Supporting Information:

Abnormal carbenes derived from the 1, 5-cycloaddition product between azides and alkynes: Structural characterization of Pd(II) complexes and their catalytic properties.

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Experimental Section

General and Instrumentation

Complex $PdCl_2(MeCN)_2$ was synthesized according to reported procedure.[i] All reagents were used as supplied until mentioned otherwise. Dichloromethane was dried over CaH_2 and degassed. All complexation reactions were carried out under inert gas atmosphere excluding light due to the silver. All catalysis experiments were carried out under inert gas atmosphere in dried solvents unless otherwise mentioned. The yields of the catalysis were determined by NMR spectroscopy.

^{1}H- and ^{13}C-NMR-Spectroscopy was performed on a Bruker AC 250 spectrometer or a Joel ECS 400 MHz spectrometer. Elemental analysis was performed on a Perkin Elmer Analyser 240. Mass spectrometry experiments were carried out on a Bruker Daltronics Mictrotof-Q mass spectrometer. Xray data was collected at 100 K using a Bruker Kappa Apex II duo diffractometer. Calculations were performed with the X-Step 32 revision 1.05f and SHELXL-97 program.[ii]

Synthesis of ligands

1,5-Diphenyl-*1H*-1,2,3-triazole (1)

The compound was synthesized according to a reported procedure.[iii]

1-Benzyl-5-phenyl-*1H*-1,2,3-triazole (2)

Triazole **2** was synthesized according to a reported procedure.[iv]

3-Methyl-1,5-diphenyl-*1H*-1,2,3-triazol-3-ium iodide (3)

Compound **1** (1 eq; 0.211 g; 0.95 mmol) was dissolved in acetonitrile (10 ml) and an excess of methyliodide (15 eq; 2.02 g; 14.3 mmol; 0.88 ml) was added. The reaction mixture was heated up to 60 °C and stirred for 24 hours. After cooling to room temperature the mixture was poured into diethylether (250 ml) upon which a white solid was precipitated. The mixture was stirred for 20 minutes and the white solids were filtered, washed with diethylether and dried under air to give a white solid in a good yield of 77% (0.268 g, 0.73 mmol). ^{1}H-NMR (400 MHz, DMSO d-$_6$, 25°C, TMS): δ 4.44 (s, 3H, N-C*H*$_3$); 7.30 – 7.37 (m, 2H, Aryl-*H*); 7.41 – 7.53 (m, 3H, Aryl-*H*); 7.55 – 7.69 (m, 5H, Aryl-*H*); 9.34 (s, 1H, Triazol-*5H*) ^{13}C-NMR (100 MHz, DMSO d-$_6$, 25°C, TMS): δ 40.9 (N-*C*H$_3$), 123.1, 126.8, 129.7, 129.8, 130.6, 130.7, 131.9, 132.5, 134.4, 143.0 ; MS (ESI) 236.1176 [$C_{15}H_{14}N_3^+$]; elemental analysis calcd for $C_{15}H_{14}N_3I$ (%) C 49.06, H 3.89, N 11.57; found C 48.90, H 3.95, N 11.20.

1-Benzyl-3-methyl-5-phenyl-1*H*-1,2,3-triazol-3-ium iodide (4)

Compound **2** (1 eq; 0.212 g; 0.9 mmol) was dissolved in acetonitrile (10 ml) and an excess of methyliodide (15 eq; 1.91 g; 13.5 mmol; 0,84 ml) was added. The reactions mixture was heated up to 60 °C and stirred for 24 hours. After cooling to room temperature the mixture was poured into diethylether (250 ml) upon which a white solid was precipitated. The mixture was stirred for 20 minutes and the white solids were filtered, washed with diethylether and dried under air to give a white solid in a good yield of 77% (0.282 g, 0.7 mmol). ^{1}H-NMR

(250 MHz, $CDCl_3$, 25°C, TMS): δ 4.60 (s, 3 H; Methyl-H); 5.64 (s, 2 H); 7.08 – 7.14 (m, 2 H); 7.30 – 7.38 (m, 3 H); 7.51 – 7.60 (m, 5 H); 9.60 (s, 1 H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25°C, TMS): δ 41.6, 55.3, 121.6, 128.2, 129.4, 129.7, 129.8, 129.9, 131.1, 131.3, 132.1, 142.9; MS (ESI) 250.1327 [$C_{16}H_{16}N_3^+$]; elemental analysis calcd for $C_{16}H_{16}N_3I$ (%) C 50.94, H 4.28, N 11.14; found C 50.87, H 4.34, N 11.15. Single crystals were grown by layering a dichloromethane solution with diethylether at 8 °C.

