Electronic Supporting Information for:

Oxidation Reactions of a Nucleophilic Palladium Carbene: Mono and Bi-radical Carbenes

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1 EPR Spectra

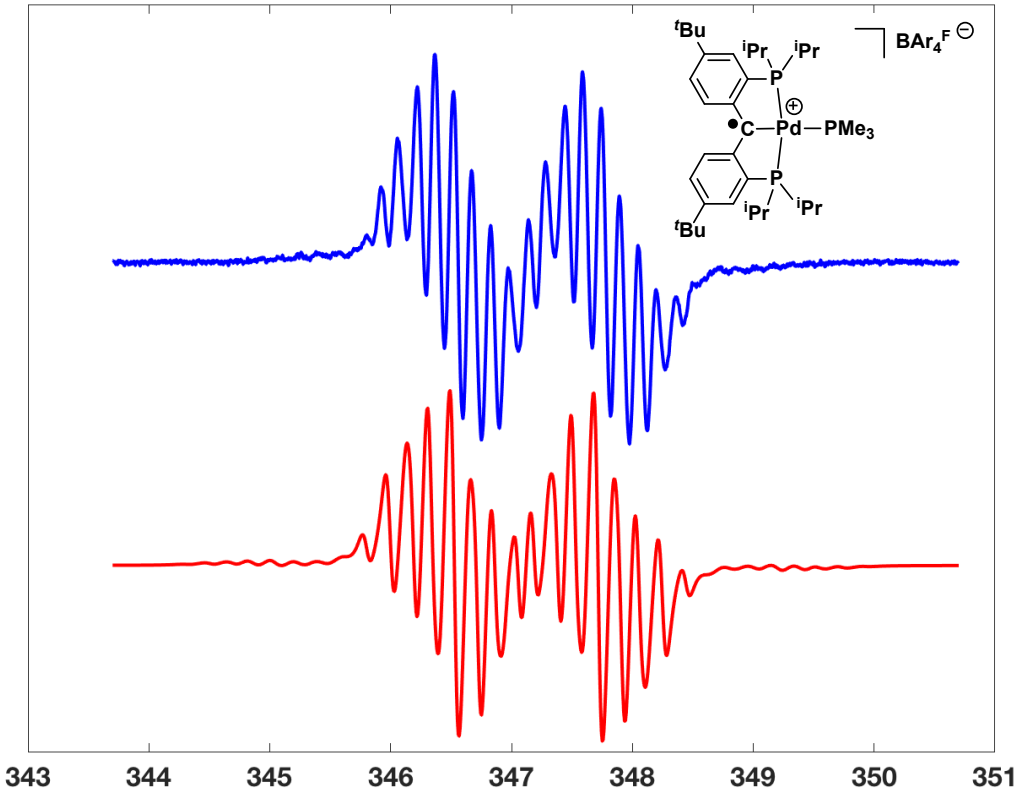

Figure S1. EPR spectrum of [{PC$^{\bullet}$(sp^2)P}$^{t\mathrm{Bu}}$Pd(PMe$_3$)][BAr$^{\mathrm{F}}_4$] (**2**) (4 mM solution in CH_2Cl_2 298 K); the blue line represents the experimental data and the red line represents the simulation with the following parameters: a_1(2H) = 0.34 mT, a_2(2H) = 0.2 mT, a_3(2H) = 0.19 mT, a(^{31}P) = 1.2 mT, g = 2.0200, individual linewidth 0.08 mT (lorentzian lineshape), relative intensity 77.67% for the nonmagnetic Pd isotope species; a_1(2H) = 0.34 mT, a_2(2H) = 0.2 mT, a_3(2H) = 0.19 mT, a(^{31}P) = 1.2 mT, a(^{105}Pd) = 0.6 mT, g = 2.0200, individual linewidth 0.12 mT, relative intensity 22.33% for the ^{105}Pd species.

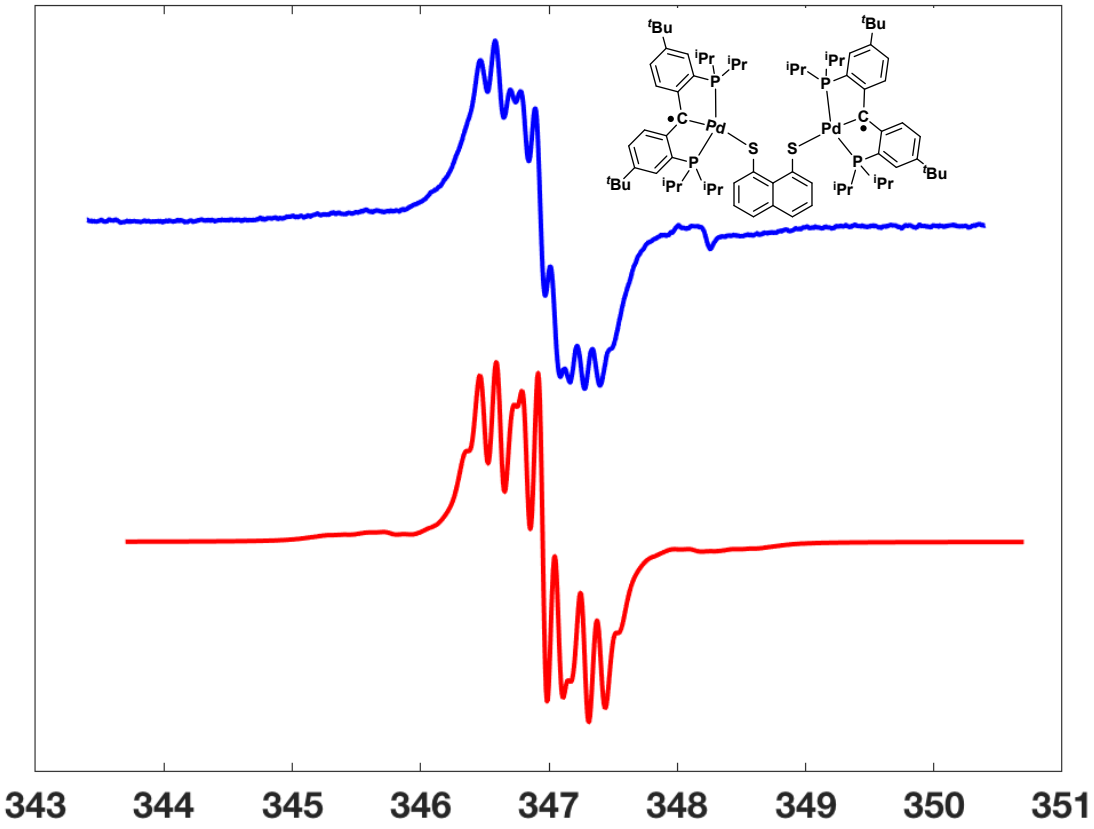

Figure S2. EPR spectrum of [{PC$^{\bullet}$(sp^2)P}$^{t\mathrm{Bu}}$PdS($C_{10}H_6$)SPd{PC$^{\bullet}$(sp^2)P}$^{t\mathrm{Bu}}$] (**4**) (1 mM solution in toluene, 298 K); the blue line represents the experimental data and the red line represents the simulation with the following parameters: a_1(2H) = 0.33 mT, a_2(2H) = 0.13 mT, a_3(2H) = 0.12 mT, g = 2.0210, individual linewidth 0.1 mT (lorentzian lineshape), relative intensity 77.67% for the nonmagnetic Pd isotope species; a_1(2H) = 0.33 mT, a_2(2H) = 0.13 mT, a_3(2H) = 0.12 mT, a(^{105}Pd) = 0.48 mT, g = 2.0210, individual linewidth 0.17 mT, relative intensity 22.33% for the ^{105}Pd species.

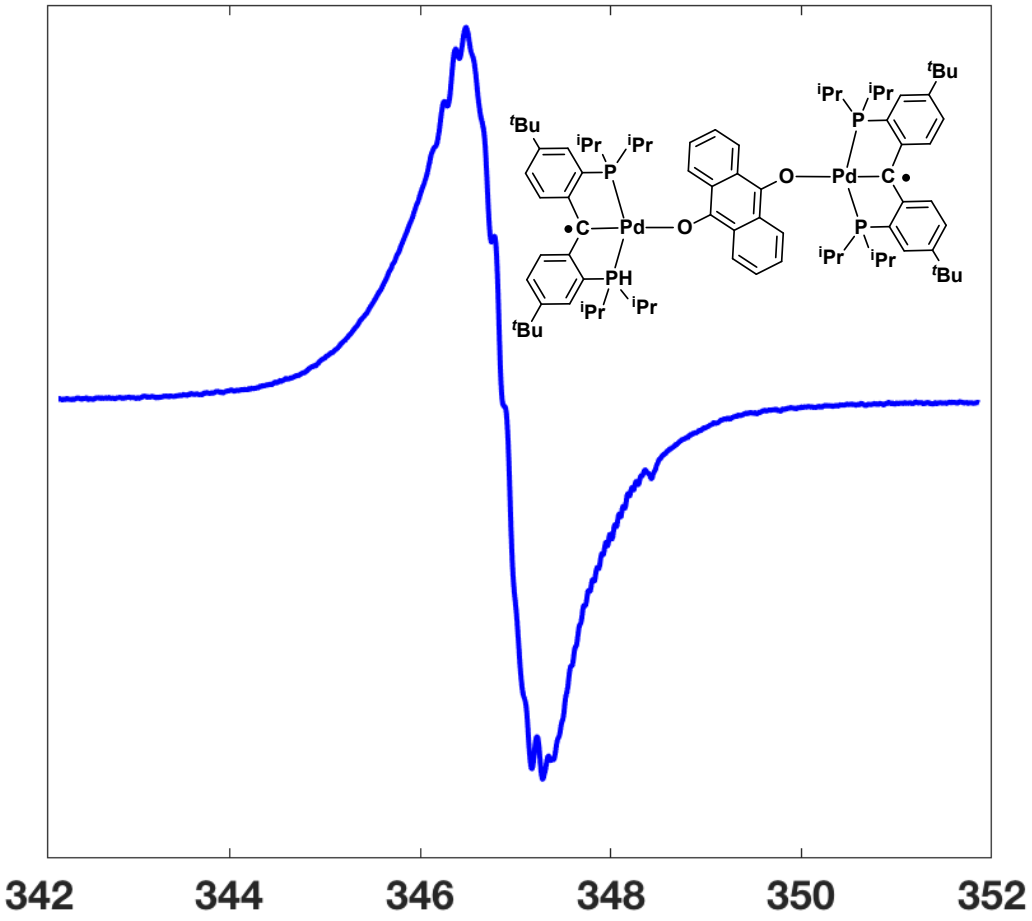

Figure S3. EPR spectrum of [{PC$^{\bullet}$(sp^2)P}$^{t\mathrm{Bu}}$PdO($C_{14}H_8$)OPd{PC$^{\bullet}$(sp^2)P}$^{t\mathrm{Bu}}$] (**5**) at 298 K(100 μM solution in toluene); g = 2.0100, ΔH_{pp} = 0.78 mT.

2 Crystallographic tables

2.1 Crystal data for [{PC•(sp²)P}$^{t\text{Bu}}$Pd(PMe$_3$)][BAr$^{\text{F}}_4$] (2)

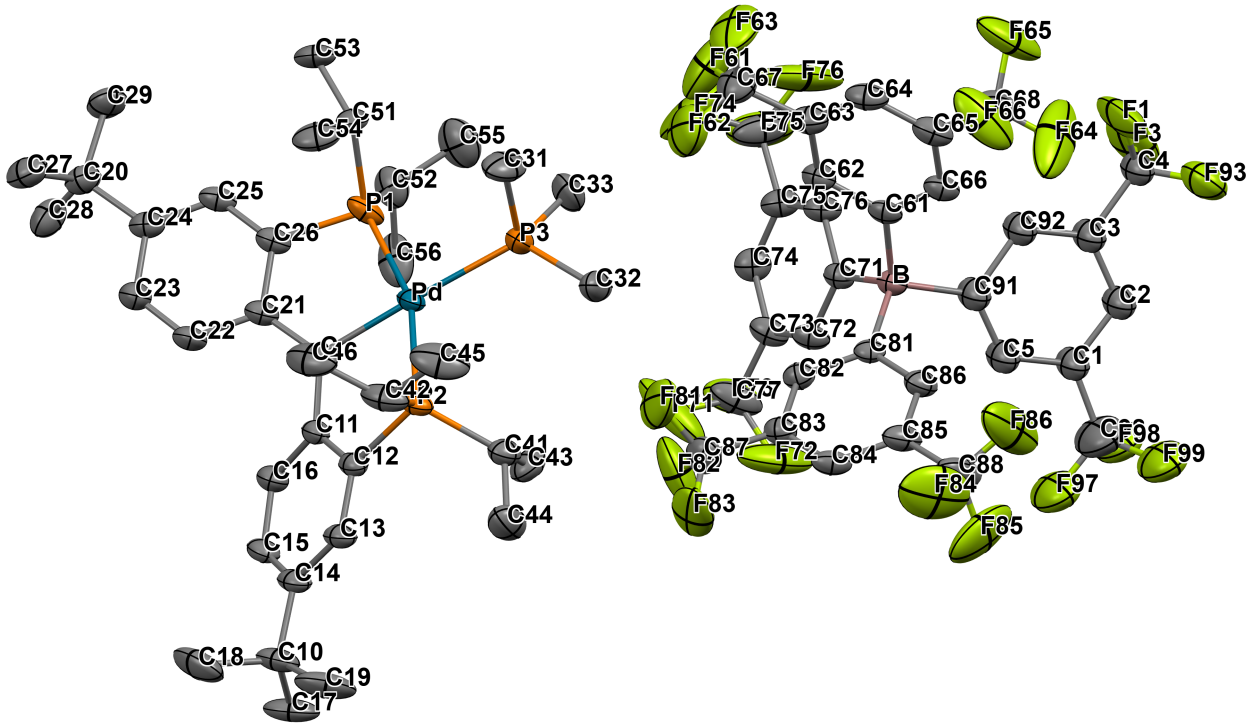

Figure S4. Thermal-ellipsoid representation of [{PC•(sp²)P}$^{t\text{Bu}}$Pd(PMe$_3$)][BAr$^{\text{F}}_4$] (**2**) at 50% probability. Hydrogen atoms were omitted for clarity.

Table S1. Crystal data and structure refinement for [{PC$^{\bullet}$(sp^2)P}$^{t\mathrm{Bu}}$Pd(PMe$_3$)][BAr$^{\mathrm{F}}_4$] (**2**).

Identification code:	pc62a	
Empirical formula:	$C_{68}H_{73}BF_{24}P_3Pd$	
Formula weight:	1556.38	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Triclinic	
Space group:	$P\bar{1}$	
Unit cell dimensions:	a = 13.6492(7) Å	α = 66.0282(14)°
	b = 17.8440(9) Å	β = 76.7560(15)°
	c = 18.4747(9) Å	γ = 88.0975(15)°
Volume:	3993.1(3) Å^3	
Z:	2	
Density (calculated):	1.294 g·cm^{-3}	
Absorption coefficient (μ):	0.384 mm^{-1}	
F(000):	1586	
Crystal size:	0.090 × 0.080 × 0.070 mm^3	
θ range for data collection:	1.354 to 24.999°	
Index ranges:	$-16 \le h \le 16$, $-21 \le k \le 21$, $-21 \le l \le 21$	
Reflections collected:	97651	
Independent reflections:	14055 [R_{int} = 0.0347]	
Completeness to θ = 25.000°:	100.0 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.7454 and 0.6770	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	14055 / 0 / 985	
Goodness-of-fit on F^2:	1.083	
Final R indices [I>2σ(I)]:	R_1 = 0.0500, wR_2 = 0.1349	
R indices (all data):	R_1 = 0.0616, wR_2 = 0.1416	
Extinction coefficient:	n/a	
Largest diff. peak and hole:	1.910 and −0.828 e$^-$·Å^{-3}	

Table S2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [{PC$^\bullet$(sp^2)P}$^{t\mathrm{Bu}}$Pd(PMe$_3$)][BAr$^{\mathrm{F}}_4$] (**2**). U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

atom	x	y	z	U(eq)
Pd	0.82662(2)	0.73644(2)	0.71679(2)	0.027(1)
C(10)	0.6107(3)	1.0980(2)	0.7302(2)	0.046(1)
P(3)	0.76282(6)	0.60028(5)	0.75535(6)	0.038(1)
P(2)	0.69537(7)	0.78267(5)	0.78933(5)	0.030(1)
P(1)	0.98511(7)	0.72999(5)	0.64021(5)	0.036(1)
C(11)	0.8091(2)	0.91820(19)	0.6792(2)	0.031(1)
C(12)	0.7191(2)	0.89290(19)	0.73893(19)	0.029(1)
C(13)	0.6569(3)	0.9498(2)	0.7569(2)	0.034(1)
C(15)	0.7609(3)	1.0585(2)	0.6451(2)	0.038(1)
C(14)	0.6769(3)	1.0339(2)	0.7107(2)	0.035(1)
C(18)	0.6720(5)	1.1456(3)	0.7591(3)	0.076(2)
C(17)	0.5796(4)	1.1571(3)	0.6538(3)	0.060(1)
C(16)	0.8261(3)	1.0036(2)	0.6289(2)	0.038(1)
C(19)	0.5151(4)	1.0580(3)	0.7968(3)	0.073(2)
C(20)	1.3150(3)	0.9303(2)	0.5717(2)	0.039(1)
C(21)	0.9865(2)	0.87771(19)	0.6469(2)	0.032(1)
C(98)	0.0624(12)	0.3941(10)	0.6317(11)	0.103(1)
F(97)	0.0520(6)	0.4657(5)	0.6345(6)	0.103(1)
F(98)	0.0726(5)	0.4192(5)	0.5471(5)	0.103(1)
F(99)	−0.0404(10)	0.3505(9)	0.6797(8)	0.103(1)
C(1)	0.1495(7)	0.3489(6)	0.6535(6)	0.044(1)
C(2)	0.1613(7)	0.2692(5)	0.6556(6)	0.044(1)
C(3)	0.2443(7)	0.2295(5)	0.6797(6)	0.044(1)
C(4)	0.2631(8)	0.1472(6)	0.6735(6)	0.044(1)
F(1)	0.3038(8)	0.0965(5)	0.7302(7)	0.115(3)
F(93)	0.1833(12)	0.1057(6)	0.6840(7)	0.075(3)
F(3)	0.3214(9)	0.1574(6)	0.6020(8)	0.114(4)
C(5)	0.2094(8)	0.3772(7)	0.6910(6)	0.044(1)
C(92)	0.3052(15)	0.2593(10)	0.7129(10)	0.044(1)
C(99)	0.0268(12)	0.3997(11)	0.6644(11)	0.103(1)
F(96)	0.0379(5)	0.4577(5)	0.5895(5)	0.103(1)
F(94)	−0.0045(5)	0.4308(5)	0.7160(5)	0.103(1)
F(95)	−0.0334(10)	0.3474(8)	0.6555(7)	0.103(1)
C(95)	0.1249(7)	0.3561(5)	0.6760(5)	0.044(1)
C(94)	0.1508(7)	0.2993(5)	0.6430(5)	0.044(1)
C(93)	0.2380(7)	0.2567(5)	0.6564(5)	0.044(1)
C(97)	0.2638(7)	0.1893(6)	0.6290(7)	0.053(2)
F(91)	0.3438(6)	0.1508(6)	0.6486(8)	0.094(3)
F(2)	0.1820(10)	0.1369(6)	0.6507(7)	0.078(3)

