207709	-2.042054	3.308492
13	6	0	-1.648550	1.649442	0.071582
14	7	0	-2.589856	2.599738	-0.186669
15	6	0	-2.031396	3.832583	0.054270
16	7	0	-0.797237	3.739418	0.462535
17	7	0	-0.586965	2.382706	0.468910
18	6	0	-3.984918	2.364518	-0.573516
19	35	0	-1.083282	-2.843294	-0.107641
20	1	0	-2.561414	4.764064	-0.080651
21	1	0	0.819108	-0.610435	4.676726
22	1	0	1.176648	2.646816	1.489894
23	1	0	1.667498	2.234013	-0.945097
24	1	0	1.063204	0.576950	-0.782037
25	1	0	2.900177	0.100909	0.906279
26	1	0	3.517361	1.754162	0.658698
27	1	0	-0.661023	-2.603689	4.068739
28	1	0	-2.157364	-1.688992	3.719970
29	1	0	-1.381549	-2.665175	2.429085
30	1	0	-4.012824	1.493299	-1.230713
31	1	0	-4.591149	2.188618	0.319477
32	1	0	-4.350823	3.248032	-1.100690
33	16	0	5.184559	-0.010736	-0.787627
34	6	0	5.312301	-0.911829	-2.332802
35	1	0	6.329036	-1.307730	-2.380618
36	1	0	4.581115	-1.721082	-2.327043
37	1	0	5.131293	-0.220932	-3.157443
38	8	0	5.225520	-0.933205	0.345558
39	8	0	6.067657	1.152259	-0.813479

7'b

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	1.634575	-1.201658	1.775082
2	7	0	0.747055	-0.546410	0.958574
3	6	0	-0.508982	-1.043617	0.992664
4	7	0	-0.404703	-2.074120	1.875336
5	6	0	0.897520	-2.132151	2.312138
6	6	0	1.117382	0.646977	0.179640
7	6	0	2.581976	1.045931	0.332299
8	6	0	3.530527	0.064228	-0.349881
9	8	0	4.830707	0.707093	-0.325061
10	46	0	-1.991577	-0.138518	-0.050984
11	35	0	-3.640625	1.126397	-1.459270
12	6	0	-1.494744	-2.940192	2.336575
13	6	0	-1.141667	1.596042	0.566028
14	7	0	-1.570311	2.785203	1.070265
15	6	0	-0.464587	3.551494	1.353356
16	7	0	0.646230	2.930655	1.073032
17	7	0	0.202937	1.726123	0.587780
18	6	0	-2.961142	3.171029	1.329491
19	35	0	-2.811037	-2.357253	-0.889248
20	1	0	-0.519220	4.552374	1.755976
21	1	0	1.261004	-2.869562	3.012852
22	1	0	0.883170	0.421365	-0.864518
23	1	0	2.840021	1.148736	1.388875
24	1	0	2.697269	2.029100	-0.131854
25	1	0	3.248157	-0.120401	-1.392330
26	1	0	3.581683	-0.883459	0.190666
27	1	0	-1.067499	-3.891395	2.660628
28	1	0	-2.017285	-2.464949	3.171304
29	1	0	-2.178838	-3.095779	1.500033
30	1	0	-3.584542	2.729616	0.549321
31	1	0	-3.268777	2.807525	2.313883
32	1	0	-3.030026	4.260439	1.299220
33	16	0	6.086532	-0.262843	-0.773799
34	6	0	7.336440	1.023821	-0.763046
35	1	0	8.279577	0.542373	-1.030271
36	1	0	7.069016	1.780787	-1.501285
37	1	0	7.394737	1.449278	0.239675
38	8	0	6.352962	-1.223568	0.293818
39	8	0	5.853943	-0.730864	-2.138014