1-Benzyl-3-isopropyl-5-phenyl-1*H*-1,2,3-triazol-3-ium iodide (5)

Compound **2** (1 eq; 0.212 g; 0.9 mmol) was dissolved in acetonitrile (10 ml) and an excess of isopropyliodide (15 eq; 2.3 g; 13.5 mmol; 1.35 ml) was added. The reactions mixture was heated up to 60 °C and stirred for 24 hours. After 24 hours the same amount of Isopropyliodide was added again and the mixture was stirred for another 24 hours. After cooling to room temperature the mixture was poured into diethylether (250 ml) upon which a white solid was precipitated. The mixture was stirred for 20 minutes and the white solids were filtered, washed with diethylether and dried under air to give a white solid in a moderate yield of 42% (0.153 g, 0.38 mmol). ^{1}H-NMR (250 MHz, $CDCl_3$, 25°C, TMS): δ 1.80 (d, J = 6.75 Hz, 6 H); 5.50 (hept, J = 6.75 Hz, 1 H); 5.68 (s, 2 H); 7.06 – 7.08 (m,2 H); 7.32 – 7.38 (m, 3 H); 7.52 – 7.60 (m, 5 H); 9.69 (s, 1 H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25°C, TMS): δ 22.4, 55.5, 59.0, 121.8, 128.0, 129.0, 129.4, 129.6, 129.7, 129.9, 131.4, 132.0, 142.8; MS (ESI) 278,1651 [$C_{18}H_{20}N_3^+$]; elemental analysis calcd for $C_{18}H_{20}N_3I$ (%) C 53.34, H 4.97, N 10.37; found C 52.65, H 5.15, N 10.13.

Synthesis of the Palladium(II)-Complexes:

2 equivalents of the Carbene-Precursor were mixed with 7 equivalent of silver(I) oxide and stirred at room temperature in dichloromethane (15 ml) excluded from air and light for 24 hours. Afterwards the mixture was filtered over Celite and trans-

bis(acetonitril)dichloropalladium(II) was added and the mixture was stirred excluded from light for another 24 hours. The crude mixture was then filtered over Celite and the solvents were evaporated. The crude products were then recrystallized from Dichloromethane/Hexane (1:9) to give a yellow microcrystalline powder in fair yields.

Bis(3-methyl-1,5-diphenyl-1*H*-1,2,3-triazol-4-yl)palladium(II)dichlorid (6)

The reaction was carried out like described above using Carbene-Precursor **3** (2 eq; 0.125 g; 0.34 mmol), silver(I) oxide (7 eq; 0.274 g; 1.19 mmol) and $PdCl_2(MeCN)_2$ (1 eq; 0.044 g; 0.17 mmol). The product was isolated as a yellow powder in 54% yield. (0.059 g; 0.09 mmol)) ^{1}H-NMR (400 MHz, DMSO d-$_6$, 25°C, TMS): 3.79 (s, 6H, N-CH_3); 7.11 – 7.16 (m, 4H, Aryl-*H*); 7.26 – 7.31 (m, 4H, Aryl-*H*); 7.35 – 7.40 (m, 4H, Aryl-*H*); 7.44 – 7.50 (m, 8H, Aryl-*H*); ^{13}C-NMR (100 MHz, DMSO d-$_6$, 25°C, TMS): 41.3 (N-*C*H$_3$), 125.4, 127.1, 129.0, 129.3, 129.8, 130.0, 131.1, 134.2, 143.0, 148.8 (all Aryl-*C*),): (carben-C not observed); MS (ESI) 611.0948 [$C_{30}H_{26}N_6ClPd^+$]; elemental analysis calcd for $C_{30}H_{26}N_6Cl_2Pd\ CH_2Cl_2$ (%) C 50.81, H 3.85, N 11.47; found C 51.41, H 4.06, N 11.68 Single crystals suitable for X-ray analysis were grown from saturated solutions of dichloromethane layered with hexane at room temperature..