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Table S2. – continued from previous page

atom	x	y	x	U(eq)
F(92)	0.2816(5)	0.2186(6)	0.5473(5)	0.091(2)
C(96)	0.1915(8)	0.3799(7)	0.7097(6)	0.044(1)
C(6)	0.3014(9)	0.2777(6)	0.6971(6)	0.033(2)
C(72)	0.4319(3)	0.5141(2)	0.64494(19)	0.033(1)
F(72)	0.3890(3)	0.67065(18)	0.5478(2)	0.116(2)
C(23)	1.1362(3)	0.9641(2)	0.6186(2)	0.038(1)
C(22)	1.0337(3)	0.9487(2)	0.6432(2)	0.038(1)
C(73)	0.5034(3)	0.5658(2)	0.57773(19)	0.036(1)
F(73)	0.5253(2)	0.68836(14)	0.45840(13)	0.063(1)
C(24)	1.2008(2)	0.9107(2)	0.5954(2)	0.034(1)
C(25)	1.1554(3)	0.8404(2)	0.59888(19)	0.033(1)
C(26)	1.0517(2)	0.82282(19)	0.62573(19)	0.031(1)
C(27)	1.3484(3)	0.9355(3)	0.6431(3)	0.051(1)
C(28)	1.3411(3)	1.0129(3)	0.4977(2)	0.051(1)
C(29)	1.3722(3)	0.8634(3)	0.5508(3)	0.051(1)
C(31)	0.8152(6)	0.5210(4)	0.8406(5)	0.058(2)
C(33)	0.7900(6)	0.5589(5)	0.6804(6)	0.060(2)
C(32)	0.6284(5)	0.5640(4)	0.8008(6)	0.063(3)
C(36)	0.6790(7)	0.6093(5)	0.6847(7)	0.051(3)
C(34)	0.6864(8)	0.5476(5)	0.8514(6)	0.052(3)
C(35)	0.8413(6)	0.5225(5)	0.7412(6)	0.040(2)
C(52)	1.0215(7)	0.7345(4)	0.5370(4)	0.048(2)
C(55)	0.9995(7)	0.6556(5)	0.5319(5)	0.073(3)
C(56)	0.9689(7)	0.8079(5)	0.4846(4)	0.062(3)
C(59)	0.8660(10)	0.7969(8)	0.5182(7)	0.061(2)
C(57)	0.9577(12)	0.7428(9)	0.5350(7)	0.061(2)
C(58)	1.0518(10)	0.7793(8)	0.4693(7)	0.061(2)
C(51)	1.0584(9)	0.6440(7)	0.7058(8)	0.035(3)
C(53)	1.1683(5)	0.6355(4)	0.6702(5)	0.050(2)
C(54)	1.0453(8)	0.6490(7)	0.7876(6)	0.054(3)
C(49)	1.0433(15)	0.6410(12)	0.6794(11)	0.034(3)
C(47)	1.1328(10)	0.6256(7)	0.6203(10)	0.074(5)
C(48)	1.0704(14)	0.6391(9)	0.7536(13)	0.055(4)
C(41)	0.5673(2)	0.7617(2)	0.7821(2)	0.036(1)
C(42)	0.6903(3)	0.7576(2)	0.8973(2)	0.049(1)
C(43)	0.5668(3)	0.7904(3)	0.6926(2)	0.048(1)
C(44)	0.4813(3)	0.7960(3)	0.8259(3)	0.057(1)
C(45)	0.6495(4)	0.6691(3)	0.9540(2)	0.070(1)
C(46)	0.7939(4)	0.7762(3)	0.9054(3)	0.067(1)
C(61)	0.4066(2)	0.29409(19)	0.83013(18)	0.029(1)
F(61)	0.7066(2)	0.2963(3)	0.8528(2)	0.110(1)
C(62)	0.4973(3)	0.3069(2)	0.8470(2)	0.033(1)

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Table S2. – continued from previous page

atom	x	y	x	U(eq)
F(62)	0.6283(2)	0.3223(2)	0.9498(2)	0.095(1)
F(63)	0.6687(3)	0.2030(2)	0.9737(3)	0.116(1)
C(63)	0.5372(3)	0.2466(2)	0.9068(2)	0.038(1)
C(64)	0.4858(3)	0.1706(2)	0.9527(2)	0.041(1)
F(64)	0.2578(4)	0.0663(2)	0.9674(3)	0.161(2)
C(68)	0.3373(3)	0.0753(2)	0.9887(2)	0.052(1)
C(67)	0.6352(3)	0.2655(3)	0.9201(3)	0.053(1)
C(66)	0.3558(3)	0.2176(2)	0.8783(2)	0.034(1)
F(66)	0.3084(3)	0.06145(18)	1.06636(17)	0.105(1)
C(65)	0.3947(3)	0.1569(2)	0.9384(2)	0.040(1)
F(65)	0.3895(3)	0.01285(16)	0.9895(2)	0.112(1)
F(71)	0.5261(4)	0.69891(17)	0.5668(2)	0.132(2)
C(71)	0.4457(2)	0.43118(19)	0.68742(18)	0.027(1)
B	0.3582(3)	0.3692(2)	0.7641(2)	0.029(1)
C(74)	0.5933(3)	0.5372(2)	0.5495(2)	0.036(1)
F(74)	0.7797(2)	0.4462(4)	0.5893(3)	0.144(2)
C(78)	0.7078(3)	0.4247(3)	0.5627(3)	0.064(1)
C(77)	0.4875(4)	0.6553(2)	0.5381(2)	0.059(1)
C(76)	0.5366(3)	0.4037(2)	0.6572(2)	0.035(1)
F(76)	0.7075(3)	0.3454(2)	0.5898(2)	0.132(2)
C(75)	0.6091(3)	0.4551(2)	0.5900(2)	0.038(1)
F(75)	0.7400(2)	0.4550(2)	0.48240(17)	0.089(1)
C(82)	0.3353(2)	0.4795(2)	0.82960(19)	0.030(1)
F(82)	0.3687(3)	0.6428(2)	0.8148(2)	0.109(1)
C(81)	0.2942(2)	0.41528(18)	0.81932(18)	0.027(1)
F(81)	0.4087(2)	0.5618(2)	0.9209(3)	0.109(1)
C(83)	0.2818(2)	0.5137(2)	0.88103(19)	0.032(1)
F(83)	0.2712(2)	0.6166(2)	0.9306(2)	0.100(1)
F(84)	0.0147(3)	0.3920(2)	1.0370(2)	0.123(2)
C(84)	0.1849(3)	0.4851(2)	0.9252(2)	0.035(1)
F(85)	−0.0285(2)	0.4336(3)	0.9306(2)	0.126(2)
C(85)	0.1428(3)	0.4203(2)	0.9176(2)	0.040(1)
F(86)	0.0216(3)	0.3109(2)	0.9857(3)	0.143(2)
C(86)	0.1961(3)	0.3860(2)	0.8660(2)	0.037(1)
C(87)	0.3304(3)	0.5833(3)	0.8872(3)	0.054(1)
C(88)	0.0378(3)	0.3893(3)	0.9636(3)	0.068(2)
C(91)	0.2841(3)	0.3370(2)	0.7231(2)	0.044(1)
C	0.8799(2)	0.85710(19)	0.6753(2)	0.033(1)
H(13)	0.5997	0.9307	0.8017	0.041
H(15)	0.7737	1.1153	0.6102	0.046
H(18A)	0.7335	1.1715	0.7167	0.114
H(18B)	0.6902	1.1078	0.8092	0.114

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Table S2. – continued from previous page

atom	x	y	x	U(eq)
H(18C)	0.6317	1.1881	0.7698	0.114
H(17A)	0.6400	1.1850	0.6110	0.090
H(17B)	0.5377	1.1980	0.6663	0.090
H(17C)	0.5410	1.1264	0.6348	0.090
H(16)	0.8828	1.0231	0.5838	0.046
H(19A)	0.4751	1.1008	0.8072	0.109
H(19B)	0.5337	1.0207	0.8469	0.109
H(19C)	0.4753	1.0271	0.7789	0.109
H(2)	0.1136	0.2437	0.6410	0.052
H(5)	0.1959	0.4287	0.6938	0.052
H(92)	0.3612	0.2300	0.7295	0.052
H(94)	0.1105	0.2893	0.6118	0.052
H(96)	0.1775	0.4249	0.7247	0.052
H(6)	0.3594	0.2477	0.7062	0.039
H(72)	0.3712	0.5358	0.6627	0.040
H(23)	1.1647	1.0127	0.6171	0.046
H(22)	0.9933	0.9868	0.6581	0.046
H(25)	1.1963	0.8033	0.5825	0.040
H(27A)	1.4211	0.9501	0.6274	0.077
H(27B)	1.3335	0.8821	0.6900	0.077
H(27C)	1.3120	0.9775	0.6577	0.077
H(28A)	1.3223	1.0089	0.4512	0.076
H(28B)	1.4138	1.0270	0.4840	0.076
H(28C)	1.3040	1.0556	0.5106	0.076
H(29A)	1.3522	0.8597	0.5046	0.076
H(29B)	1.3559	0.8104	0.5981	0.076
H(29C)	1.4449	0.8774	0.5363	0.076
H(31A)	0.7894	0.4658	0.8520	0.087
H(31B)	0.7941	0.5315	0.8898	0.087
H(31C)	0.8890	0.5249	0.8238	0.087
H(33A)	0.7591	0.5912	0.6352	0.090
H(33B)	0.7626	0.5017	0.7048	0.090
H(33C)	0.8632	0.5612	0.6599	0.090
H(32A)	0.5876	0.5964	0.7630	0.095
H(32B)	0.6064	0.5704	0.8522	0.095
H(32C)	0.6199	0.5059	0.8112	0.095
H(36A)	0.7170	0.6382	0.6281	0.077
H(36B)	0.6208	0.6401	0.6956	0.077
H(36C)	0.6555	0.5542	0.6936	0.077
H(34A)	0.6376	0.5843	0.8647	0.062
H(34B)	0.7280	0.5283	0.8915	0.062
H(34C)	0.6505	0.5004	0.8525	0.062

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Table S2. – continued from previous page

atom	x	y	x	U(eq)
H(35A)	0.8805	0.5431	0.6846	0.060
H(35B)	0.7990	0.4735	0.7536	0.060
H(35C)	0.8873	0.5083	0.7778	0.060
H(52)	1.0960	0.7480	0.5168	0.058
H(55A)	1.0239	0.6616	0.4755	0.110
H(55B)	0.9265	0.6419	0.5494	0.110
H(55C)	1.0336	0.6117	0.5674	0.110
H(56A)	0.9794	0.8556	0.4961	0.093
H(56B)	0.8965	0.7932	0.4977	0.093
H(56C)	0.9976	0.8213	0.4267	0.093
H(59A)	0.8684	0.8203	0.4598	0.092
H(59B)	0.8692	0.8415	0.5359	0.092
H(59C)	0.8030	0.7629	0.5486	0.092
H(57)	0.9405	0.6873	0.5384	0.073
H(58A)	1.0398	0.7858	0.4169	0.092
H(58B)	1.1066	0.7429	0.4817	0.092
H(58C)	1.0705	0.8332	0.4665	0.092
H(51)	1.0218	0.5911	0.7179	0.042
H(53A)	1.1775	0.6468	0.6124	0.075
H(53B)	1.1864	0.5795	0.6996	0.075
H(53C)	1.2115	0.6748	0.6755	0.075
H(54A)	1.0805	0.6996	0.7799	0.081
H(54B)	1.0735	0.6014	0.8243	0.081
H(54C)	0.9733	0.6491	0.8113	0.081
H(49)	0.9913	0.5947	0.6982	0.041
H(47A)	1.1117	0.6299	0.5716	0.112
H(47B)	1.1553	0.5704	0.6471	0.112
H(47C)	1.1885	0.6666	0.6045	0.112
H(48A)	1.1249	0.6811	0.7377	0.083
H(48B)	1.0927	0.5848	0.7835	0.083
H(48C)	1.0113	0.6503	0.7885	0.083
H(41)	0.5540	0.7006	0.8075	0.043
H(42)	0.6433	0.7950	0.9139	0.059
H(43A)	0.5762	0.8506	0.6659	0.071
H(43B)	0.5021	0.7727	0.6881	0.071
H(43C)	0.6217	0.7666	0.6662	0.071
H(44A)	0.4846	0.8560	0.7968	0.086
H(44B)	0.4875	0.7815	0.8818	0.086
H(44C)	0.4166	0.7727	0.8272	0.086
H(45A)	0.5830	0.6594	0.9466	0.105
H(45B)	0.6435	0.6606	1.0107	0.105
H(45C)	0.6958	0.6308	0.9410	0.105

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Table S2. – continued from previous page

atom	x	y	x	U(eq)
H(46A)	0.8417	0.7398	0.8903	0.100
H(46B)	0.7903	0.7672	0.9620	0.100
H(46C)	0.8166	0.8336	0.8693	0.100
H(62)	0.5336	0.3590	0.8166	0.040
H(64)	0.5127	0.1288	0.9931	0.050
H(66)	0.2927	0.2064	0.8701	0.041
H(74)	0.6426	0.5728	0.5037	0.044
H(76)	0.5493	0.3476	0.6837	0.042
H(82)	0.4023	0.5007	0.8004	0.036
H(84)	0.1482	0.5091	0.9597	0.042
H(86)	0.1649	0.3412	0.8624	0.044

Table S3. Anisotropic displacement parameters (Å^2) for [{PC$^\bullet$(sp^2)P}$^{t\mathrm{Bu}}$Pd(PMe$_3$)][BAr$^{\mathrm{F}}_4$] (**2**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ...+ 2hka^*b^*U_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	0.0337(2)	0.0205(1)	0.0333(2)	−0.0131(1)	−0.0145(1)	0.0098(1)
C(10)	0.064(2)	0.0363(19)	0.046(2)	−0.0229(17)	−0.0222(19)	0.0304(18)
P(3)	0.0304(4)	0.0272(4)	0.0591(6)	−0.0221(4)	−0.0106(4)	0.0049(3)
P(2)	0.0398(5)	0.0233(4)	0.0292(4)	−0.0109(3)	−0.0140(4)	0.0129(3)
P(1)	0.0531(5)	0.0240(4)	0.0294(4)	−0.0140(4)	−0.0020(4)	0.0075(4)
C(11)	0.0335(17)	0.0244(16)	0.0418(19)	−0.0167(14)	−0.0174(14)	0.0095(13)
C(12)	0.0351(17)	0.0269(16)	0.0330(17)	−0.0160(14)	−0.0185(14)	0.0121(13)
C(13)	0.0395(18)	0.0325(17)	0.0391(18)	−0.0199(15)	−0.0197(15)	0.0179(14)
C(15)	0.045(2)	0.0218(16)	0.052(2)	−0.0146(15)	−0.0210(17)	0.0126(14)
C(14)	0.0450(19)	0.0298(17)	0.0413(19)	−0.0191(15)	−0.0239(16)	0.0198(15)
C(18)	0.123(5)	0.053(3)	0.086(4)	−0.051(3)	−0.052(3)	0.043(3)
C(17)	0.079(3)	0.053(2)	0.047(2)	−0.020(2)	−0.020(2)	0.048(2)
C(16)	0.0364(18)	0.0265(17)	0.053(2)	−0.0164(16)	−0.0144(16)	0.0086(14)
C(19)	0.095(4)	0.057(3)	0.057(3)	−0.025(2)	−0.005(3)	0.047(3)
C(20)	0.0332(17)	0.048(2)	0.0390(19)	−0.0215(17)	−0.0099(15)	0.0125(15)
C(21)	0.0372(17)	0.0247(16)	0.0336(17)	−0.0116(14)	−0.0084(14)	0.0103(13)
C(98)	0.0963(19)	0.107(2)	0.143(3)	−0.065(2)	−0.082(2)	0.0478(15)
F(97)	0.0963(19)	0.107(2)	0.143(3)	−0.065(2)	−0.082(2)	0.0478(15)
F(98)	0.0963(19)	0.107(2)	0.143(3)	−0.065(2)	−0.082(2)	0.0478(15)
F(99)	0.0963(19)	0.107(2)	0.143(3)	−0.065(2)	−0.082(2)	0.0478(15)
C(1)	0.0560(13)	0.0414(12)	0.0477(15)	−0.0254(12)	−0.0267(11)	0.0118(11)
C(2)	0.0560(13)	0.0414(12)	0.0477(15)	−0.0254(12)	−0.0267(11)	0.0118(11)
C(3)	0.0560(13)	0.0414(12)	0.0477(15)	−0.0254(12)	−0.0267(11)	0.0118(11)
C(4)	0.0560(13)	0.0414(12)	0.0477(15)	−0.0254(12)	−0.0267(11)	0.0118(11)
F(1)	0.178(8)	0.072(5)	0.173(9)	−0.093(6)	−0.111(7)	0.059(5)
F(93)	0.097(6)	0.054(6)	0.089(7)	−0.043(5)	−0.028(5)	0.021(5)
F(3)	0.119(8)	0.096(6)	0.152(10)	−0.100(8)	0.018(7)	0.002(5)
C(5)	0.0560(13)	0.0414(12)	0.0477(15)	−0.0254(12)	−0.0267(11)	0.0118(11)
C(92)	0.0560(13)	0.0414(12)	0.0477(15)	−0.0254(12)	−0.0267(11)	0.0118(11)
C(99)	0.0963(19)	0.107(2)	0.143(3)	−0.065(2)	−0.082(2)	0.0478(15)
F(96)	0.0963(19)	0.107(2)	0.143(3)	−0.065(2)	−0.082(2)	0.0478(15)
F(94)	0.0963(19)	0.107(2)	0.143(3)	−0.065(2)	−0.082(2)	0.0478(15)
F(95)	0.0963(19)	0.107(2)	0.143(3)	−0.065(2)	−0.082(2)	0.0478(15)
C(95)	0.0560(13)	0.0414(12)	0.0477(15)	−0.0254(12)	−0.0267(11)	0.0118(11)
C(94)	0.0560(13)	0.0414(12)	0.0477(15)	−0.0254(12)	−0.0267(11)	0.0118(11)
C(93)	0.0560(13)	0.0414(12)	0.0477(15)	−0.0254(12)	−0.0267(11)	0.0118(11)
C(97)	0.058(5)	0.052(5)	0.069(6)	−0.039(5)	−0.025(5)	0.008(4)
F(91)	0.091(5)	0.103(6)	0.167(9)	−0.118(7)	−0.065(6)	0.044(4)
F(2)	0.080(5)	0.061(6)	0.129(10)	−0.069(6)	−0.042(7)	0.016(5)
F(92)	0.079(4)	0.142(7)	0.099(5)	−0.098(5)	−0.018(4)	0.022(4)