Electrochemical properties

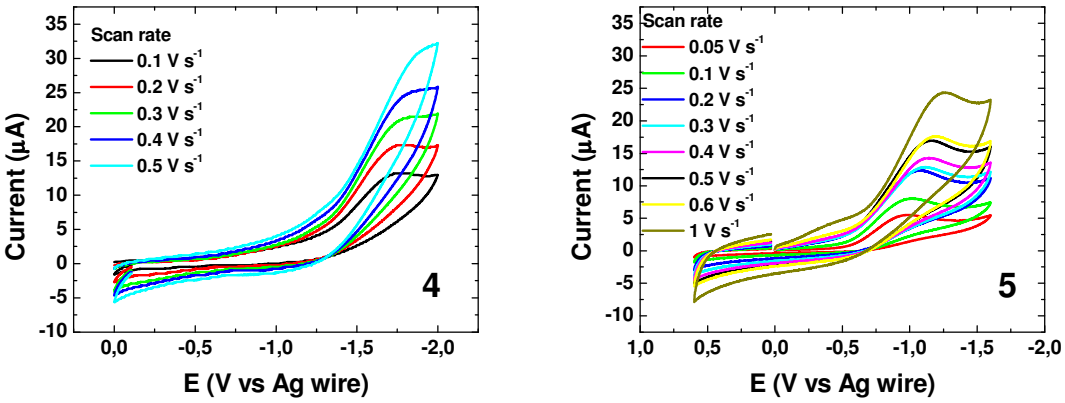


Figure S1. Cyclic voltammogram of 1,1'-(3-hydroxypropane-1,1-diyl)bis(4-butyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene)palladium(II) dibromide (**4**) and 1,1'-(3-hydroxypropane-1-1diyl)bis(4-butyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene)palladium(II) diiodide (**5**). [Pd(II)] = 1.5 mM in DMF. Electrolyte = (*n*-$Bu_4N)_3(PO_4)$ (0.1 M). Platinum electrode vs silver wire pseudo-reference electrode at a different scan rates (V s^{-1}).

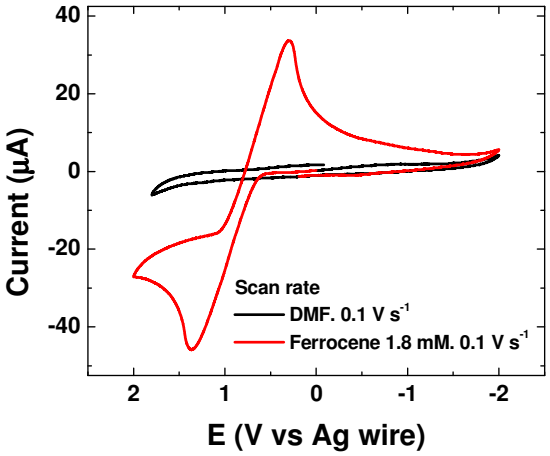


Figure S2. Control experiments. 1.8 mM in DMF. Electrolyte = (*n*-$Bu_4N)_3(PO_4)$ (0.1 M). Platinum electrode vs silver wire pseudo-reference electrode at a scan rate of 0.1 V s^{-1}.

The reduction potential is 0.303 V. The ferrocinium/ferrocene redox couple has been reported to be 0.46 V vs a saturated calomel electrode.[3] The anodic to cathodic peak separation ($\Delta Ep = Epa - Epc$) is 1.08 eV.

UV-Vis spectra

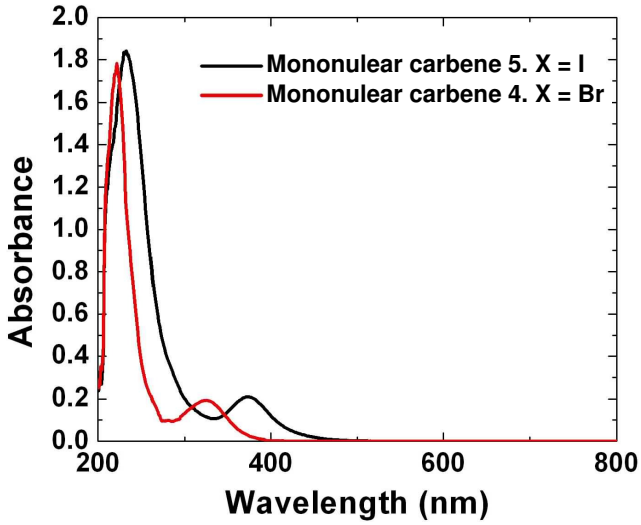


Figure S3. Absorption spectra of 1,1'-(3-hydroxypropane-1,1-diyl)bis(4-butyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene)palladium(II) dibromide (**4**) and 1,1'-(3-hydroxypropane-1,1-diyl)bis(4-butyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene)palladium(II) diiodide (**5**). 0.3 mM in THF (spectroscopic grade).

References

1 G. M. Sheldrick, *A computer Program for the Determination of Crystal Structure*, University of Göttingen, Germany, 1997.

2 *International Tables of X-ray Crystallography*, ed. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99–100 and 149.

3 T. Nyokong, *Synth. Met.*, 1994, *66,* 107–116.