Bis(1-benzyl-3-methyl-5-phenyl-1*H*-1,2,3-triazol-4-yl)palladium(II)di-chlorid (7)

The reaction was carried out like described above using Carbene-Precursor **4** (2 eq; 0.200 g; 0.5 mmol), silver(I) oxide (7 eq; 0.404 g; 1.75 mmol) and $PdCl_2(MeCN)_2$ (1 eq; 0.068 g; 0.25 mmol). The product was isolated as a yellow powder in 60% yield. (0.109 g; 0.16 mmol)) ^{1}H-NMR (400 MHz, DMSO d-$_6$, 120°C, TMS): δ 3.56 (s, 6H, N-CH_3, *cis*); 4.35 – 4.47 (m, 6H, N-CH_3, *trans*); 5.33 (s, 4H, CH_2-Ph, *cis*); 5.62 (s, 4H, CH_2-Ph, *trans*); 6.85 – 6.94 (m, 4H, Aryl-*H*); 6.96 – 7.06 (m, 4H, Aryl-*H*); 7.10 – 7.20 (m, 4H, Aryl-*H*); 7.22 – 7.33 (m, 12H, Aryl-*H*); 7.43 – 7.57 (m, 12H, Aryl-*H*); 7.62 – 7.71 (m, 2H, Aryl-*H*); 7.72 – 7.80 (m, 2H, Aryl-*H*) (Aryl *cis*/*trans* mixture) ^{13}C-NMR (125 MHz, DMSO d-$_6$, 25°C, TMS): δ 41.2 42.1, 42.3 (N-*C*H$_3$, cis/trans- syn/anti), 53.9, 54.2, 54.4, 55.8 (N-*C*H$_2$-Ph, cis/trans - syn/anti), 127.1 127.6 127.8,, 128.2, 128.3, 128.6, 128.7, 128.8, 128.9, 129.3, 129.5, 129.6, 129.7, 129.8, 12.9., 130.9, 131.0, 131.1, 131.4, 134.4, 134.6, 134.7, 143.6, 143.7, 149.8, 154.5 (all Aryl-*C*, cis/trans – syn/anti), 172.4(Carbene-trans), 172.6 (Carbene-cis); MS (ESI) 639.1246 [$C_{32}H_{30}N_6ClPd^+$]; elemental analysis calcd for $C_{32}H_{30}N_6Cl_2Pd$ (%) C 56.86, H 4.47, N 12.43; found C 56.01, H 4.73, N 12.04. Single crystals suitable for X-ray analysis were grown from saturated solutions of dichloromethane layered with hexane at 8°C.

Bis(1-benzyl-3-isopropyl-5-phenyl-1*H*-1,2,3-triazol-4-yl)palladium(II)-di-chlorid (8)

The reaction was carried out like described above using Carbene-Precursor **5** (2 eq; 0.152 g; 0.38 mmol), silver(I) oxide (7 eq; 0.307 g; 1.33 mmol) and $PdCl_2(MeCN)_2$ (1 eq; 0.049 g; 0.19 mmol). The product was isolated as a yellow powder in 67% yield. (0.093 g; 0.13 mmol)) ^{1}H-NMR (400 MHz, DMSO d-$_6$, 100°C, TMS): δ 1.50 – 1.71 (m, 12H, C*H*$_3$); 5.51 – 5.76 (m, 6H. 2x C*H*$_2$-Ph, 2x C*H*-Me$_2$); 6.82 – 7.00 (m, 4H, Aryl-*H*); 7.19 – 7.28 (m, 6H, Aryl-*H*); 7.41 – 7.57 (m, 6H, Aryl-*H*); 7.69 – 7.83 (m, 2H, Aryl-*H*); 7.88 – 8.08 (m, 2H, Aryl-*H*) ^{13}C-NMR (125 MHz, DMSO d-$_6$, 25°C, TMS): δ 21.9, 22.3, 22.3, 22.4, 22.8, 22.9, 23.1, 23.7, 23.9 (C-(*C*H$_3$)$_2$, 54.2, 54.3 (N-*C*H$_2$-Ph, cis/trans), 58.7, 58.8 (N-*C*H), 126.9, 127.3, 127.5, 127.7, 128.7, 129.0, 129.3, 129.4, 129.5, 129.6, 130.4, 130.6, 131.1, 134.1, 134.4, 134.5, 142.1, 144.4, 148.7 (all Aryl-*C*, cis/trans – syn/anti) ; MS (ESI) 695.1874 [$C_{36}H_{38}N_6ClPd^+$]; elemental analysis calcd for $C_{36}H_{38}N_6Cl_2Pd$ CH_3CN 1.5 CH_2Cl_2 (%) for C 52.68, H 4.92, N 10.89; found C 52.80, H 4.90, N 11.08. Single crystals suitable for X-ray analysis were grown from saturated solutions of dichloromethane layered with hexane at 8°C.