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Table S3. – continued from previous page

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(96)	0.0560(13)	0.0414(12)	0.0477(15)	−0.0254(12)	−0.0267(11)	0.0118(11)
C(6)	0.029(3)	0.039(6)	0.034(6)	−0.022(5)	−0.002(4)	0.008(4)
C(72)	0.0425(18)	0.0325(17)	0.0257(16)	−0.0152(14)	−0.0058(14)	0.0146(14)
F(72)	0.102(2)	0.0503(17)	0.115(3)	0.0128(17)	0.037(2)	0.0411(17)
C(23)	0.0367(18)	0.0329(18)	0.051(2)	−0.0212(16)	−0.0139(16)	0.0094(14)
C(22)	0.0374(18)	0.0305(17)	0.054(2)	−0.0237(16)	−0.0131(16)	0.0140(14)
C(73)	0.053(2)	0.0316(17)	0.0232(16)	−0.0125(14)	−0.0055(15)	0.0108(15)
F(73)	0.0893(18)	0.0449(13)	0.0322(12)	−0.0007(10)	−0.0014(12)	0.0237(12)
C(24)	0.0356(18)	0.0364(18)	0.0315(17)	−0.0152(15)	−0.0098(14)	0.0139(14)
C(25)	0.0416(18)	0.0294(17)	0.0272(16)	−0.0122(14)	−0.0053(14)	0.0133(14)
C(26)	0.0403(18)	0.0246(16)	0.0254(16)	−0.0099(13)	−0.0057(13)	0.0094(13)
C(27)	0.043(2)	0.070(3)	0.054(2)	−0.034(2)	−0.0225(18)	0.0232(19)
C(28)	0.0354(19)	0.059(2)	0.051(2)	−0.016(2)	−0.0094(17)	−0.0026(17)
C(29)	0.0338(19)	0.067(3)	0.062(3)	−0.040(2)	−0.0064(18)	0.0156(18)
C(31)	0.051(4)	0.029(3)	0.070(5)	0.002(3)	−0.011(4)	0.010(3)
C(33)	0.058(5)	0.051(4)	0.090(6)	−0.048(4)	−0.016(4)	0.001(4)
C(32)	0.031(4)	0.035(4)	0.119(8)	−0.031(4)	−0.011(4)	0.001(3)
C(36)	0.058(6)	0.037(5)	0.077(7)	−0.028(5)	−0.041(5)	0.008(4)
C(34)	0.061(6)	0.022(4)	0.058(6)	−0.013(4)	0.008(5)	−0.007(4)
C(35)	0.040(4)	0.020(4)	0.061(6)	−0.019(4)	−0.011(4)	0.006(3)
C(52)	0.063(5)	0.054(4)	0.037(4)	−0.027(3)	−0.015(3)	0.000(4)
C(55)	0.094(6)	0.079(6)	0.064(5)	−0.047(5)	−0.017(4)	0.001(5)
C(56)	0.093(7)	0.057(5)	0.032(4)	−0.006(3)	−0.028(4)	−0.019(4)
C(59)	0.079(6)	0.071(5)	0.038(4)	−0.027(4)	−0.013(4)	−0.005(4)
C(57)	0.079(6)	0.071(5)	0.038(4)	−0.027(4)	−0.013(4)	−0.005(4)
C(58)	0.079(6)	0.071(5)	0.038(4)	−0.027(4)	−0.013(4)	−0.005(4)
C(51)	0.033(5)	0.028(4)	0.048(9)	−0.016(5)	−0.020(5)	0.015(3)
C(53)	0.039(4)	0.046(4)	0.069(5)	−0.028(4)	−0.016(3)	0.025(3)
C(54)	0.055(5)	0.061(6)	0.039(6)	−0.011(4)	−0.021(4)	0.030(4)
C(49)	0.027(7)	0.027(5)	0.044(10)	−0.013(6)	−0.006(6)	0.009(5)
C(47)	0.056(7)	0.039(6)	0.104(11)	−0.028(7)	0.027(7)	0.002(5)
C(48)	0.056(10)	0.038(7)	0.069(16)	−0.009(9)	−0.036(10)	0.005(6)
C(41)	0.0348(17)	0.0251(16)	0.0428(19)	−0.0103(15)	−0.0071(15)	0.0063(13)
C(42)	0.076(3)	0.046(2)	0.0340(19)	−0.0212(17)	−0.0241(19)	0.034(2)
C(43)	0.0366(19)	0.054(2)	0.053(2)	−0.0172(19)	−0.0232(17)	0.0106(17)
C(44)	0.040(2)	0.051(2)	0.077(3)	−0.032(2)	0.007(2)	−0.0005(18)
C(45)	0.108(4)	0.054(3)	0.031(2)	−0.0048(19)	−0.011(2)	0.033(3)
C(46)	0.099(4)	0.072(3)	0.058(3)	−0.040(2)	−0.053(3)	0.048(3)
C(61)	0.0367(17)	0.0283(16)	0.0246(15)	−0.0158(13)	−0.0055(13)	0.0118(13)
F(61)	0.0455(15)	0.211(4)	0.074(2)	−0.057(2)	−0.0128(15)	−0.011(2)
C(62)	0.0417(18)	0.0310(17)	0.0311(17)	−0.0150(14)	−0.0119(14)	0.0115(14)
F(62)	0.083(2)	0.120(3)	0.126(3)	−0.080(2)	−0.051(2)	0.0113(19)

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Table S3. – continued from previous page

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F(63)	0.099(2)	0.086(2)	0.153(3)	−0.006(2)	−0.094(3)	0.0206(19)
C(63)	0.0447(19)	0.042(2)	0.0311(18)	−0.0186(16)	−0.0138(15)	0.0165(16)
C(64)	0.055(2)	0.040(2)	0.0288(18)	−0.0134(16)	−0.0134(16)	0.0223(17)
F(64)	0.159(4)	0.081(2)	0.172(4)	0.065(3)	−0.111(3)	−0.069(3)
C(68)	0.061(3)	0.037(2)	0.045(2)	−0.0061(18)	−0.0090(19)	0.0077(18)
C(67)	0.058(3)	0.058(3)	0.050(2)	−0.020(2)	−0.029(2)	0.015(2)
C(66)	0.0379(18)	0.0304(17)	0.0318(17)	−0.0140(14)	−0.0043(14)	0.0101(14)
F(66)	0.177(4)	0.0525(17)	0.0517(17)	−0.0140(14)	0.0273(19)	−0.0244(19)
C(65)	0.052(2)	0.0291(17)	0.0309(18)	−0.0101(14)	−0.0025(16)	0.0108(15)
F(65)	0.137(3)	0.0332(14)	0.123(3)	−0.0252(16)	0.038(2)	0.0056(16)
F(71)	0.299(6)	0.0362(15)	0.071(2)	−0.0238(15)	−0.060(3)	0.011(2)
C(71)	0.0353(16)	0.0290(16)	0.0234(15)	−0.0146(13)	−0.0107(13)	0.0097(13)
B	0.0335(18)	0.0265(18)	0.0286(18)	−0.0131(15)	−0.0098(15)	0.0088(14)
C(74)	0.0401(18)	0.0417(19)	0.0232(16)	−0.0120(15)	−0.0028(14)	0.0048(15)
F(74)	0.0490(19)	0.248(6)	0.155(4)	−0.096(4)	−0.041(2)	0.052(3)
C(78)	0.049(2)	0.065(3)	0.047(2)	−0.003(2)	0.006(2)	0.023(2)
C(77)	0.084(3)	0.037(2)	0.036(2)	−0.0109(18)	0.010(2)	0.015(2)
C(76)	0.0384(18)	0.0335(18)	0.0313(17)	−0.0127(14)	−0.0087(14)	0.0148(14)
F(76)	0.104(3)	0.074(2)	0.121(3)	0.011(2)	0.051(2)	0.061(2)
C(75)	0.0374(18)	0.0415(19)	0.0322(18)	−0.0135(15)	−0.0080(15)	0.0143(15)
F(75)	0.0766(19)	0.096(2)	0.0573(17)	−0.0142(15)	0.0171(14)	0.0426(17)
C(82)	0.0293(16)	0.0336(17)	0.0266(16)	−0.0135(14)	−0.0057(13)	0.0059(13)
F(82)	0.159(3)	0.074(2)	0.095(2)	−0.0495(19)	0.002(2)	−0.054(2)
C(81)	0.0300(15)	0.0226(15)	0.0240(15)	−0.0053(12)	−0.0081(12)	0.0078(12)
F(81)	0.076(2)	0.142(3)	0.184(4)	−0.122(3)	−0.068(2)	0.025(2)
C(83)	0.0361(17)	0.0362(18)	0.0284(16)	−0.0166(14)	−0.0105(14)	0.0104(14)
F(83)	0.0734(19)	0.122(3)	0.156(3)	−0.123(3)	0.0027(19)	0.0023(18)
F(84)	0.095(3)	0.120(3)	0.090(2)	−0.020(2)	0.054(2)	0.005(2)
C(84)	0.0401(18)	0.0330(18)	0.0267(17)	−0.0100(14)	−0.0015(14)	0.0149(14)
F(85)	0.0306(14)	0.165(4)	0.117(3)	−0.002(3)	0.0012(16)	−0.0064(19)
C(85)	0.0359(18)	0.0262(17)	0.041(2)	−0.0049(15)	0.0061(15)	0.0073(14)
F(86)	0.076(2)	0.071(2)	0.232(5)	−0.067(3)	0.073(3)	−0.0332(17)
C(86)	0.0344(18)	0.0241(16)	0.045(2)	−0.0104(15)	−0.0028(15)	0.0045(13)
C(87)	0.049(2)	0.066(3)	0.064(3)	−0.047(2)	−0.010(2)	0.007(2)
C(88)	0.041(2)	0.040(2)	0.098(4)	−0.023(2)	0.020(2)	0.0047(19)
C(91)	0.0560(13)	0.0414(12)	0.0477(15)	−0.0254(12)	−0.0267(11)	0.0118(11)
C	0.0370(18)	0.0252(16)	0.0406(19)	−0.0148(14)	−0.0128(15)	0.0121(13)

Table S4. Distances [Å] for [{PC$^{\bullet}$(sp^2)P}$^{t\mathrm{Bu}}$Pd(PMe$_3$)][BAr$^{\mathrm{F}}_4$] (**2**).

atom – atom	distance	atom – atom	distance
Pd – C	2.064(3)	Pd – P(2)	2.3208(8)
Pd – P(1)	2.3256(9)	Pd – P(3)	2.3704(9)
C(10) – C(17)	1.524(5)	C(10) – C(18)	1.525(6)
C(10) – C(19)	1.528(6)	C(10) – C(14)	1.541(4)
P(3) – C(34)	1.727(9)	P(3) – C(33)	1.783(7)
P(3) – C(35)	1.792(7)	P(3) – C(32)	1.850(7)
P(3) – C(36)	1.881(8)	P(3) – C(31)	1.906(7)
P(2) – C(12)	1.805(3)	P(2) – C(42)	1.843(4)
P(2) – C(41)	1.846(4)	P(1) – C(49)	1.71(2)
P(1) – C(26)	1.808(3)	P(1) – C(52)	1.827(6)
P(1) – C(51)	1.941(11)	P(1) – C(57)	1.983(12)
C(11) – C(12)	1.394(5)	C(11) – C(16)	1.418(5)
C(11) – C	1.445(4)	C(12) – C(13)	1.397(4)
C(13) – C(14)	1.390(5)	C(13) – H(13)	0.9500
C(15) – C(16)	1.378(5)	C(15) – C(14)	1.393(5)
C(15) – H(15)	0.9500	C(18) – H(18A)	0.9800
C(18) – H(18B)	0.9800	C(18) – H(18C)	0.9800
C(17) – H(17A)	0.9800	C(17) – H(17B)	0.9800
C(17) – H(17C)	0.9800	C(16) – H(16)	0.9500
C(19) – H(19A)	0.9800	C(19) – H(19B)	0.9800
C(19) – H(19C)	0.9800	C(20) – C(27)	1.526(5)
C(20) – C(28)	1.530(5)	C(20) – C(24)	1.531(5)
C(20) – C(29)	1.535(5)	C(21) – C(22)	1.409(5)
C(21) – C(26)	1.414(4)	C(21) – C	1.434(5)
C(98) – F(97)	1.302(17)	C(98) – F(98)	1.414(18)
C(98) – C(1)	1.455(15)	C(98) – F(99)	1.52(3)
C(1) – C(5)	1.405(13)	C(1) – C(2)	1.412(12)
C(2) – C(3)	1.380(12)	C(2) – H(2)	0.9500
C(3) – C(92)	1.37(2)	C(3) – C(4)	1.528(12)
C(4) – F(93)	1.270(16)	C(4) – F(1)	1.299(13)
C(4) – F(3)	1.321(14)	C(5) – C(91)	1.336(12)
C(5) – H(5)	0.9500	C(92) – C(91)	1.484(18)
C(92) – H(92)	0.9500	C(99) – F(94)	1.275(16)
C(99) – F(96)	1.326(19)	C(99) – F(95)	1.35(2)
C(99) – C(95)	1.540(15)	C(95) – C(96)	1.376(12)
C(95) – C(94)	1.379(11)	C(94) – C(93)	1.407(11)
C(94) – H(94)	0.9500	C(93) – C(6)	1.416(16)
C(93) – C(97)	1.487(11)	C(97) – F(91)	1.313(12)
C(97) – F(92)	1.345(13)	C(97) – F(2)	1.357(15)
C(96) – C(91)	1.472(11)	C(96) – H(96)	0.9500
C(6) – C(91)	1.323(13)	C(6) – H(6)	0.9500

Continued on next page

Table S4. – continued from previous page

atom – atom	distance	atom – atom	distance
C(72) – C(73)	1.385(5)	C(72) – C(71)	1.395(4)
C(72) – H(72)	0.9500	F(72) – C(77)	1.348(6)
C(23) – C(22)	1.368(5)	C(23) – C(24)	1.404(5)
C(23) – H(23)	0.9500	C(22) – H(22)	0.9500
C(73) – C(74)	1.387(5)	C(73) – C(77)	1.494(5)
F(73) – C(77)	1.322(4)	C(24) – C(25)	1.389(5)
C(25) – C(26)	1.389(5)	C(25) – H(25)	0.9500
C(27) – H(27A)	0.9800	C(27) – H(27B)	0.9800
C(27) – H(27C)	0.9800	C(28) – H(28A)	0.9800
C(28) – H(28B)	0.9800	C(28) – H(28C)	0.9800
C(29) – H(29A)	0.9800	C(29) – H(29B)	0.9800
C(29) – H(29C)	0.9800	C(31) – H(31A)	0.9800
C(31) – H(31B)	0.9800	C(31) – H(31C)	0.9800
C(33) – H(33A)	0.9800	C(33) – H(33B)	0.9800
C(33) – H(33C)	0.9800	C(32) – H(32A)	0.9800
C(32) – H(32B)	0.9800	C(32) – H(32C)	0.9800
C(36) – H(36A)	0.9800	C(36) – H(36B)	0.9800
C(36) – H(36C)	0.9800	C(34) – H(34A)	0.9800
C(34) – H(34B)	0.9800	C(34) – H(34C)	0.9800
C(35) – H(35A)	0.9800	C(35) – H(35B)	0.9800
C(35) – H(35C)	0.9800	C(52) – C(55)	1.491(10)
C(52) – C(56)	1.548(11)	C(52) – H(52)	1.0000
C(55) – H(55A)	0.9800	C(55) – H(55B)	0.9800
C(55) – H(55C)	0.9800	C(56) – H(56A)	0.9800
C(56) – H(56B)	0.9800	C(56) – H(56C)	0.9800
C(59) – C(57)	1.56(2)	C(59) – H(59A)	0.9800
C(59) – H(59B)	0.9800	C(59) – H(59C)	0.9800
C(57) – C(58)	1.499(19)	C(57) – H(57)	1.0000
C(58) – H(58A)	0.9800	C(58) – H(58B)	0.9800
C(58) – H(58C)	0.9800	C(51) – C(54)	1.519(12)
C(51) – C(53)	1.522(14)	C(51) – H(51)	1.0000
C(53) – H(53A)	0.9800	C(53) – H(53B)	0.9800
C(53) – H(53C)	0.9800	C(54) – H(54A)	0.9800
C(54) – H(54B)	0.9800	C(54) – H(54C)	0.9800
C(49) – C(48)	1.486(19)	C(49) – C(47)	1.54(2)
C(49) – H(49)	1.0000	C(47) – H(47A)	0.9800
C(47) – H(47B)	0.9800	C(47) – H(47C)	0.9800
C(48) – H(48A)	0.9800	C(48) – H(48B)	0.9800
C(48) – H(48C)	0.9800	C(41) – C(43)	1.521(5)
C(41) – C(44)	1.525(5)	C(41) – H(41)	1.0000
C(42) – C(46)	1.517(7)	C(42) – C(45)	1.532(6)
C(42) – H(42)	1.0000	C(43) – H(43A)	0.9800

Continued on next page

Table S4. – continued from previous page

atom – atom	distance	atom – atom	distance
C(43) – H(43B)	0.9800	C(43) – H(43C)	0.9800
C(44) – H(44A)	0.9800	C(44) – H(44B)	0.9800
C(44) – H(44C)	0.9800	C(45) – H(45A)	0.9800
C(45) – H(45B)	0.9800	C(45) – H(45C)	0.9800
C(46) – H(46A)	0.9800	C(46) – H(46B)	0.9800
C(46) – H(46C)	0.9800	C(61) – C(66)	1.388(5)
C(61) – C(62)	1.392(5)	C(61) – B	1.644(4)
F(61) – C(67)	1.312(5)	C(62) – C(63)	1.394(5)
C(62) – H(62)	0.9500	F(62) – C(67)	1.328(5)
F(63) – C(67)	1.308(5)	C(63) – C(64)	1.381(5)
C(63) – C(67)	1.487(5)	C(64) – C(65)	1.378(5)
C(64) – H(64)	0.9500	F(64) – C(68)	1.272(5)
C(68) – F(65)	1.300(5)	C(68) – F(66)	1.316(5)
C(68) – C(65)	1.496(5)	C(66) – C(65)	1.394(5)
C(66) – H(66)	0.9500	F(71) – C(77)	1.288(6)
C(71) – C(76)	1.398(4)	C(71) – B	1.642(5)
B – C(91)	1.635(5)	B – C(81)	1.645(4)
C(74) – C(75)	1.383(5)	C(74) – H(74)	0.9500
F(74) – C(78)	1.323(7)	C(78) – F(76)	1.294(6)
C(78) – F(75)	1.323(5)	C(78) – C(75)	1.493(5)
C(76) – C(75)	1.391(5)	C(76) – H(76)	0.9500
C(82) – C(81)	1.389(4)	C(82) – C(83)	1.390(4)
C(82) – H(82)	0.9500	F(82) – C(87)	1.324(6)
C(81) – C(86)	1.401(5)	F(81) – C(87)	1.327(5)
C(83) – C(84)	1.374(5)	C(83) – C(87)	1.482(5)
F(83) – C(87)	1.307(5)	F(84) – C(88)	1.340(7)
C(84) – C(85)	1.378(5)	C(84) – H(84)	0.9500
F(85) – C(88)	1.276(6)	C(85) – C(86)	1.392(5)
C(85) – C(88)	1.481(5)	F(86) – C(88)	1.300(5)
C(86) – H(86)	0.9500		