Catalysis

Suzuki-Miyaura Couplings using Aryl-bromides

4-bromobenzaldehyde (1 eq, 0.185 g, 1 mmol), the corresponding boronic acid (1.2 eq, 1.2 mmol) and potassium carbonate (1.5 eq, 0.207 g, 1.5 mmol) were mixed in a small vessel and dissolved in water (ca. 3 ml). After that, the corresponding catalyst (0.5 mol%) was added. The mixtures were stirred under air at room temperature for 5 hours. The crude reaction mixture were poured into 30 ml of DCM and extracted with water (20 ml) for 5 times. Finally, the combined aqueous layers were extracted one last time with 20 ml of DCM. The combined organic layers were dried over sodium sulfate (20 g), filtered and evaporated to dryness. Yields were determined via proton NMR spectroscopy with the help of the integrals of the aldehyde protons.

Suzuki-Miyaura Cpouplings using Aryl-chlorides

4-chlorobenzaldehyde (1 eq, 0.141 g, 1 mmol), boronic acid (1.2 eq, 0.146 g, 1.2 mmol) and Cs_2CO_3 (2 eq, 0.650 g, 2 mmol) were mixed in a small tube under inert gas atmosphere. Afterwards 5ml of solvent was added. After that, the corresponding catalyst (1 or 2 mol%) was added. The mixtures were stirred under argon atmosphere overnight (15 hours). The crude reaction mixture were poured into 30 ml of DCM and extracted with water (20 ml) for 5 times. Finally, the combined aqueous layers were extracted one last time with 20 ml of DCM. The combined organic layers were dried over sodium sulfate (20 g), filtered and evaporated to dryness. Yields were determined via proton NMR spectroscopy with the help of the integrals of the aldehyde protons.

X-ray structural analyses

Single crystals of **4** were grown by layering a dichloromethane solution with diethylether at 8 °C. Single crystals of **7** and **8** suitable for X-ray analysis were grown from saturated solutions of dichloromethane layered with hexane at 8°C. X-ray data were collected at 100 K using a Bruker Kappa Apex II duo diffractometer. Calculations were performed with the X-Step 32 revision 1.05f and SHELXL-97 program. *The quality of the data set for **8** is not very high because of the small size of its crystals. Despite several attempts we were not able to grow better crystals for **8**. We have used the data set of **8** here just to discuss connectivity, and not bond lengths.* CCDC-846888 (**4**), 929861 (**6**), 846894 (**7**) and 892296 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.uk/data_request.cif.

Table S1: Crystallographic details for **4**, **6** **7** and **8**.

	4	**6**	**7**	**8**
Chemical formula	$C_{16}H_{16}N_3I$	$C_{30}H_{28}N_6Cl_2Pd_2$ 0.5 H_2O	$C_{32}H_{30}Cl_2N_6Pd$	$C_{36}H_{38}Cl_2N_6Pd$
M_r	377.22 g mol^{-1}	657.88	675.92 g mol^{-1}	732.02 g mol^{-1}
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/n	C2	P2(1)/c
a (Å)	9.3307(6);	13.4987(18)	16.427(3);	24.7893(14);
b (Å)	18.6233(13);	14.889(2)	8.2599(12);	15.1436(9);
c (Å)	9.6719(7)	14.0557(19)	12.1501(17)	19.3799(11)
β (°)	114.796(3)	97.797(3)	116.214(7)	113.010(2)
V (Å^3)	1525.72(18)	2798.8(7)	1479.0(4)	6696.4(7)
Z	4	2	2	8
Densitiy (g cm^{-3})	1.642	1.561	1.518	1.452
F(000)	744	1336	688	3008
Radiation Type	Mo K_α	Mo K_α	Mo K_α	Cu K_α
μ (mm^{-1})	2.093	0.888	0.841	6.210
Crystal size	0.28 x 0.24 x 0.18	0.42 x 0.38 x 0.32	0.18 x 0.14 x 0.09	0.20 x 0.12 x 0.10
Meas. Refl.	32385	36889	4408	38116
Indep. Refl.	4690	6416	2328	10976
Obsvd. [$I > 2\sigma(I)$] refl.	4336	5871	1868	9820
R_{int}	0.0180	0.0153	0.0983	0.0942
R [$F^2 > 2\sigma(F^2)$], wR(F^2)	0.0158, 0.0389	0.0246, 0.0669	0.0620, 0.1314	0.0877, 0.2283
S	1.053	1.054	1.069	1.073
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.525; -0.275	1.042; -0.373	1.521; -2.666	3.104; -0.698

Table S2: Selected bonds lengths (Å) and bond angles (°) for **4**.