Table S5. Angles [°] for [{PC$^{\bullet}$(sp^2)P}$^{t\mathrm{Bu}}$Pd(PMe$_3$)][BAr$^{\mathrm{F}}_4$] (**2**).

atom – atom – atom	angle	atom – atom – atom	angle
C – Pd – P(2)	80.50(9)	C – Pd – P(1)	81.07(9)
P(2) – Pd – P(1)	160.65(3)	C – Pd – P(3)	175.97(10)
P(2) – Pd – P(3)	100.61(3)	P(1) – Pd – P(3)	98.18(3)
C(17) – C(10) – C(18)	109.5(4)	C(17) – C(10) – C(19)	108.3(4)
C(18) – C(10) – C(19)	108.8(4)	C(17) – C(10) – C(14)	109.6(3)
C(18) – C(10) – C(14)	108.5(3)	C(19) – C(10) – C(14)	112.0(3)
C(34) – P(3) – C(35)	102.4(4)	C(33) – P(3) – C(32)	99.8(4)
C(34) – P(3) – C(36)	103.9(5)	C(35) – P(3) – C(36)	100.0(4)
C(33) – P(3) – C(31)	101.5(4)	C(32) – P(3) – C(31)	96.9(4)
C(34) – P(3) – Pd	119.5(3)	C(33) – P(3) – Pd	117.7(3)
C(35) – P(3) – Pd	122.6(3)	C(32) – P(3) – Pd	124.0(2)
C(36) – P(3) – Pd	105.2(3)	C(31) – P(3) – Pd	112.9(3)
C(12) – P(2) – C(42)	104.69(16)	C(12) – P(2) – C(41)	105.64(14)
C(42) – P(2) – C(41)	107.57(19)	C(12) – P(2) – Pd	102.79(11)
C(42) – P(2) – Pd	118.44(12)	C(41) – P(2) – Pd	116.18(11)
C(49) – P(1) – C(26)	115.8(6)	C(26) – P(1) – C(52)	100.4(3)
C(26) – P(1) – C(51)	102.8(4)	C(52) – P(1) – C(51)	106.9(4)
C(49) – P(1) – C(57)	109.6(7)	C(26) – P(1) – C(57)	109.0(4)
C(49) – P(1) – Pd	116.0(7)	C(26) – P(1) – Pd	102.39(10)
C(52) – P(1) – Pd	129.6(3)	C(51) – P(1) – Pd	111.0(4)
C(57) – P(1) – Pd	103.1(5)	C(12) – C(11) – C(16)	116.7(3)
C(12) – C(11) – C	118.3(3)	C(16) – C(11) – C	124.9(3)
C(11) – C(12) – C(13)	121.2(3)	C(11) – C(12) – P(2)	113.5(2)
C(13) – C(12) – P(2)	125.3(3)	C(14) – C(13) – C(12)	121.4(3)
C(14) – C(13) – H(13)	119.3	C(12) – C(13) – H(13)	119.3
C(16) – C(15) – C(14)	122.5(3)	C(16) – C(15) – H(15)	118.7
C(14) – C(15) – H(15)	118.7	C(13) – C(14) – C(15)	116.9(3)
C(13) – C(14) – C(10)	122.4(3)	C(15) – C(14) – C(10)	120.6(3)
C(10) – C(18) – H(18A)	109.5	C(10) – C(18) – H(18B)	109.5
H(18A) – C(18) – H(18B)	109.5	C(10) – C(18) – H(18C)	109.5
H(18A) – C(18) – H(18C)	109.5	H(18B) – C(18) – H(18C)	109.5
C(10) – C(17) – H(17A)	109.5	C(10) – C(17) – H(17B)	109.5
H(17A) – C(17) – H(17B)	109.5	C(10) – C(17) – H(17C)	109.5
H(17A) – C(17) – H(17C)	109.5	H(17B) – C(17) – H(17C)	109.5
C(15) – C(16) – C(11)	120.5(3)	C(15) – C(16) – H(16)	119.8
C(11) – C(16) – H(16)	119.8	C(10) – C(19) – H(19A)	109.5
C(10) – C(19) – H(19B)	109.5	H(19A) – C(19) – H(19B)	109.5
C(10) – C(19) – H(19C)	109.5	H(19A) – C(19) – H(19C)	109.5
H(19B) – C(19) – H(19C)	109.5	C(27) – C(20) – C(28)	109.4(3)
C(27) – C(20) – C(24)	109.3(3)	C(28) – C(20) – C(24)	109.2(3)
C(27) – C(20) – C(29)	108.4(3)	C(28) – C(20) – C(29)	109.2(3)

Continued on next page

Table S5. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(24) – C(20) – C(29)	111.3(3)	C(22) – C(21) – C(26)	115.9(3)
C(22) – C(21) – C	123.9(3)	C(26) – C(21) – C	120.0(3)
F(97) – C(98) – F(98)	98.6(13)	F(97) – C(98) – C(1)	119.4(11)
F(98) – C(98) – C(1)	108.1(12)	F(97) – C(98) – F(99)	101.9(12)
F(98) – C(98) – F(99)	111.1(10)	C(1) – C(98) – F(99)	116.5(13)
C(5) – C(1) – C(2)	118.7(8)	C(5) – C(1) – C(98)	118.1(9)
C(2) – C(1) – C(98)	121.5(10)	C(3) – C(2) – C(1)	117.8(8)
C(3) – C(2) – H(2)	121.1	C(1) – C(2) – H(2)	121.1
C(92) – C(3) – C(2)	122.0(10)	C(92) – C(3) – C(4)	120.1(10)
C(2) – C(3) – C(4)	117.8(8)	F(93) – C(4) – F(1)	101.7(10)
F(93) – C(4) – F(3)	107.6(10)	F(1) – C(4) – F(3)	108.4(11)
F(93) – C(4) – C(3)	114.1(10)	F(1) – C(4) – C(3)	113.2(7)
F(3) – C(4) – C(3)	111.3(9)	C(91) – C(5) – C(1)	124.8(8)
C(91) – C(5) – H(5)	117.6	C(1) – C(5) – H(5)	117.6
C(3) – C(92) – C(91)	120.4(13)	C(3) – C(92) – H(92)	119.8
C(91) – C(92) – H(92)	119.8	F(94) – C(99) – F(96)	109.6(14)
F(94) – C(99) – F(95)	121.1(17)	F(96) – C(99) – F(95)	95.9(11)
F(94) – C(99) – C(95)	112.3(11)	F(96) – C(99) – C(95)	111.4(13)
F(95) – C(99) – C(95)	105.3(12)	C(96) – C(95) – C(94)	120.1(8)
C(96) – C(95) – C(99)	121.0(9)	C(94) – C(95) – C(99)	118.5(9)
C(95) – C(94) – C(93)	118.7(7)	C(95) – C(94) – H(94)	120.6
C(93) – C(94) – H(94)	120.6	C(94) – C(93) – C(6)	119.5(8)
C(94) – C(93) – C(97)	120.8(7)	C(6) – C(93) – C(97)	119.6(8)
F(91) – C(97) – F(92)	106.1(9)	F(91) – C(97) – F(2)	112.6(9)
F(92) – C(97) – F(2)	100.3(8)	F(91) – C(97) – C(93)	115.5(7)
F(92) – C(97) – C(93)	110.4(8)	F(2) – C(97) – C(93)	110.8(9)
C(95) – C(96) – C(91)	121.3(7)	C(95) – C(96) – H(96)	119.4
C(91) – C(96) – H(96)	119.4	C(91) – C(6) – C(93)	123.4(8)
C(91) – C(6) – H(6)	118.3	C(93) – C(6) – H(6)	118.3
C(73) – C(72) – C(71)	122.4(3)	C(73) – C(72) – H(72)	118.8
C(71) – C(72) – H(72)	118.8	C(22) – C(23) – C(24)	122.3(3)
C(22) – C(23) – H(23)	118.8	C(24) – C(23) – H(23)	118.8
C(23) – C(22) – C(21)	121.8(3)	C(23) – C(22) – H(22)	119.1
C(21) – C(22) – H(22)	119.1	C(72) – C(73) – C(74)	121.0(3)
C(72) – C(73) – C(77)	120.0(3)	C(74) – C(73) – C(77)	118.8(3)
C(25) – C(24) – C(23)	116.6(3)	C(25) – C(24) – C(20)	124.0(3)
C(23) – C(24) – C(20)	119.4(3)	C(24) – C(25) – C(26)	121.8(3)
C(24) – C(25) – H(25)	119.1	C(26) – C(25) – H(25)	119.1
C(25) – C(26) – C(21)	121.6(3)	C(25) – C(26) – P(1)	125.8(2)
C(21) – C(26) – P(1)	112.6(2)	C(20) – C(27) – H(27A)	109.5
C(20) – C(27) – H(27B)	109.5	H(27A) – C(27) – H(27B)	109.5
C(20) – C(27) – H(27C)	109.5	H(27A) – C(27) – H(27C)	109.5

Continued on next page

Table S5. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(27B) – C(27) – H(27C)	109.5	C(20) – C(28) – H(28A)	109.5
C(20) – C(28) – H(28B)	109.5	H(28A) – C(28) – H(28B)	109.5
C(20) – C(28) – H(28C)	109.5	H(28A) – C(28) – H(28C)	109.5
H(28B) – C(28) – H(28C)	109.5	C(20) – C(29) – H(29A)	109.5
C(20) – C(29) – H(29B)	109.5	H(29A) – C(29) – H(29B)	109.5
C(20) – C(29) – H(29C)	109.5	H(29A) – C(29) – H(29C)	109.5
H(29B) – C(29) – H(29C)	109.5	P(3) – C(31) – H(31A)	109.5
P(3) – C(31) – H(31B)	109.5	H(31A) – C(31) – H(31B)	109.5
P(3) – C(31) – H(31C)	109.5	H(31A) – C(31) – H(31C)	109.5
H(31B) – C(31) – H(31C)	109.5	P(3) – C(33) – H(33A)	109.5
P(3) – C(33) – H(33B)	109.5	H(33A) – C(33) – H(33B)	109.5
P(3) – C(33) – H(33C)	109.5	H(33A) – C(33) – H(33C)	109.5
H(33B) – C(33) – H(33C)	109.5	P(3) – C(32) – H(32A)	109.5
P(3) – C(32) – H(32B)	109.5	H(32A) – C(32) – H(32B)	109.5
P(3) – C(32) – H(32C)	109.5	H(32A) – C(32) – H(32C)	109.5
H(32B) – C(32) – H(32C)	109.5	P(3) – C(36) – H(36A)	109.5
P(3) – C(36) – H(36B)	109.5	H(36A) – C(36) – H(36B)	109.5
P(3) – C(36) – H(36C)	109.5	H(36A) – C(36) – H(36C)	109.5
H(36B) – C(36) – H(36C)	109.5	P(3) – C(34) – H(34A)	109.5
P(3) – C(34) – H(34B)	109.5	H(34A) – C(34) – H(34B)	109.5
P(3) – C(34) – H(34C)	109.5	H(34A) – C(34) – H(34C)	109.5
H(34B) – C(34) – H(34C)	109.5	P(3) – C(35) – H(35A)	109.5
P(3) – C(35) – H(35B)	109.5	H(35A) – C(35) – H(35B)	109.5
P(3) – C(35) – H(35C)	109.5	H(35A) – C(35) – H(35C)	109.5
H(35B) – C(35) – H(35C)	109.5	C(55) – C(52) – C(56)	113.8(6)
C(55) – C(52) – P(1)	113.8(5)	C(56) – C(52) – P(1)	105.8(5)
C(55) – C(52) – H(52)	107.7	C(56) – C(52) – H(52)	107.7
P(1) – C(52) – H(52)	107.7	C(52) – C(55) – H(55A)	109.5
C(52) – C(55) – H(55B)	109.5	H(55A) – C(55) – H(55B)	109.5
C(52) – C(55) – H(55C)	109.5	H(55A) – C(55) – H(55C)	109.5
H(55B) – C(55) – H(55C)	109.5	C(52) – C(56) – H(56A)	109.5
C(52) – C(56) – H(56B)	109.5	H(56A) – C(56) – H(56B)	109.5
C(52) – C(56) – H(56C)	109.5	H(56A) – C(56) – H(56C)	109.5
H(56B) – C(56) – H(56C)	109.5	C(57) – C(59) – H(59A)	109.5
C(57) – C(59) – H(59B)	109.5	H(59A) – C(59) – H(59B)	109.5
C(57) – C(59) – H(59C)	109.5	H(59A) – C(59) – H(59C)	109.5
H(59B) – C(59) – H(59C)	109.5	C(58) – C(57) – C(59)	112.3(12)
C(58) – C(57) – P(1)	108.3(10)	C(59) – C(57) – P(1)	110.0(8)
C(58) – C(57) – H(57)	108.7	C(59) – C(57) – H(57)	108.7
P(1) – C(57) – H(57)	108.7	C(57) – C(58) – H(58A)	109.5
C(57) – C(58) – H(58B)	109.5	H(58A) – C(58) – H(58B)	109.5
C(57) – C(58) – H(58C)	109.5	H(58A) – C(58) – H(58C)	109.5

Continued on next page

Table S5. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(58B) – C(58) – H(58C)	109.5	C(54) – C(51) – C(53)	111.4(8)
C(54) – C(51) – P(1)	108.3(8)	C(53) – C(51) – P(1)	119.5(8)
C(54) – C(51) – H(51)	105.5	C(53) – C(51) – H(51)	105.5
P(1) – C(51) – H(51)	105.5	C(51) – C(53) – H(53A)	109.5
C(51) – C(53) – H(53B)	109.5	H(53A) – C(53) – H(53B)	109.5
C(51) – C(53) – H(53C)	109.5	H(53A) – C(53) – H(53C)	109.5
H(53B) – C(53) – H(53C)	109.5	C(51) – C(54) – H(54A)	109.5
C(51) – C(54) – H(54B)	109.5	H(54A) – C(54) – H(54B)	109.5
C(51) – C(54) – H(54C)	109.5	H(54A) – C(54) – H(54C)	109.5
H(54B) – C(54) – H(54C)	109.5	C(48) – C(49) – C(47)	112.9(17)
C(48) – C(49) – P(1)	106.8(14)	C(47) – C(49) – P(1)	116.4(12)
C(48) – C(49) – H(49)	106.7	C(47) – C(49) – H(49)	106.7
P(1) – C(49) – H(49)	106.7	C(49) – C(47) – H(47A)	109.5
C(49) – C(47) – H(47B)	109.5	H(47A) – C(47) – H(47B)	109.5
C(49) – C(47) – H(47C)	109.5	H(47A) – C(47) – H(47C)	109.5
H(47B) – C(47) – H(47C)	109.5	C(49) – C(48) – H(48A)	109.5
C(49) – C(48) – H(48B)	109.5	H(48A) – C(48) – H(48B)	109.5
C(49) – C(48) – H(48C)	109.5	H(48A) – C(48) – H(48C)	109.5
H(48B) – C(48) – H(48C)	109.5	C(43) – C(41) – C(44)	111.1(3)
C(43) – C(41) – P(2)	108.6(2)	C(44) – C(41) – P(2)	116.4(3)
C(43) – C(41) – H(41)	106.7	C(44) – C(41) – H(41)	106.7
P(2) – C(41) – H(41)	106.7	C(46) – C(42) – C(45)	112.0(4)
C(46) – C(42) – P(2)	109.2(3)	C(45) – C(42) – P(2)	113.1(3)
C(46) – C(42) – H(42)	107.5	C(45) – C(42) – H(42)	107.5
P(2) – C(42) – H(42)	107.5	C(41) – C(43) – H(43A)	109.5
C(41) – C(43) – H(43B)	109.5	H(43A) – C(43) – H(43B)	109.5
C(41) – C(43) – H(43C)	109.5	H(43A) – C(43) – H(43C)	109.5
H(43B) – C(43) – H(43C)	109.5	C(41) – C(44) – H(44A)	109.5
C(41) – C(44) – H(44B)	109.5	H(44A) – C(44) – H(44B)	109.5
C(41) – C(44) – H(44C)	109.5	H(44A) – C(44) – H(44C)	109.5
H(44B) – C(44) – H(44C)	109.5	C(42) – C(45) – H(45A)	109.5
C(42) – C(45) – H(45B)	109.5	H(45A) – C(45) – H(45B)	109.5
C(42) – C(45) – H(45C)	109.5	H(45A) – C(45) – H(45C)	109.5
H(45B) – C(45) – H(45C)	109.5	C(42) – C(46) – H(46A)	109.5
C(42) – C(46) – H(46B)	109.5	H(46A) – C(46) – H(46B)	109.5
C(42) – C(46) – H(46C)	109.5	H(46A) – C(46) – H(46C)	109.5
H(46B) – C(46) – H(46C)	109.5	C(66) – C(61) – C(62)	115.8(3)
C(66) – C(61) – B	122.8(3)	C(62) – C(61) – B	121.0(3)
C(61) – C(62) – C(63)	122.7(3)	C(61) – C(62) – H(62)	118.6
C(63) – C(62) – H(62)	118.6	C(64) – C(63) – C(62)	120.1(3)
C(64) – C(63) – C(67)	120.8(3)	C(62) – C(63) – C(67)	119.1(3)
C(65) – C(64) – C(63)	118.3(3)	C(65) – C(64) – H(64)	120.8

Continued on next page

Table S5. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(63) – C(64) – H(64)	120.8	F(64) – C(68) – F(65)	105.9(5)
F(64) – C(68) – F(66)	105.9(4)	F(65) – C(68) – F(66)	103.3(4)
F(64) – C(68) – C(65)	114.4(3)	F(65) – C(68) – C(65)	114.0(4)
F(66) – C(68) – C(65)	112.3(4)	F(63) – C(67) – F(61)	108.8(4)
F(63) – C(67) – F(62)	103.8(4)	F(61) – C(67) – F(62)	104.2(4)
F(63) – C(67) – C(63)	114.0(4)	F(61) – C(67) – C(63)	113.5(3)
F(62) – C(67) – C(63)	111.8(4)	C(61) – C(66) – C(65)	122.0(3)
C(61) – C(66) – H(66)	119.0	C(65) – C(66) – H(66)	119.0
C(64) – C(65) – C(66)	121.0(3)	C(64) – C(65) – C(68)	118.9(3)
C(66) – C(65) – C(68)	120.0(4)	C(72) – C(71) – C(76)	115.4(3)
C(72) – C(71) – B	122.1(3)	C(76) – C(71) – B	122.4(3)
C(91) – B – C(71)	105.5(3)	C(91) – B – C(61)	113.2(3)
C(71) – B – C(61)	112.0(3)	C(91) – B – C(81)	110.7(3)
C(71) – B – C(81)	112.4(3)	C(61) – B – C(81)	103.2(2)
C(75) – C(74) – C(73)	118.0(3)	C(75) – C(74) – H(74)	121.0
C(73) – C(74) – H(74)	121.0	F(76) – C(78) – F(74)	104.8(4)
F(76) – C(78) – F(75)	107.6(4)	F(74) – C(78) – F(75)	105.7(4)
F(76) – C(78) – C(75)	113.9(4)	F(74) – C(78) – C(75)	111.2(4)
F(75) – C(78) – C(75)	113.0(3)	F(71) – C(77) – F(73)	106.4(4)
F(71) – C(77) – F(72)	105.2(4)	F(73) – C(77) – F(72)	105.1(4)
F(71) – C(77) – C(73)	113.2(4)	F(73) – C(77) – C(73)	113.5(3)
F(72) – C(77) – C(73)	112.6(4)	C(75) – C(76) – C(71)	122.8(3)
C(75) – C(76) – H(76)	118.6	C(71) – C(76) – H(76)	118.6
C(74) – C(75) – C(76)	120.4(3)	C(74) – C(75) – C(78)	118.4(3)
C(76) – C(75) – C(78)	121.1(3)	C(81) – C(82) – C(83)	122.4(3)
C(81) – C(82) – H(82)	118.8	C(83) – C(82) – H(82)	118.8
C(82) – C(81) – C(86)	115.3(3)	C(82) – C(81) – B	123.4(3)
C(86) – C(81) – B	120.9(3)	C(84) – C(83) – C(82)	121.4(3)
C(84) – C(83) – C(87)	119.6(3)	C(82) – C(83) – C(87)	119.0(3)
C(83) – C(84) – C(85)	117.6(3)	C(83) – C(84) – H(84)	121.2
C(85) – C(84) – H(84)	121.2	C(84) – C(85) – C(86)	121.1(3)
C(84) – C(85) – C(88)	118.5(3)	C(86) – C(85) – C(88)	120.3(4)
C(85) – C(86) – C(81)	122.1(3)	C(85) – C(86) – H(86)	118.9
C(81) – C(86) – H(86)	118.9	F(83) – C(87) – F(82)	107.3(4)
F(83) – C(87) – F(81)	105.1(4)	F(82) – C(87) – F(81)	104.0(4)
F(83) – C(87) – C(83)	114.6(4)	F(82) – C(87) – C(83)	112.3(3)
F(81) – C(87) – C(83)	112.7(4)	F(85) – C(88) – F(86)	114.7(5)
F(85) – C(88) – F(84)	101.0(4)	F(86) – C(88) – F(84)	99.6(4)
F(85) – C(88) – C(85)	113.5(4)	F(86) – C(88) – C(85)	113.1(3)
F(84) – C(88) – C(85)	113.4(5)	C(6) – C(91) – C(96)	116.1(7)
C(5) – C(91) – C(92)	115.0(9)	C(6) – C(91) – B	126.0(6)
C(5) – C(91) – B	126.3(5)	C(96) – C(91) – B	117.8(4)

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Table S5. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(92) – C(91) – B	118.4(8)	C(21) – C – C(11)	121.5(3)
C(21) – C – Pd	119.3(2)	C(11) – C – Pd	119.1(2)

2.2 Crystal data for [{PC•(sp²)P}$^{t\mathrm{Bu}}$PdS($C_{10}H_6$)SPd{PC•(sp²)P}$^{t\mathrm{Bu}}$] (4)

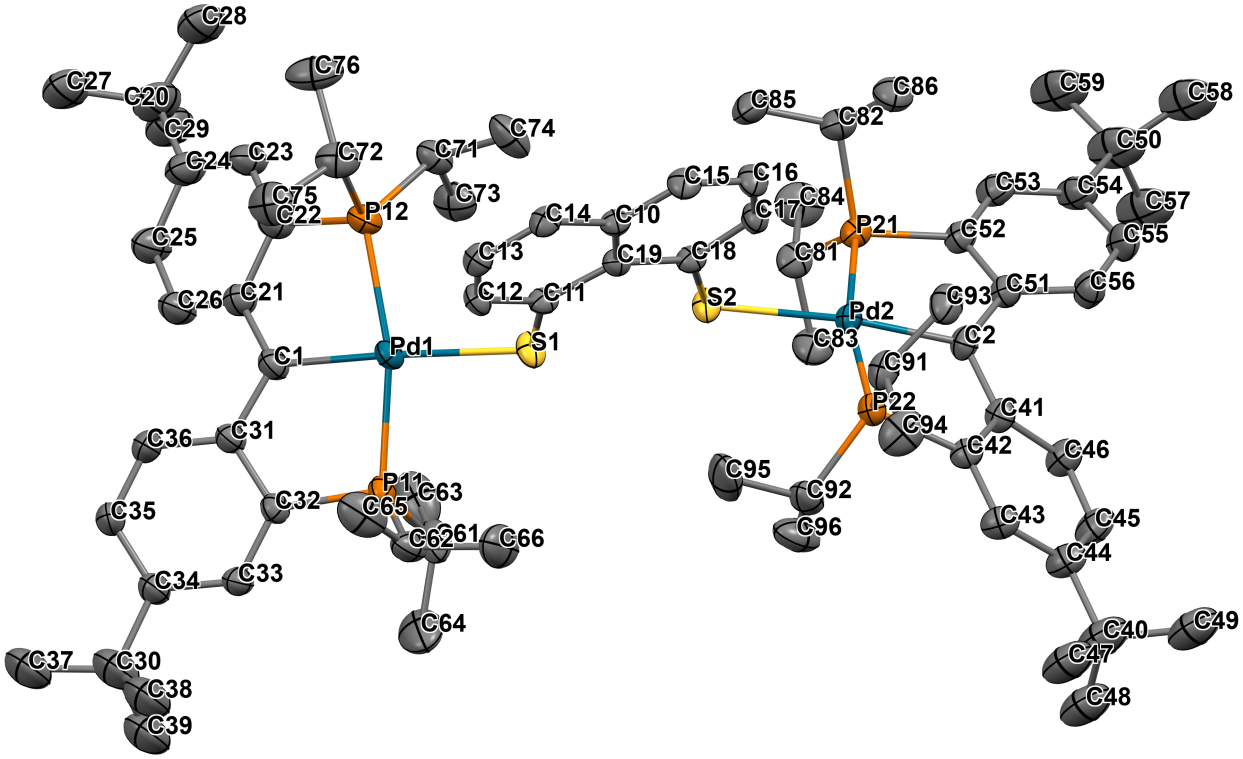

Figure S5. Thermal-ellipsoid representation of [{PC•(sp²)P}$^{t\mathrm{Bu}}$PdS($C_{10}H_6$)SPd{PC•(sp²)P}$^{t\mathrm{Bu}}$] (**4**) at 50% probability. Hydrogen atoms were omitted for clarity.

Table S6. Crystal data and structure refinement for [{PC$^{\bullet}$(sp^2)P}$^{t\mathrm{Bu}}$PdS(C$_{10}$H$_6$)SPd{PC$^{\bullet}$(sp^2)P}$^{t\mathrm{Bu}}$] (**4**).

Identification code:	pc64a	
Empirical formula:	$C_{76}H_{110}P_4Pd_2S_2$	
Formula weight:	1424.43	
Temperature:	120(2) K	
Wavelength:	1.54178 Å	
Crystal system:	Monoclinic	
Space group:	$P_2(1)/c$	
Unit cell dimensions:	a = 14.6121(3) Å	α = 90°
	b = 36.4414(8) Å	β = 90.1128(12)°
	c = 15.6562(3) Å	γ = 90°
Volume:	8336.7(3) Å^3	
Z:	4	
Density (calculated):	1.135 g·cm^{-3}	
Absorption coefficient (μ):	4.931 mm^{-1}	
F(000):	3000	
Crystal size:	0.130 × 0.080 × 0.080 mm^3	
θ range for data collection:	2.425 to 65.138°	
Index ranges:	$-16 \le h \le 17$, $-42 \le k \le 42$, $-18 \le l \le 18$	
Reflections collected:	184805	
Independent reflections:	14180 [R_{int} = 0.0617]	
Completeness to θ = 67.679°:	93.9 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.7526 and 0.5706	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	14180 / 0 / 713	
Goodness-of-fit on F^2:	1.057	
Final R indices [I>2σ(I)]:	R_1 = 0.0401, wR_2 = 0.0966	
R indices (all data):	R_1 = 0.0479, wR_2 = 0.1009	
Extinction coefficient:	n/a	
Largest diff. peak and hole:	1.146 and −1.083 e$^-$·Å^{-3}	

Table S7. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [{PC$^\bullet$(sp^2)P}$^{t\mathrm{Bu}}$PdS(C$_{10}$H$_6$)SPd{PC$^\bullet$(sp^2)P}$^{t\mathrm{Bu}}$] (**4**). U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

atom	x	y	z	U(eq)
Pd(1)	0.82924(2)	0.33450(2)	0.78033(2)	0.025(1)
C(1)	0.8913(2)	0.38182(10)	0.8173(2)	0.032(1)
S(1)	0.74929(6)	0.27791(2)	0.76079(5)	0.029(1)
S(2)	0.59606(6)	0.22113(2)	0.76173(5)	0.027(1)
Pd(2)	0.51623(2)	0.16455(2)	0.78463(2)	0.023(1)
C(2)	0.4547(2)	0.11786(9)	0.8264(2)	0.028(1)
P(11)	0.95351(6)	0.30821(2)	0.84289(5)	0.027(1)
C(10)	0.6733(2)	0.24890(9)	0.51596(19)	0.023(1)
C(11)	0.7400(2)	0.27246(9)	0.64897(19)	0.023(1)
P(12)	0.71984(6)	0.37444(3)	0.72834(5)	0.029(1)
C(12)	0.8007(2)	0.29227(9)	0.5988(2)	0.026(1)
P(21)	0.39121(6)	0.19220(2)	0.84118(5)	0.026(1)
C(21)	0.8352(2)	0.41397(10)	0.8292(2)	0.036(1)
C(20)	0.6466(4)	0.50595(13)	0.8739(4)	0.066(1)
C(19)	0.6733(2)	0.24897(9)	0.60795(19)	0.022(1)
C(18)	0.6064(2)	0.22585(9)	0.64984(19)	0.023(1)
C(17)	0.5457(2)	0.20585(9)	0.6000(2)	0.027(1)
C(16)	0.5482(2)	0.20579(9)	0.5105(2)	0.030(1)
C(15)	0.6112(2)	0.22669(9)	0.4691(2)	0.030(1)
C(14)	0.7351(2)	0.27081(9)	0.4685(2)	0.027(1)
C(13)	0.7978(2)	0.29189(9)	0.5096(2)	0.027(1)
P(22)	0.62540(6)	0.12451(2)	0.73378(5)	0.025(1)
C(22)	0.7486(2)	0.41567(10)	0.7883(2)	0.035(1)
C(23)	0.6901(3)	0.44538(11)	0.8011(2)	0.040(1)
C(24)	0.7113(3)	0.47417(11)	0.8559(3)	0.046(1)
C(30)	1.2781(3)	0.37174(16)	0.9048(4)	0.075(1)
C(29)	0.6224(3)	0.50602(13)	0.9689(3)	0.066(1)
C(28)	0.5587(3)	0.50319(13)	0.8226(4)	0.066(1)
C(27)	0.6956(3)	0.54231(13)	0.8532(4)	0.066(1)
C(26)	0.8555(3)	0.44326(11)	0.8850(3)	0.045(1)
C(25)	0.7958(3)	0.47200(11)	0.8979(3)	0.049(1)
C(33)	1.1199(2)	0.34508(9)	0.8827(2)	0.030(1)
C(32)	1.0288(2)	0.34738(9)	0.8593(2)	0.026(1)
C(31)	0.9875(2)	0.38134(9)	0.8396(2)	0.030(1)
C(34)	1.1768(2)	0.37603(10)	0.8843(2)	0.035(1)
C(35)	1.1370(2)	0.40927(10)	0.8612(3)	0.038(1)
C(36)	1.0460(3)	0.41200(10)	0.8398(3)	0.039(1)
C(43)	0.6466(2)	0.05080(10)	0.7918(2)	0.033(1)
C(42)	0.5924(2)	0.08217(9)	0.7873(2)	0.028(1)

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Table S7. – continued from previous page

atom	x	y	x	U(eq)
C(41)	0.5094(2)	0.08509(9)	0.8343(2)	0.029(1)
C(40)	0.6833(4)	−0.01320(14)	0.8538(3)	0.066(1)
C(39)	1.2911(3)	0.35261(16)	0.9899(4)	0.075(1)
C(38)	1.3197(3)	0.34397(15)	0.8411(4)	0.075(1)
C(37)	1.3299(3)	0.40623(15)	0.9032(4)	0.075(1)
C(44)	0.6242(3)	0.02115(11)	0.8448(2)	0.040(1)
C(45)	0.5465(3)	0.02541(11)	0.8954(2)	0.042(1)
C(46)	0.4913(3)	0.05568(10)	0.8912(2)	0.037(1)
C(53)	0.2320(3)	0.15690(11)	0.9051(2)	0.038(1)
C(52)	0.3197(2)	0.15377(9)	0.8721(2)	0.030(1)
C(51)	0.3604(2)	0.11921(9)	0.8555(2)	0.029(1)
C(50)	0.0858(3)	0.12856(17)	0.9667(4)	0.078(1)
C(49)	0.6244(4)	−0.04767(13)	0.8427(3)	0.066(1)
C(48)	0.7251(4)	−0.01354(14)	0.9435(3)	0.066(1)
C(47)	0.7606(4)	−0.01422(14)	0.7882(3)	0.066(1)
C(54)	0.1790(3)	0.12626(12)	0.9230(3)	0.045(1)
C(61)	0.9300(3)	0.28647(12)	0.9464(2)	0.048(1)
C(59)	0.0523(3)	0.16762(16)	0.9762(4)	0.078(1)
C(58)	0.0148(3)	0.10717(16)	0.9152(4)	0.078(1)
C(57)	0.0945(3)	0.11169(17)	1.0560(4)	0.078(1)
C(56)	0.3024(3)	0.08843(10)	0.8679(3)	0.039(1)
C(55)	0.2158(3)	0.09215(11)	0.9010(3)	0.046(1)
C(62)	1.0263(3)	0.27533(10)	0.7842(3)	0.041(1)
C(63)	0.8705(4)	0.31125(16)	1.0002(3)	0.068(2)
C(64)	1.0144(4)	0.27371(15)	0.9956(3)	0.074(2)
C(65)	1.0576(3)	0.29176(13)	0.7000(3)	0.054(1)
C(66)	0.9787(4)	0.23828(12)	0.7705(4)	0.067(2)
C(72)	0.7234(3)	0.38690(12)	0.6141(2)	0.043(1)
C(71)	0.5986(2)	0.36696(11)	0.7533(2)	0.035(1)
C(75)	0.8209(3)	0.39799(14)	0.5910(3)	0.054(1)
C(74)	0.5566(3)	0.33644(13)	0.6984(3)	0.052(1)
C(73)	0.5910(3)	0.35862(12)	0.8483(3)	0.046(1)
C(76)	0.6544(3)	0.41633(14)	0.5876(3)	0.059(1)
C(81)	0.4140(3)	0.22054(10)	0.9360(2)	0.034(1)
C(82)	0.3156(2)	0.21971(10)	0.7711(2)	0.033(1)
C(83)	0.4674(3)	0.19787(11)	1.0008(2)	0.043(1)
C(84)	0.3311(3)	0.23882(13)	0.9775(3)	0.054(1)
C(85)	0.3620(3)	0.25509(10)	0.7423(3)	0.045(1)
C(86)	0.2859(3)	0.19691(11)	0.6940(2)	0.043(1)
C(91)	0.6287(3)	0.11620(10)	0.6174(2)	0.033(1)
C(92)	0.7450(2)	0.13043(11)	0.7678(3)	0.039(1)
C(93)	0.5339(3)	0.10577(11)	0.5862(2)	0.043(1)

Continued on next page

Table S7. – continued from previous page

atom	x	y	x	U(eq)
C(94)	0.7005(3)	0.08837(12)	0.5878(3)	0.050(1)
C(95)	0.7926(3)	0.16186(12)	0.7197(4)	0.063(1)
C(96)	0.7472(3)	0.13624(13)	0.8639(3)	0.057(1)
H(12)	0.8463	0.3067	0.6263	0.031
H(17)	0.5003	0.1915	0.6278	0.033
H(16)	0.5062	0.1912	0.4789	0.036
H(15)	0.6137	0.2264	0.4084	0.035
H(14)	0.7327	0.2707	0.4079	0.032
H(13)	0.8396	0.3064	0.4778	0.033
H(23)	0.6336	0.4460	0.7711	0.048
H(29A)	0.5817	0.5267	0.9811	0.099
H(29B)	0.6785	0.5084	1.0028	0.099
H(29C)	0.5917	0.4830	0.9835	0.099
H(28A)	0.5730	0.5035	0.7615	0.099
H(28B)	0.5190	0.5240	0.8364	0.099
H(28C)	0.5273	0.4802	0.8368	0.099
H(27A)	0.7140	0.5424	0.7930	0.099
H(27B)	0.7500	0.5448	0.8894	0.099
H(27C)	0.6540	0.5629	0.8639	0.099
H(26)	0.9123	0.4432	0.9147	0.054
H(25)	0.8125	0.4909	0.9366	0.058
H(33)	1.1446	0.3219	0.8981	0.036
H(35)	1.1739	0.4307	0.8601	0.045
H(36)	1.0218	0.4353	0.8248	0.047
H(43)	0.7004	0.0495	0.7580	0.040
H(39A)	1.2593	0.3289	0.9890	0.113
H(39B)	1.2658	0.3679	1.0356	0.113
H(39C)	1.3565	0.3486	1.0002	0.113
H(38A)	1.2813	0.3219	0.8390	0.113
H(38B)	1.3815	0.3373	0.8598	0.113
H(38C)	1.3225	0.3551	0.7842	0.113
H(37A)	1.3944	0.4012	0.9159	0.113
H(37B)	1.3051	0.4231	0.9460	0.113
H(37C)	1.3249	0.4174	0.8464	0.113
H(45)	0.5312	0.0065	0.9346	0.050
H(46)	0.4393	0.0570	0.9274	0.044
H(53)	0.2076	0.1806	0.9156	0.046
H(49A)	0.5988	−0.0482	0.7848	0.098
H(49B)	0.5745	−0.0474	0.8844	0.098
H(49C)	0.6622	−0.0695	0.8518	0.098
H(48A)	0.7605	−0.0361	0.9515	0.098
H(48B)	0.6761	−0.0124	0.9861	0.098