N1 – N2	1.329(2)
N2 – N3	1.314(2)
N3 – C1	1.343(2)
C1 – C2	1.380(2)

C2 – N1	1.372(2)
N3 – C16	1.460(2)
C2 – C3	1.467(2)
N1 – C9	1.468(2)

C2 – C1 – N3	106.4(1)

Table S3: Selected bond lengths (Å) and bond angles (°) for **6**.

	6
Pd – Cl1	2.3775(5)
Pd1 – C1	1.9894(19)
C1 – C2	1.388(2)
N1 – C2	1.366(2)
N1 – N2	1.321(2)
N2 – N3	1.327(2)
N3 – C16	1.471(2)
C2 – C3	1.470(2)
N1 – C9	1.449(2)

C1 – Pd1 – Cl1	91.33(5)
C1 – Pd1 – Cl2	174.26(5)
C2 – C1 – N3	102.86(16)

Table S4: Selected bond lengths (Å) and bond angles (°) for **7**.

	7
Pd – Cl1	2.373(3)
Pd1 – C1	1.99(1)
C1 – C2	1.39(2)
N1 – C2	1.37(1)
N1 – N2	1.31(2)
N2 – N3	1.32(1)
N3 – C16	1.44(2)
C2 – C3	1.50(2)
N1 – C9	1.45(2)

C1 – Pd1 – Cl1	90.7(4)°
C1 – Pd1 – Cl1	174.3(4)°
C2 – C1 – N3	104(1)