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Table S7. – continued from previous page

atom	x	y	x	U(eq)
H(48C)	0.7654	0.0077	0.9504	0.098
H(47A)	0.7348	−0.0124	0.7306	0.098
H(47B)	0.7943	−0.0373	0.7938	0.098
H(47C)	0.8023	0.0064	0.7983	0.098
H(61)	0.8930	0.2640	0.9340	0.057
H(59A)	0.0424	0.1783	0.9196	0.117
H(59B)	0.0981	0.1821	1.0072	0.117
H(59C)	−0.0054	0.1677	1.0080	0.117
H(58A)	0.0098	0.1177	0.8578	0.117
H(58B)	−0.0447	0.1087	0.9438	0.117
H(58C)	0.0336	0.0814	0.9110	0.117
H(57A)	0.1108	0.0857	1.0509	0.117
H(57B)	0.0361	0.1140	1.0861	0.117
H(57C)	0.1423	0.1246	1.0881	0.117
H(56)	0.3239	0.0647	0.8530	0.047
H(55)	0.1797	0.0708	0.9091	0.055
H(62)	1.0821	0.2708	0.8197	0.050
H(63A)	0.8167	0.3188	0.9671	0.101
H(63B)	0.9055	0.3330	1.0171	0.101
H(63C)	0.8507	0.2980	1.0514	0.101
H(64A)	1.0498	0.2567	0.9602	0.111
H(64B)	0.9953	0.2612	1.0481	0.111
H(64C)	1.0523	0.2950	1.0103	0.111
H(65A)	1.0985	0.2745	0.6710	0.081
H(65B)	1.0902	0.3148	0.7109	0.081
H(65C)	1.0042	0.2966	0.6637	0.081
H(66A)	0.9233	0.2419	0.7361	0.100
H(66B)	0.9620	0.2278	0.8259	0.100
H(66C)	1.0202	0.2215	0.7406	0.100
H(72)	0.7086	0.3643	0.5807	0.051
H(71)	0.5647	0.3902	0.7415	0.043
H(75A)	0.8239	0.4041	0.5301	0.081
H(75B)	0.8626	0.3776	0.6031	0.081
H(75C)	0.8390	0.4194	0.6249	0.081
H(74A)	0.5655	0.3422	0.6378	0.077
H(74B)	0.4910	0.3346	0.7104	0.077
H(74C)	0.5865	0.3131	0.7117	0.077
H(73A)	0.5264	0.3558	0.8636	0.070
H(73B)	0.6177	0.3788	0.8812	0.070
H(73C)	0.6239	0.3359	0.8612	0.070
H(76A)	0.6596	0.4209	0.5261	0.089
H(76B)	0.6671	0.4391	0.6189	0.089

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Table S7. – continued from previous page

atom	x	y	x	U(eq)
H(76C)	0.5924	0.4079	0.6008	0.089
H(81)	0.4555	0.2408	0.9172	0.041
H(82)	0.2596	0.2264	0.8043	0.039
H(83A)	0.5223	0.1878	0.9737	0.065
H(83B)	0.4289	0.1777	1.0216	0.065
H(83C)	0.4854	0.2135	1.0489	0.065
H(84A)	0.2964	0.2523	0.9340	0.081
H(84B)	0.3518	0.2559	1.0219	0.081
H(84C)	0.2919	0.2200	1.0031	0.081
H(85A)	0.4154	0.2491	0.7072	0.067
H(85B)	0.3815	0.2691	0.7925	0.067
H(85C)	0.3187	0.2697	0.7086	0.067
H(86A)	0.2421	0.2110	0.6596	0.064
H(86B)	0.2569	0.1742	0.7137	0.064
H(86C)	0.3395	0.1909	0.6592	0.064
H(91)	0.6443	0.1401	0.5898	0.040
H(92)	0.7786	0.1072	0.7549	0.047
H(93A)	0.5331	0.1056	0.5236	0.064
H(93B)	0.4893	0.1236	0.6073	0.064
H(93C)	0.5182	0.0813	0.6076	0.064
H(94A)	0.7019	0.0877	0.5252	0.075
H(94B)	0.6847	0.0640	0.6096	0.075
H(94C)	0.7608	0.0956	0.6096	0.075
H(95A)	0.7918	0.1567	0.6583	0.094
H(95B)	0.8561	0.1640	0.7394	0.094
H(95C)	0.7603	0.1849	0.7309	0.094
H(96A)	0.8107	0.1392	0.8828	0.085
H(96B)	0.7201	0.1149	0.8924	0.085
H(96C)	0.7122	0.1583	0.8783	0.085

Table S8. Anisotropic displacement parameters (Å^2) for [{PC$^\bullet$(sp^2)P}$^{t\mathrm{Bu}}$PdS(C$_{10}$H$_6$)SPd{PC$^\bullet$(sp^2)P}$^{t\mathrm{Bu}}$] (**4**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ...+ 2hka^*b^*U_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd(1)	0.0238(1)	0.0281(1)	0.0246(1)	−0.0043(1)	−0.0021(1)	−0.0023(1)
C(1)	0.0277(18)	0.0312(19)	0.0364(19)	−0.0058(15)	−0.0061(14)	−0.0012(14)
S(1)	0.0353(5)	0.0355(5)	0.0168(4)	−0.0016(3)	−0.0019(3)	−0.0115(4)
S(2)	0.0349(4)	0.0289(4)	0.0161(4)	0.0002(3)	0.0009(3)	−0.0079(3)
Pd(2)	0.0249(1)	0.0236(1)	0.0201(1)	0.0008(1)	0.0022(1)	−0.0017(1)
C(2)	0.0310(18)	0.0268(17)	0.0262(17)	0.0033(14)	0.0064(13)	−0.0037(14)
P(11)	0.0305(5)	0.0245(4)	0.0248(4)	−0.0004(3)	−0.0048(3)	−0.0038(3)
C(10)	0.0259(17)	0.0256(16)	0.0191(15)	0.0011(12)	−0.0011(12)	0.0017(13)
C(11)	0.0284(17)	0.0244(16)	0.0160(14)	−0.0013(12)	−0.0036(12)	0.0015(13)
P(12)	0.0242(4)	0.0371(5)	0.0270(4)	−0.0034(4)	−0.0024(3)	0.0023(4)
C(12)	0.0249(17)	0.0300(18)	0.0230(16)	−0.0035(13)	−0.0016(13)	−0.0049(13)
P(21)	0.0297(5)	0.0251(4)	0.0221(4)	−0.0005(3)	0.0009(3)	0.0019(3)
C(21)	0.032(2)	0.032(2)	0.043(2)	−0.0039(16)	−0.0049(15)	0.0029(15)
C(20)	0.0620(16)	0.0462(13)	0.0895(19)	−0.0096(13)	−0.0098(14)	0.0208(12)
C(19)	0.0234(16)	0.0228(16)	0.0205(15)	−0.0017(12)	−0.0006(12)	0.0018(12)
C(18)	0.0274(17)	0.0244(16)	0.0173(15)	0.0000(12)	−0.0005(12)	0.0012(13)
C(17)	0.0299(18)	0.0268(17)	0.0249(17)	0.0024(13)	0.0002(13)	−0.0057(14)
C(16)	0.036(2)	0.0318(19)	0.0221(17)	−0.0010(14)	−0.0069(14)	−0.0068(15)
C(15)	0.037(2)	0.0344(19)	0.0169(15)	0.0004(13)	−0.0042(13)	−0.0017(15)
C(14)	0.0345(19)	0.0283(17)	0.0179(15)	0.0017(13)	0.0015(13)	−0.0002(14)
C(13)	0.0297(18)	0.0288(18)	0.0232(16)	0.0022(13)	0.0063(13)	−0.0008(14)
P(22)	0.0249(4)	0.0271(4)	0.0225(4)	−0.0013(3)	0.0039(3)	−0.0022(3)
C(22)	0.030(2)	0.038(2)	0.036(2)	−0.0025(16)	−0.0034(15)	0.0054(16)
C(23)	0.033(2)	0.043(2)	0.043(2)	−0.0008(17)	−0.0055(16)	0.0092(17)
C(24)	0.047(2)	0.039(2)	0.054(3)	−0.0013(19)	−0.0082(19)	0.0122(18)
C(30)	0.0410(14)	0.0770(19)	0.108(2)	−0.0034(16)	−0.0220(14)	−0.0022(12)
C(29)	0.0620(16)	0.0462(13)	0.0895(19)	−0.0096(13)	−0.0098(14)	0.0208(12)
C(28)	0.0620(16)	0.0462(13)	0.0895(19)	−0.0096(13)	−0.0098(14)	0.0208(12)
C(27)	0.0620(16)	0.0462(13)	0.0895(19)	−0.0096(13)	−0.0098(14)	0.0208(12)
C(26)	0.036(2)	0.039(2)	0.060(3)	−0.0124(19)	−0.0151(18)	0.0068(17)
C(25)	0.050(3)	0.037(2)	0.059(3)	−0.0153(19)	−0.015(2)	0.0101(19)
C(33)	0.0282(19)	0.0276(18)	0.0349(19)	−0.0028(14)	−0.0077(14)	0.0028(14)
C(32)	0.0275(18)	0.0266(17)	0.0248(16)	−0.0036(13)	−0.0023(13)	−0.0018(14)
C(31)	0.0258(18)	0.0290(18)	0.0337(18)	−0.0046(14)	−0.0044(14)	0.0011(14)
C(34)	0.0269(19)	0.033(2)	0.045(2)	−0.0042(16)	−0.0051(15)	0.0004(15)
C(35)	0.031(2)	0.0275(19)	0.055(2)	−0.0004(17)	−0.0084(17)	−0.0038(15)
C(36)	0.036(2)	0.0238(18)	0.058(2)	0.0014(17)	−0.0105(17)	−0.0005(15)
C(43)	0.035(2)	0.037(2)	0.0276(18)	0.0008(15)	0.0054(14)	0.0078(16)
C(42)	0.0312(19)	0.0304(18)	0.0234(17)	0.0019(14)	0.0015(13)	0.0018(14)

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Table S8. – continued from previous page

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(41)	0.0314(19)	0.0293(18)	0.0261(17)	0.0011(14)	0.0052(13)	−0.0011(14)
C(40)	0.0707(17)	0.0538(14)	0.0726(17)	0.0157(13)	0.0140(13)	0.0262(12)
C(39)	0.0410(14)	0.0770(19)	0.108(2)	−0.0034(16)	−0.0220(14)	−0.0022(12)
C(38)	0.0410(14)	0.0770(19)	0.108(2)	−0.0034(16)	−0.0220(14)	−0.0022(12)
C(37)	0.0410(14)	0.0770(19)	0.108(2)	−0.0034(16)	−0.0220(14)	−0.0022(12)
C(44)	0.046(2)	0.037(2)	0.035(2)	0.0058(16)	0.0049(16)	0.0089(17)
C(45)	0.052(2)	0.037(2)	0.037(2)	0.0136(17)	0.0118(17)	0.0065(18)
C(46)	0.038(2)	0.036(2)	0.037(2)	0.0067(16)	0.0148(16)	0.0057(16)
C(53)	0.038(2)	0.039(2)	0.038(2)	0.0101(16)	0.0059(16)	0.0067(16)
C(52)	0.0310(19)	0.0304(18)	0.0277(17)	0.0045(14)	0.0050(14)	0.0007(14)
C(51)	0.0290(18)	0.0307(18)	0.0279(17)	0.0022(14)	0.0031(13)	0.0005(14)
C(50)	0.0419(14)	0.098(2)	0.093(2)	0.0391(17)	0.0285(13)	0.0219(13)
C(49)	0.0707(17)	0.0538(14)	0.0726(17)	0.0157(13)	0.0140(13)	0.0262(12)
C(48)	0.0707(17)	0.0538(14)	0.0726(17)	0.0157(13)	0.0140(13)	0.0262(12)
C(47)	0.0707(17)	0.0538(14)	0.0726(17)	0.0157(13)	0.0140(13)	0.0262(12)
C(54)	0.029(2)	0.052(3)	0.054(2)	0.017(2)	0.0093(17)	0.0073(18)
C(61)	0.057(3)	0.054(3)	0.033(2)	0.0134(18)	−0.0070(18)	−0.024(2)
C(59)	0.0419(14)	0.098(2)	0.093(2)	0.0391(17)	0.0285(13)	0.0219(13)
C(58)	0.0419(14)	0.098(2)	0.093(2)	0.0391(17)	0.0285(13)	0.0219(13)
C(57)	0.0419(14)	0.098(2)	0.093(2)	0.0391(17)	0.0285(13)	0.0219(13)
C(56)	0.035(2)	0.032(2)	0.050(2)	0.0045(17)	0.0094(17)	−0.0021(16)
C(55)	0.032(2)	0.044(2)	0.061(3)	0.018(2)	0.0061(18)	−0.0071(17)
C(62)	0.036(2)	0.033(2)	0.055(2)	−0.0127(18)	−0.0166(18)	0.0071(16)
C(63)	0.072(3)	0.099(4)	0.031(2)	−0.002(2)	0.008(2)	−0.032(3)
C(64)	0.090(4)	0.076(4)	0.055(3)	0.038(3)	−0.026(3)	−0.022(3)
C(65)	0.048(3)	0.070(3)	0.044(2)	−0.027(2)	0.0039(19)	0.009(2)
C(66)	0.068(3)	0.034(2)	0.096(4)	−0.024(2)	−0.026(3)	0.004(2)
C(72)	0.042(2)	0.055(3)	0.0301(19)	0.0004(17)	0.0021(16)	0.0082(19)
C(71)	0.0277(19)	0.043(2)	0.036(2)	−0.0080(16)	−0.0014(15)	0.0020(16)
C(75)	0.048(3)	0.068(3)	0.047(2)	0.010(2)	0.015(2)	0.004(2)
C(74)	0.029(2)	0.067(3)	0.059(3)	−0.019(2)	−0.0012(18)	−0.0069(19)
C(73)	0.035(2)	0.058(3)	0.046(2)	0.002(2)	0.0096(17)	0.0043(19)
C(76)	0.059(3)	0.080(3)	0.039(2)	0.013(2)	0.002(2)	0.028(3)
C(81)	0.043(2)	0.035(2)	0.0236(17)	−0.0067(14)	−0.0023(15)	0.0013(16)
C(82)	0.035(2)	0.0327(19)	0.0304(18)	0.0007(15)	−0.0009(14)	0.0059(15)
C(83)	0.053(3)	0.050(2)	0.0270(19)	−0.0006(17)	−0.0072(17)	−0.0015(19)
C(84)	0.063(3)	0.060(3)	0.038(2)	−0.021(2)	0.002(2)	0.012(2)
C(85)	0.054(3)	0.032(2)	0.048(2)	0.0080(17)	−0.0084(19)	0.0051(18)
C(86)	0.044(2)	0.049(2)	0.035(2)	0.0012(18)	−0.0102(17)	−0.0011(18)
C(91)	0.045(2)	0.0301(19)	0.0241(17)	0.0001(14)	0.0070(15)	−0.0043(16)
C(92)	0.0261(19)	0.037(2)	0.055(2)	−0.0077(18)	−0.0029(16)	0.0025(15)
C(93)	0.062(3)	0.035(2)	0.031(2)	−0.0016(16)	−0.0091(18)	−0.0095(18)

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Table S8. – continued from previous page

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(94)	0.068(3)	0.049(3)	0.032(2)	−0.0058(18)	0.0152(19)	0.010(2)
C(95)	0.030(2)	0.047(3)	0.112(4)	−0.011(3)	0.010(2)	−0.0091(19)
C(96)	0.049(3)	0.058(3)	0.063(3)	−0.021(2)	−0.028(2)	0.012(2)

Table S9. Distances [Å] for [{PC$^{\bullet}$(sp^2)P}$^{t\mathrm{Bu}}$PdS(C$_{10}$H$_6$)SPd{PC$^{\bullet}$(sp^2)P}$^{t\mathrm{Bu}}$] (**4**).

atom – atom	distance	atom – atom	distance
Pd(1) – C(1)	2.031(3)	Pd(1) – P(11)	2.2732(9)
Pd(1) – P(12)	2.3089(9)	Pd(1) – S(1)	2.3895(8)
C(1) – C(21)	1.442(5)	C(1) – C(31)	1.448(5)
S(1) – C(11)	1.767(3)	S(2) – C(18)	1.767(3)
S(2) – Pd(2)	2.3961(8)	Pd(2) – C(2)	2.033(3)
Pd(2) – P(21)	2.2677(9)	Pd(2) – P(22)	2.3051(9)
C(2) – C(41)	1.442(5)	C(2) – C(51)	1.453(5)
P(11) – C(32)	1.820(3)	P(11) – C(61)	1.836(4)
P(11) – C(62)	1.848(4)	C(10) – C(14)	1.418(4)
C(10) – C(15)	1.419(5)	C(10) – C(19)	1.440(4)
C(11) – C(12)	1.389(4)	C(11) – C(19)	1.447(4)
P(12) – C(22)	1.820(4)	P(12) – C(71)	1.835(4)
P(12) – C(72)	1.847(4)	C(12) – C(13)	1.397(4)
C(12) – H(12)	0.9500	P(21) – C(52)	1.814(3)
P(21) – C(81)	1.838(3)	P(21) – C(82)	1.851(3)
C(21) – C(26)	1.411(5)	C(21) – C(22)	1.419(5)
C(20) – C(28)	1.517(7)	C(20) – C(24)	1.521(6)
C(20) – C(29)	1.530(7)	C(20) – C(27)	1.541(7)
C(19) – C(18)	1.448(4)	C(18) – C(17)	1.387(4)
C(17) – C(16)	1.401(4)	C(17) – H(17)	0.9500
C(16) – C(15)	1.360(5)	C(16) – H(16)	0.9500
C(15) – H(15)	0.9500	C(14) – C(13)	1.356(5)
C(14) – H(14)	0.9500	C(13) – H(13)	0.9500
P(22) – C(42)	1.822(3)	P(22) – C(92)	1.839(4)
P(22) – C(91)	1.848(3)	C(22) – C(23)	1.394(5)
C(23) – C(24)	1.390(6)	C(23) – H(23)	0.9500
C(24) – C(25)	1.400(6)	C(30) – C(37)	1.468(7)
C(30) – C(39)	1.516(8)	C(30) – C(34)	1.522(6)
C(30) – C(38)	1.546(8)	C(29) – H(29A)	0.9800
C(29) – H(29B)	0.9800	C(29) – H(29C)	0.9800
C(28) – H(28A)	0.9800	C(28) – H(28B)	0.9800
C(28) – H(28C)	0.9800	C(27) – H(27A)	0.9800
C(27) – H(27B)	0.9800	C(27) – H(27C)	0.9800
C(26) – C(25)	1.378(5)	C(26) – H(26)	0.9500
C(25) – H(25)	0.9500	C(33) – C(32)	1.383(5)
C(33) – C(34)	1.402(5)	C(33) – H(33)	0.9500
C(32) – C(31)	1.411(5)	C(31) – C(36)	1.407(5)
C(34) – C(35)	1.391(5)	C(35) – C(36)	1.374(5)
C(35) – H(35)	0.9500	C(36) – H(36)	0.9500
C(43) – C(42)	1.392(5)	C(43) – C(44)	1.401(5)
C(43) – H(43)	0.9500	C(42) – C(41)	1.423(5)

Continued on next page

Table S9. – continued from previous page

atom – atom	distance	atom – atom	distance
C(41) – C(46)	1.419(5)	C(40) – C(44)	1.527(6)
C(40) – C(47)	1.529(7)	C(40) – C(48)	1.530(7)
C(40) – C(49)	1.532(7)	C(39) – H(39A)	0.9800
C(39) – H(39B)	0.9800	C(39) – H(39C)	0.9800
C(38) – H(38A)	0.9800	C(38) – H(38B)	0.9800
C(38) – H(38C)	0.9800	C(37) – H(37A)	0.9800
C(37) – H(37B)	0.9800	C(37) – H(37C)	0.9800
C(44) – C(45)	1.396(5)	C(45) – C(46)	1.368(5)
C(45) – H(45)	0.9500	C(46) – H(46)	0.9500
C(53) – C(54)	1.388(6)	C(53) – C(52)	1.388(5)
C(53) – H(53)	0.9500	C(52) – C(51)	1.417(5)
C(51) – C(56)	1.420(5)	C(50) – C(59)	1.513(8)
C(50) – C(58)	1.527(9)	C(50) – C(54)	1.527(6)
C(50) – C(57)	1.532(7)	C(49) – H(49A)	0.9800
C(49) – H(49B)	0.9800	C(49) – H(49C)	0.9800
C(48) – H(48A)	0.9800	C(48) – H(48B)	0.9800
C(48) – H(48C)	0.9800	C(47) – H(47A)	0.9800
C(47) – H(47B)	0.9800	C(47) – H(47C)	0.9800
C(54) – C(55)	1.398(6)	C(61) – C(63)	1.512(7)
C(61) – C(64)	1.526(6)	C(61) – H(61)	1.0000
C(59) – H(59A)	0.9800	C(59) – H(59B)	0.9800
C(59) – H(59C)	0.9800	C(58) – H(58A)	0.9800
C(58) – H(58B)	0.9800	C(58) – H(58C)	0.9800
C(57) – H(57A)	0.9800	C(57) – H(57B)	0.9800
C(57) – H(57C)	0.9800	C(56) – C(55)	1.374(5)
C(56) – H(56)	0.9500	C(55) – H(55)	0.9500
C(62) – C(65)	1.520(6)	C(62) – C(66)	1.534(6)
C(62) – H(62)	1.0000	C(63) – H(63A)	0.9800
C(63) – H(63B)	0.9800	C(63) – H(63C)	0.9800
C(64) – H(64A)	0.9800	C(64) – H(64B)	0.9800
C(64) – H(64C)	0.9800	C(65) – H(65A)	0.9800
C(65) – H(65B)	0.9800	C(65) – H(65C)	0.9800
C(66) – H(66A)	0.9800	C(66) – H(66B)	0.9800
C(66) – H(66C)	0.9800	C(72) – C(75)	1.525(6)
C(72) – C(76)	1.529(6)	C(72) – H(72)	1.0000
C(71) – C(73)	1.522(5)	C(71) – C(74)	1.534(5)
C(71) – H(71)	1.0000	C(75) – H(75A)	0.9800
C(75) – H(75B)	0.9800	C(75) – H(75C)	0.9800
C(74) – H(74A)	0.9800	C(74) – H(74B)	0.9800
C(74) – H(74C)	0.9800	C(73) – H(73A)	0.9800
C(73) – H(73B)	0.9800	C(73) – H(73C)	0.9800
C(76) – H(76A)	0.9800	C(76) – H(76B)	0.9800

Continued on next page

Table S9. – continued from previous page

atom – atom	distance	atom – atom	distance
C(76) – H(76C)	0.9800	C(81) – C(83)	1.523(5)
C(81) – C(84)	1.529(5)	C(81) – H(81)	1.0000
C(82) – C(85)	1.525(5)	C(82) – C(86)	1.527(5)
C(82) – H(82)	1.0000	C(83) – H(83A)	0.9800
C(83) – H(83B)	0.9800	C(83) – H(83C)	0.9800
C(84) – H(84A)	0.9800	C(84) – H(84B)	0.9800
C(84) – H(84C)	0.9800	C(85) – H(85A)	0.9800
C(85) – H(85B)	0.9800	C(85) – H(85C)	0.9800
C(86) – H(86A)	0.9800	C(86) – H(86B)	0.9800
C(86) – H(86C)	0.9800	C(91) – C(93)	1.516(5)
C(91) – C(94)	1.532(5)	C(91) – H(91)	1.0000
C(92) – C(96)	1.519(6)	C(92) – C(95)	1.538(6)
C(92) – H(92)	1.0000	C(93) – H(93A)	0.9800
C(93) – H(93B)	0.9800	C(93) – H(93C)	0.9800
C(94) – H(94A)	0.9800	C(94) – H(94B)	0.9800
C(94) – H(94C)	0.9800	C(95) – H(95A)	0.9800
C(95) – H(95B)	0.9800	C(95) – H(95C)	0.9800
C(96) – H(96A)	0.9800	C(96) – H(96B)	0.9800
C(96) – H(96C)	0.9800		

Table S10. Angles [°] for [{PC$^{\bullet}$(sp^2)P}$^{t\mathrm{Bu}}$PdS(C$_{10}$H$_6$)SPd{PC$^{\bullet}$(sp^2)P}$^{t\mathrm{Bu}}$] (**4**).

atom – atom – atom	angle	atom – atom – atom	angle
C(1) – Pd(1) – P(11)	83.09(10)	C(1) – Pd(1) – P(12)	82.73(10)
P(11) – Pd(1) – P(12)	165.81(3)	C(1) – Pd(1) – S(1)	170.65(10)
P(11) – Pd(1) – S(1)	94.67(3)	P(12) – Pd(1) – S(1)	99.25(3)
C(21) – C(1) – C(31)	122.0(3)	C(21) – C(1) – Pd(1)	118.2(2)
C(31) – C(1) – Pd(1)	119.4(2)	C(11) – S(1) – Pd(1)	105.10(11)
C(18) – S(2) – Pd(2)	105.95(11)	C(2) – Pd(2) – P(21)	83.64(10)
C(2) – Pd(2) – P(22)	83.57(10)	P(21) – Pd(2) – P(22)	167.09(3)
C(2) – Pd(2) – S(2)	169.70(10)	P(21) – Pd(2) – S(2)	93.95(3)
P(22) – Pd(2) – S(2)	98.95(3)	C(41) – C(2) – C(51)	121.8(3)
C(41) – C(2) – Pd(2)	118.4(2)	C(51) – C(2) – Pd(2)	119.5(2)
C(32) – P(11) – C(61)	109.12(17)	C(32) – P(11) – C(62)	103.34(17)
C(61) – P(11) – C(62)	105.5(2)	C(32) – P(11) – Pd(1)	102.25(11)
C(61) – P(11) – Pd(1)	114.29(15)	C(62) – P(11) – Pd(1)	121.29(12)
C(14) – C(10) – C(15)	117.2(3)	C(14) – C(10) – C(19)	121.6(3)
C(15) – C(10) – C(19)	121.2(3)	C(12) – C(11) – C(19)	119.2(3)
C(12) – C(11) – S(1)	117.0(2)	C(19) – C(11) – S(1)	123.8(2)
C(22) – P(12) – C(71)	103.58(17)	C(22) – P(12) – C(72)	106.82(19)
C(71) – P(12) – C(72)	105.80(17)	C(22) – P(12) – Pd(1)	100.35(12)
C(71) – P(12) – Pd(1)	119.94(13)	C(72) – P(12) – Pd(1)	118.40(13)
C(11) – C(12) – C(13)	122.8(3)	C(11) – C(12) – H(12)	118.6
C(13) – C(12) – H(12)	118.6	C(52) – P(21) – C(81)	108.77(17)
C(52) – P(21) – C(82)	103.48(16)	C(81) – P(21) – C(82)	106.36(16)
C(52) – P(21) – Pd(2)	103.05(11)	C(81) – P(21) – Pd(2)	114.85(12)
C(82) – P(21) – Pd(2)	119.31(12)	C(26) – C(21) – C(22)	115.7(3)
C(26) – C(21) – C(1)	125.2(3)	C(22) – C(21) – C(1)	118.9(3)
C(28) – C(20) – C(24)	112.2(4)	C(28) – C(20) – C(29)	108.5(5)
C(24) – C(20) – C(29)	109.0(4)	C(28) – C(20) – C(27)	109.8(4)
C(24) – C(20) – C(27)	109.1(4)	C(29) – C(20) – C(27)	108.1(4)
C(10) – C(19) – C(11)	116.3(3)	C(10) – C(19) – C(18)	116.9(3)
C(11) – C(19) – C(18)	126.7(3)	C(17) – C(18) – C(19)	118.8(3)
C(17) – C(18) – S(2)	116.8(2)	C(19) – C(18) – S(2)	124.4(2)
C(18) – C(17) – C(16)	123.1(3)	C(18) – C(17) – H(17)	118.5
C(16) – C(17) – H(17)	118.5	C(15) – C(16) – C(17)	119.7(3)
C(15) – C(16) – H(16)	120.2	C(17) – C(16) – H(16)	120.2
C(16) – C(15) – C(10)	120.3(3)	C(16) – C(15) – H(15)	119.8
C(10) – C(15) – H(15)	119.8	C(13) – C(14) – C(10)	120.1(3)
C(13) – C(14) – H(14)	120.0	C(10) – C(14) – H(14)	120.0
C(14) – C(13) – C(12)	120.0(3)	C(14) – C(13) – H(13)	120.0
C(12) – C(13) – H(13)	120.0	C(42) – P(22) – C(92)	102.64(17)
C(42) – P(22) – C(91)	108.82(16)	C(92) – P(22) – C(91)	106.16(18)
C(42) – P(22) – Pd(2)	101.13(11)	C(92) – P(22) – Pd(2)	118.93(13)

Continued on next page

Table S10. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(91) – P(22) – Pd(2)	117.61(12)	C(23) – C(22) – C(21)	121.0(3)
C(23) – C(22) – P(12)	125.1(3)	C(21) – C(22) – P(12)	113.7(3)
C(24) – C(23) – C(22)	122.6(4)	C(24) – C(23) – H(23)	118.7
C(22) – C(23) – H(23)	118.7	C(23) – C(24) – C(25)	116.3(4)
C(23) – C(24) – C(20)	123.5(4)	C(25) – C(24) – C(20)	120.2(4)
C(37) – C(30) – C(39)	110.2(5)	C(37) – C(30) – C(34)	114.2(4)
C(39) – C(30) – C(34)	110.6(5)	C(37) – C(30) – C(38)	110.3(5)
C(39) – C(30) – C(38)	102.6(5)	C(34) – C(30) – C(38)	108.3(4)
C(20) – C(29) – H(29A)	109.5	C(20) – C(29) – H(29B)	109.5
H(29A) – C(29) – H(29B)	109.5	C(20) – C(29) – H(29C)	109.5
H(29A) – C(29) – H(29C)	109.5	H(29B) – C(29) – H(29C)	109.5
C(20) – C(28) – H(28A)	109.5	C(20) – C(28) – H(28B)	109.5
H(28A) – C(28) – H(28B)	109.5	C(20) – C(28) – H(28C)	109.5
H(28A) – C(28) – H(28C)	109.5	H(28B) – C(28) – H(28C)	109.5
C(20) – C(27) – H(27A)	109.5	C(20) – C(27) – H(27B)	109.5
H(27A) – C(27) – H(27B)	109.5	C(20) – C(27) – H(27C)	109.5
H(27A) – C(27) – H(27C)	109.5	H(27B) – C(27) – H(27C)	109.5
C(25) – C(26) – C(21)	122.2(4)	C(25) – C(26) – H(26)	118.9
C(21) – C(26) – H(26)	118.9	C(26) – C(25) – C(24)	122.1(4)
C(26) – C(25) – H(25)	118.9	C(24) – C(25) – H(25)	118.9
C(32) – C(33) – C(34)	121.8(3)	C(32) – C(33) – H(33)	119.1
C(34) – C(33) – H(33)	119.1	C(33) – C(32) – C(31)	121.5(3)
C(33) – C(32) – P(11)	124.8(3)	C(31) – C(32) – P(11)	113.5(2)
C(36) – C(31) – C(32)	115.9(3)	C(36) – C(31) – C(1)	125.5(3)
C(32) – C(31) – C(1)	118.5(3)	C(35) – C(34) – C(33)	116.6(3)
C(35) – C(34) – C(30)	123.4(4)	C(33) – C(34) – C(30)	119.9(4)
C(36) – C(35) – C(34)	122.0(3)	C(36) – C(35) – H(35)	119.0
C(34) – C(35) – H(35)	119.0	C(35) – C(36) – C(31)	122.1(3)
C(35) – C(36) – H(36)	119.0	C(31) – C(36) – H(36)	119.0
C(42) – C(43) – C(44)	122.0(3)	C(42) – C(43) – H(43)	119.0
C(44) – C(43) – H(43)	119.0	C(43) – C(42) – C(41)	121.4(3)
C(43) – C(42) – P(22)	124.6(3)	C(41) – C(42) – P(22)	113.7(2)
C(46) – C(41) – C(42)	115.4(3)	C(46) – C(41) – C(2)	125.1(3)
C(42) – C(41) – C(2)	119.3(3)	C(44) – C(40) – C(47)	112.1(4)
C(44) – C(40) – C(48)	108.4(4)	C(47) – C(40) – C(48)	108.8(4)
C(44) – C(40) – C(49)	110.1(4)	C(47) – C(40) – C(49)	108.6(4)
C(48) – C(40) – C(49)	108.7(4)	C(30) – C(39) – H(39A)	109.5
C(30) – C(39) – H(39B)	109.5	H(39A) – C(39) – H(39B)	109.5
C(30) – C(39) – H(39C)	109.5	H(39A) – C(39) – H(39C)	109.5
H(39B) – C(39) – H(39C)	109.5	C(30) – C(38) – H(38A)	109.5
C(30) – C(38) – H(38B)	109.5	H(38A) – C(38) – H(38B)	109.5
C(30) – C(38) – H(38C)	109.5	H(38A) – C(38) – H(38C)	109.5

Continued on next page

Table S10. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(38B) – C(38) – H(38C)	109.5	C(30) – C(37) – H(37A)	109.5
C(30) – C(37) – H(37B)	109.5	H(37A) – C(37) – H(37B)	109.5
C(30) – C(37) – H(37C)	109.5	H(37A) – C(37) – H(37C)	109.5
H(37B) – C(37) – H(37C)	109.5	C(45) – C(44) – C(43)	116.2(3)
C(45) – C(44) – C(40)	119.9(4)	C(43) – C(44) – C(40)	123.7(4)
C(46) – C(45) – C(44)	122.9(3)	C(46) – C(45) – H(45)	118.6
C(44) – C(45) – H(45)	118.6	C(45) – C(46) – C(41)	121.9(3)
C(45) – C(46) – H(46)	119.0	C(41) – C(46) – H(46)	119.0
C(54) – C(53) – C(52)	121.7(4)	C(54) – C(53) – H(53)	119.1
C(52) – C(53) – H(53)	119.1	C(53) – C(52) – C(51)	122.0(3)
C(53) – C(52) – P(21)	124.7(3)	C(51) – C(52) – P(21)	113.3(2)
C(52) – C(51) – C(56)	115.2(3)	C(52) – C(51) – C(2)	119.1(3)
C(56) – C(51) – C(2)	125.7(3)	C(59) – C(50) – C(58)	108.2(4)
C(59) – C(50) – C(54)	112.6(4)	C(58) – C(50) – C(54)	109.9(5)
C(59) – C(50) – C(57)	108.3(5)	C(58) – C(50) – C(57)	109.4(5)
C(54) – C(50) – C(57)	108.3(4)	C(40) – C(49) – H(49A)	109.5
C(40) – C(49) – H(49B)	109.5	H(49A) – C(49) – H(49B)	109.5
C(40) – C(49) – H(49C)	109.5	H(49A) – C(49) – H(49C)	109.5
H(49B) – C(49) – H(49C)	109.5	C(40) – C(48) – H(48A)	109.5
C(40) – C(48) – H(48B)	109.5	H(48A) – C(48) – H(48B)	109.5
C(40) – C(48) – H(48C)	109.5	H(48A) – C(48) – H(48C)	109.5
H(48B) – C(48) – H(48C)	109.5	C(40) – C(47) – H(47A)	109.5
C(40) – C(47) – H(47B)	109.5	H(47A) – C(47) – H(47B)	109.5
C(40) – C(47) – H(47C)	109.5	H(47A) – C(47) – H(47C)	109.5
H(47B) – C(47) – H(47C)	109.5	C(53) – C(54) – C(55)	116.7(3)
C(53) – C(54) – C(50)	123.0(4)	C(55) – C(54) – C(50)	120.2(4)
C(63) – C(61) – C(64)	111.4(4)	C(63) – C(61) – P(11)	110.1(3)
C(64) – C(61) – P(11)	115.2(3)	C(63) – C(61) – H(61)	106.6
C(64) – C(61) – H(61)	106.6	P(11) – C(61) – H(61)	106.6
C(50) – C(59) – H(59A)	109.5	C(50) – C(59) – H(59B)	109.5
H(59A) – C(59) – H(59B)	109.5	C(50) – C(59) – H(59C)	109.5
H(59A) – C(59) – H(59C)	109.5	H(59B) – C(59) – H(59C)	109.5
C(50) – C(58) – H(58A)	109.5	C(50) – C(58) – H(58B)	109.5
H(58A) – C(58) – H(58B)	109.5	C(50) – C(58) – H(58C)	109.5
H(58A) – C(58) – H(58C)	109.5	H(58B) – C(58) – H(58C)	109.5
C(50) – C(57) – H(57A)	109.5	C(50) – C(57) – H(57B)	109.5
H(57A) – C(57) – H(57B)	109.5	C(50) – C(57) – H(57C)	109.5
H(57A) – C(57) – H(57C)	109.5	H(57B) – C(57) – H(57C)	109.5
C(55) – C(56) – C(51)	121.6(4)	C(55) – C(56) – H(56)	119.2
C(51) – C(56) – H(56)	119.2	C(56) – C(55) – C(54)	122.4(4)
C(56) – C(55) – H(55)	118.8	C(54) – C(55) – H(55)	118.8
C(65) – C(62) – C(66)	111.2(4)	C(65) – C(62) – P(11)	110.5(3)