Figure S1: Temperature depended NMR of **7** in dmso-d_6

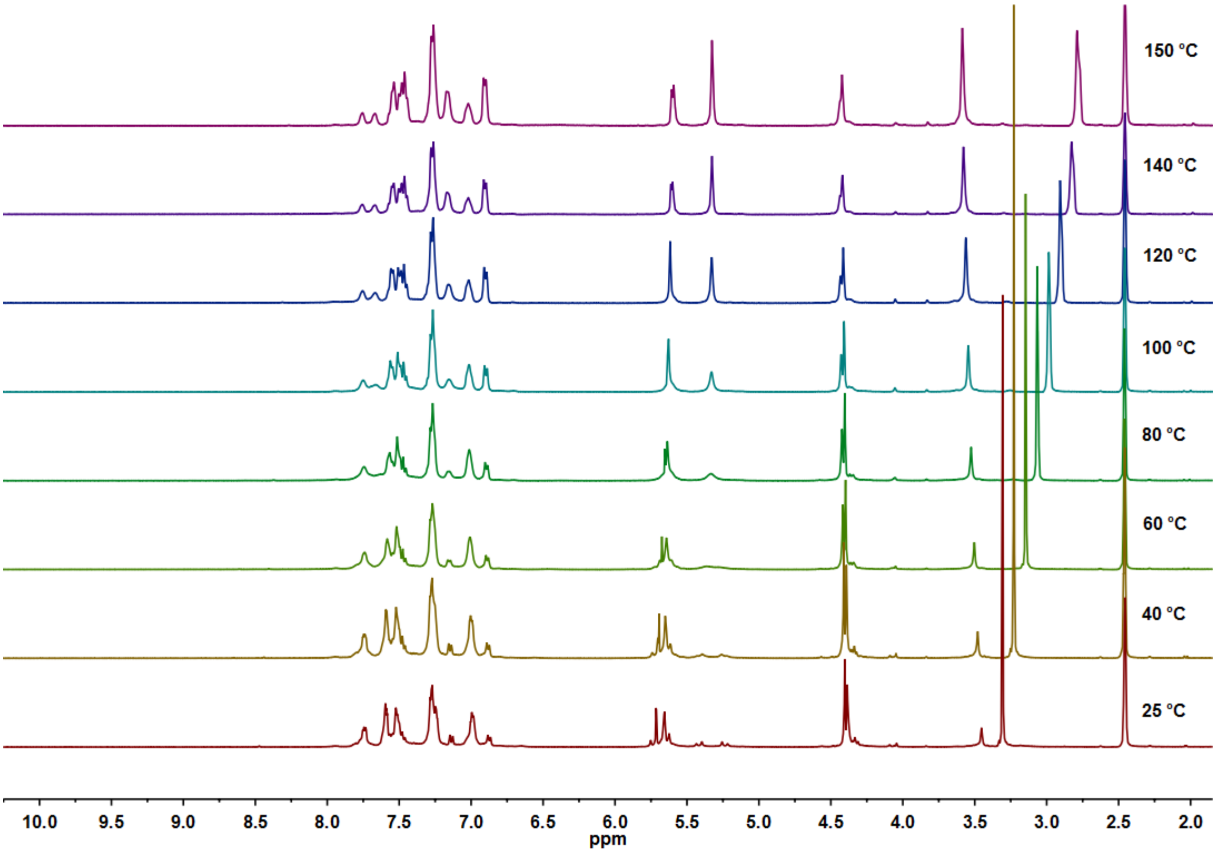


Figure S2: ORTEP plot of **4**.

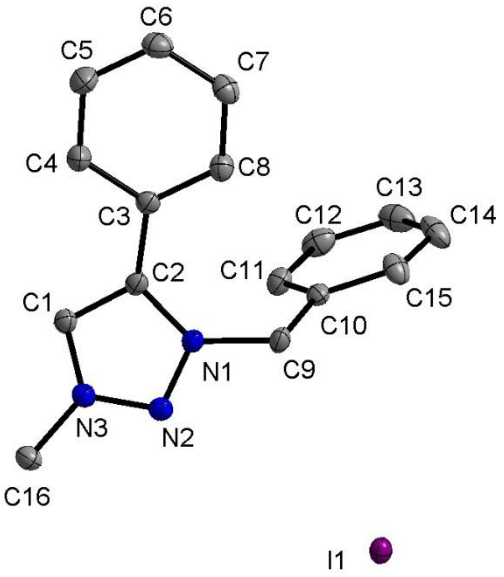


Figure S3: ORTEP plot of **6**

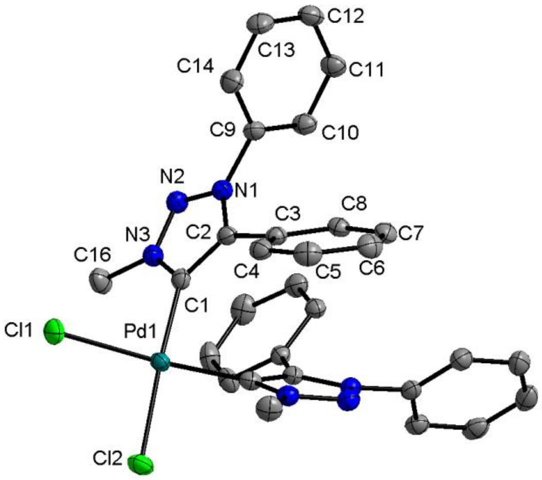
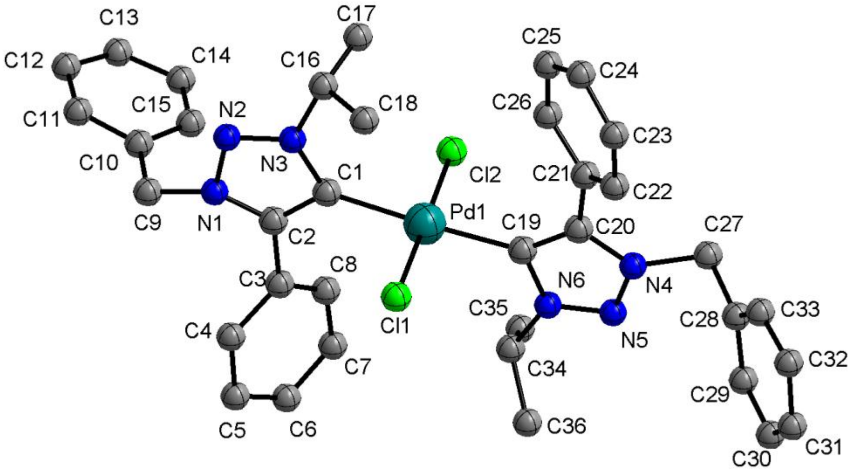


Figure S4: X-ray structure of **8**.



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[iv] L. Zhang, X. Chen, P. Xue, H.H.Y. Sun, I.D. Williams, K.B. Sharpless, V.V. Fokin, G. Jia, *J. Am. Chem. Soc.*, 2005, **127**, 15998 - 15999