Continued on next page

Table S10. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(66) – C(62) – P(11)	112.3(3)	C(65) – C(62) – H(62)	107.5
C(66) – C(62) – H(62)	107.5	P(11) – C(62) – H(62)	107.5
C(61) – C(63) – H(63A)	109.5	C(61) – C(63) – H(63B)	109.5
H(63A) – C(63) – H(63B)	109.5	C(61) – C(63) – H(63C)	109.5
H(63A) – C(63) – H(63C)	109.5	H(63B) – C(63) – H(63C)	109.5
C(61) – C(64) – H(64A)	109.5	C(61) – C(64) – H(64B)	109.5
H(64A) – C(64) – H(64B)	109.5	C(61) – C(64) – H(64C)	109.5
H(64A) – C(64) – H(64C)	109.5	H(64B) – C(64) – H(64C)	109.5
C(62) – C(65) – H(65A)	109.5	C(62) – C(65) – H(65B)	109.5
H(65A) – C(65) – H(65B)	109.5	C(62) – C(65) – H(65C)	109.5
H(65A) – C(65) – H(65C)	109.5	H(65B) – C(65) – H(65C)	109.5
C(62) – C(66) – H(66A)	109.5	C(62) – C(66) – H(66B)	109.5
H(66A) – C(66) – H(66B)	109.5	C(62) – C(66) – H(66C)	109.5
H(66A) – C(66) – H(66C)	109.5	H(66B) – C(66) – H(66C)	109.5
C(75) – C(72) – C(76)	111.5(4)	C(75) – C(72) – P(12)	108.8(3)
C(76) – C(72) – P(12)	114.5(3)	C(75) – C(72) – H(72)	107.2
C(76) – C(72) – H(72)	107.2	P(12) – C(72) – H(72)	107.2
C(73) – C(71) – C(74)	111.9(4)	C(73) – C(71) – P(12)	108.1(3)
C(74) – C(71) – P(12)	111.9(3)	C(73) – C(71) – H(71)	108.3
C(74) – C(71) – H(71)	108.3	P(12) – C(71) – H(71)	108.3
C(72) – C(75) – H(75A)	109.5	C(72) – C(75) – H(75B)	109.5
H(75A) – C(75) – H(75B)	109.5	C(72) – C(75) – H(75C)	109.5
H(75A) – C(75) – H(75C)	109.5	H(75B) – C(75) – H(75C)	109.5
C(71) – C(74) – H(74A)	109.5	C(71) – C(74) – H(74B)	109.5
H(74A) – C(74) – H(74B)	109.5	C(71) – C(74) – H(74C)	109.5
H(74A) – C(74) – H(74C)	109.5	H(74B) – C(74) – H(74C)	109.5
C(71) – C(73) – H(73A)	109.5	C(71) – C(73) – H(73B)	109.5
H(73A) – C(73) – H(73B)	109.5	C(71) – C(73) – H(73C)	109.5
H(73A) – C(73) – H(73C)	109.5	H(73B) – C(73) – H(73C)	109.5
C(72) – C(76) – H(76A)	109.5	C(72) – C(76) – H(76B)	109.5
H(76A) – C(76) – H(76B)	109.5	C(72) – C(76) – H(76C)	109.5
H(76A) – C(76) – H(76C)	109.5	H(76B) – C(76) – H(76C)	109.5
C(83) – C(81) – C(84)	111.0(3)	C(83) – C(81) – P(21)	109.0(3)
C(84) – C(81) – P(21)	116.5(3)	C(83) – C(81) – H(81)	106.6
C(84) – C(81) – H(81)	106.6	P(21) – C(81) – H(81)	106.6
C(85) – C(82) – C(86)	110.6(3)	C(85) – C(82) – P(21)	111.6(3)
C(86) – C(82) – P(21)	110.0(3)	C(85) – C(82) – H(82)	108.2
C(86) – C(82) – H(82)	108.2	P(21) – C(82) – H(82)	108.2
C(81) – C(83) – H(83A)	109.5	C(81) – C(83) – H(83B)	109.5
H(83A) – C(83) – H(83B)	109.5	C(81) – C(83) – H(83C)	109.5
H(83A) – C(83) – H(83C)	109.5	H(83B) – C(83) – H(83C)	109.5
C(81) – C(84) – H(84A)	109.5	C(81) – C(84) – H(84B)	109.5

Continued on next page

Table S10. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(84A) – C(84) – H(84B)	109.5	C(81) – C(84) – H(84C)	109.5
H(84A) – C(84) – H(84C)	109.5	H(84B) – C(84) – H(84C)	109.5
C(82) – C(85) – H(85A)	109.5	C(82) – C(85) – H(85B)	109.5
H(85A) – C(85) – H(85B)	109.5	C(82) – C(85) – H(85C)	109.5
H(85A) – C(85) – H(85C)	109.5	H(85B) – C(85) – H(85C)	109.5
C(82) – C(86) – H(86A)	109.5	C(82) – C(86) – H(86B)	109.5
H(86A) – C(86) – H(86B)	109.5	C(82) – C(86) – H(86C)	109.5
H(86A) – C(86) – H(86C)	109.5	H(86B) – C(86) – H(86C)	109.5
C(93) – C(91) – C(94)	111.2(3)	C(93) – C(91) – P(22)	109.5(2)
C(94) – C(91) – P(22)	115.2(3)	C(93) – C(91) – H(91)	106.8
C(94) – C(91) – H(91)	106.8	P(22) – C(91) – H(91)	106.8
C(96) – C(92) – C(95)	111.8(4)	C(96) – C(92) – P(22)	108.7(3)
C(95) – C(92) – P(22)	112.1(3)	C(96) – C(92) – H(92)	108.0
C(95) – C(92) – H(92)	108.0	P(22) – C(92) – H(92)	108.0
C(91) – C(93) – H(93A)	109.5	C(91) – C(93) – H(93B)	109.5
H(93A) – C(93) – H(93B)	109.5	C(91) – C(93) – H(93C)	109.5
H(93A) – C(93) – H(93C)	109.5	H(93B) – C(93) – H(93C)	109.5
C(91) – C(94) – H(94A)	109.5	C(91) – C(94) – H(94B)	109.5
H(94A) – C(94) – H(94B)	109.5	C(91) – C(94) – H(94C)	109.5
H(94A) – C(94) – H(94C)	109.5	H(94B) – C(94) – H(94C)	109.5
C(92) – C(95) – H(95A)	109.5	C(92) – C(95) – H(95B)	109.5
H(95A) – C(95) – H(95B)	109.5	C(92) – C(95) – H(95C)	109.5
H(95A) – C(95) – H(95C)	109.5	H(95B) – C(95) – H(95C)	109.5
C(92) – C(96) – H(96A)	109.5	C(92) – C(96) – H(96B)	109.5
H(96A) – C(96) – H(96B)	109.5	C(92) – C(96) – H(96C)	109.5
H(96A) – C(96) – H(96C)	109.5	H(96B) – C(96) – H(96C)	109.5

2.3 Crystal data for [{PC•(sp^2)P}$^{t\mathrm{Bu}}$PdO($C_{14}H_8$)OPd{PC•(sp^2)P}$^{t\mathrm{Bu}}$]·C_6H_{12} (**5**·C_6H_{14})

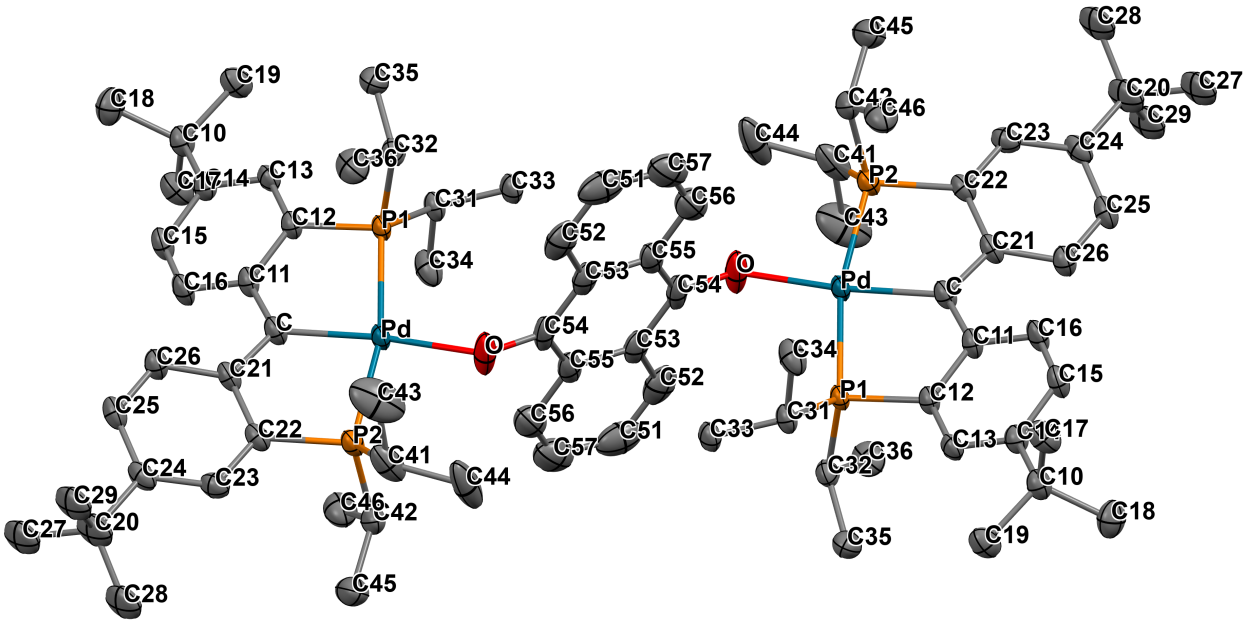

Figure S6. Thermal-ellipsoid representation of [{PC•(sp^2)P}$^{t\mathrm{Bu}}$PdO($C_{14}H_8$)OPd{PC•(sp^2)P}$^{t\mathrm{Bu}}$]·C_6H_{12} (**5**·$\mathbf{C_6H_{14}}$) at 50% probability. Hydrogen atoms and the solvent were omitted for clarity.

Table S11. Crystal data and structure refinement for [{PC$^{\bullet}$(sp^2)P}$^{t\mathrm{Bu}}$PdO($C_{14}H_8$)OPd{PC$^{\bullet}$(sp^2)P}$^{t\mathrm{Bu}}$]·C_6H_{12} (**5**·$\mathbf{C_6H_{14}}$).

Identification code:	pc65b	
Empirical formula:	$C_{85}H_{123}O_2P_4Pd_2$	
Formula weight:	1513.51	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Triclinic	
Space group:	$P\bar{1}$	
Unit cell dimensions:	a = 11.8407(12) Å	α = 100.199(3)°
	b = 13.4567(13) Å	β = 109.735(2)°
	c = 13.9043(13) Å	γ = 98.037(3)°
Volume:	2004.2(3) Å^3	
Z:	1	
Density (calculated):	1.254 g·cm^{-3}	
Absorption coefficient (μ):	0.573 mm^{-1}	
F(000):	801	
Crystal size:	0.110 × 0.100 × 0.090 mm^3	
θ range for data collection:	1.575 to 24.999°	
Index ranges:	$-14 \le h \le 14$, $-16 \le k \le 16$, $-16 \le l \le 16$	
Reflections collected:	48850	
Independent reflections:	7042 [R_{int} = 0.0384]	
Completeness to θ = 25.000°:	100.0 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.7456 and 0.6895	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	7042 / 0 / 434	
Goodness-of-fit on F^2:	1.045	
Final R indices [I>2σ(I)]:	R_1 = 0.0287, wR_2 = 0.0698	
R indices (all data):	R_1 = 0.0361, wR_2 = 0.0724	
Extinction coefficient:	n/a	
Largest diff. peak and hole:	0.554 and −0.330 e$^-$·Å^{-3}	

Table S12. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [{PC$^\bullet$(sp^2)P}$^{t\mathrm{Bu}}$PdO(C$_{14}$H$_8$)OPd{PC$^\bullet$(sp^2)P}$^{t\mathrm{Bu}}$]·C$_6$H$_{12}$ (**5·C$_6$H$_{14}$**). U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

atom	x	y	z	U(eq)
Pd	0.14223(2)	0.22633(2)	0.30749(2)	0.022(1)
C(24)	0.4641(2)	0.3898(2)	0.72024(18)	0.030(1)
P(2)	0.32016(5)	0.20064(5)	0.41963(5)	0.026(1)
C(25)	0.3787(2)	0.45329(19)	0.70664(18)	0.030(1)
C(26)	0.2860(2)	0.44410(18)	0.61107(18)	0.029(1)
C	0.1844(2)	0.35963(18)	0.41565(18)	0.027(1)
C(11)	0.1275(2)	0.44367(18)	0.38610(17)	0.026(1)
C(12)	0.0177(2)	0.42169(17)	0.29658(17)	0.025(1)
C(13)	−0.0382(2)	0.50021(18)	0.26303(17)	0.026(1)
C(15)	0.1235(2)	0.62578(18)	0.39888(18)	0.030(1)
C(14)	0.0128(2)	0.60390(18)	0.31155(18)	0.026(1)
C(16)	0.1786(2)	0.54937(18)	0.43535(18)	0.031(1)
C(17)	0.0566(2)	0.7522(2)	0.2369(2)	0.037(1)
C(63)	0.4799(8)	−0.0462(6)	0.1998(6)	0.077(2)
C(62)	0.5206(4)	0.0106(3)	0.1469(3)	0.071(1)
C(61)	0.4710(3)	−0.0311(2)	0.0285(3)	0.061(1)
C(10)	−0.0383(2)	0.69217(18)	0.26916(18)	0.029(1)
C(18)	−0.0642(3)	0.7650(2)	0.3533(2)	0.040(1)
C(19)	−0.1572(2)	0.6514(2)	0.1720(2)	0.035(1)
C(21)	0.2739(2)	0.37046(17)	0.52024(17)	0.025(1)
C(20)	0.5678(3)	0.4035(3)	0.8262(2)	0.048(1)
C(22)	0.3541(2)	0.30129(18)	0.53623(17)	0.025(1)
C(23)	0.4464(2)	0.3116(2)	0.63335(18)	0.029(1)
P(1)	−0.02747(5)	0.28794(4)	0.22196(4)	0.021(1)
O	0.1141(2)	0.08089(14)	0.21455(14)	0.051(1)
C(27)	0.6237(5)	0.5266(5)	0.8752(4)	0.048(1)
C(28)	0.6731(6)	0.3615(5)	0.8187(4)	0.048(1)
C(29)	0.5189(4)	0.3653(5)	0.9019(4)	0.048(1)
C(73)	0.6878(8)	0.3907(8)	0.8033(7)	0.048(1)
C(72)	0.5861(7)	0.4952(7)	0.9029(6)	0.048(1)
C(71)	0.5352(7)	0.3017(7)	0.8681(5)	0.048(1)
C(31)	−0.0714(2)	0.30231(18)	0.08509(17)	0.025(1)
C(32)	−0.1714(2)	0.22656(18)	0.23264(18)	0.027(1)
C(33)	−0.1408(2)	0.20226(18)	0.00260(18)	0.029(1)
C(34)	0.0442(2)	0.3502(2)	0.0693(2)	0.038(1)
C(35)	−0.2733(2)	0.2856(2)	0.2039(2)	0.037(1)
C(36)	−0.1423(3)	0.2094(2)	0.3430(2)	0.042(1)
C(42)	0.4497(2)	0.2196(2)	0.37574(19)	0.034(1)
C(43)	0.2095(3)	0.0533(3)	0.4909(3)	0.076(1)

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Table S12. – continued from previous page

atom	x	y	x	U(eq)
C(44)	0.3174(3)	−0.0090(2)	0.3717(3)	0.071(1)
C(45)	0.5710(2)	0.2065(3)	0.4521(2)	0.048(1)
C(46)	0.4632(3)	0.3245(2)	0.3491(2)	0.045(1)
C(51)	−0.2348(3)	−0.1142(3)	0.0942(3)	0.060(1)
C(52)	−0.1216(3)	−0.0478(2)	0.1356(2)	0.049(1)
C(53)	−0.0569(3)	−0.02297(19)	0.0698(2)	0.035(1)
C(54)	0.0591(3)	0.04460(19)	0.11152(19)	0.036(1)
C(55)	0.1161(2)	0.06803(18)	0.0414(2)	0.036(1)
C(56)	0.2311(3)	0.1376(2)	0.0784(3)	0.049(1)
C(57)	0.2875(3)	0.1602(2)	0.0139(3)	0.060(1)
C(41)	0.3185(3)	0.0778(2)	0.4601(2)	0.045(1)
H(25)	0.3849	0.5048	0.7656	0.036
H(26)	0.2293	0.4882	0.6063	0.034
H(13)	−0.1141	0.4821	0.2047	0.031
H(15)	0.1617	0.6959	0.4341	0.036
H(16)	0.2530	0.5682	0.4953	0.037
H(17A)	0.1315	0.7836	0.2991	0.056
H(17B)	0.0232	0.8066	0.2055	0.056
H(17C)	0.0761	0.7050	0.1854	0.056
H(63A)	0.5195	−0.0134	0.2752	0.092
H(63B)	0.4986	−0.1148	0.1859	0.092
H(63C)	0.3907	−0.0533	0.1781	0.092
H(62A)	0.6113	0.0207	0.1733	0.086
H(62B)	0.5011	0.0795	0.1621	0.086
H(61A)	0.4832	−0.1026	0.0130	0.073
H(61B)	0.3815	−0.0343	0.0008	0.073
H(18A)	0.0117	0.7926	0.4154	0.060
H(18B)	−0.1264	0.7270	0.3730	0.060
H(18C)	−0.0944	0.8222	0.3252	0.060
H(19A)	−0.1849	0.7095	0.1442	0.052
H(19B)	−0.2207	0.6151	0.1917	0.052
H(19C)	−0.1422	0.6035	0.1181	0.052
H(23)	0.4988	0.2637	0.6405	0.035
H(27A)	0.6933	0.5376	0.9417	0.072
H(27B)	0.5600	0.5602	0.8878	0.072
H(27C)	0.6514	0.5563	0.8255	0.072
H(28A)	0.6496	0.2858	0.7978	0.072
H(28B)	0.7412	0.3834	0.8873	0.072
H(28C)	0.6991	0.3872	0.7661	0.072
H(29A)	0.4570	0.4034	0.9112	0.072
H(29B)	0.5862	0.3761	0.9699	0.072
H(29C)	0.4812	0.2914	0.8744	0.072

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Table S12. – continued from previous page

atom	x	y	x	U(eq)
H(73A)	0.7548	0.3933	0.8692	0.072
H(73B)	0.7111	0.4467	0.7728	0.072
H(73C)	0.6718	0.3240	0.7537	0.072
H(72A)	0.5164	0.4918	0.9260	0.057
H(72B)	0.5926	0.5550	0.8722	0.057
H(72C)	0.6619	0.5022	0.9633	0.057
H(71A)	0.4547	0.2976	0.8742	0.072
H(71B)	0.5979	0.3066	0.9371	0.072
H(71C)	0.5333	0.2396	0.8181	0.072
H(31)	−0.1268	0.3525	0.0765	0.030
H(32)	−0.2016	0.1570	0.1823	0.032
H(33A)	−0.2149	0.1746	0.0142	0.043
H(33B)	−0.0882	0.1518	0.0081	0.043
H(33C)	−0.1641	0.2159	−0.0677	0.043
H(34A)	0.0970	0.3002	0.0706	0.058
H(34B)	0.0888	0.4123	0.1260	0.058
H(34C)	0.0207	0.3689	0.0014	0.058
H(35A)	−0.2477	0.3536	0.2534	0.055
H(35B)	−0.3477	0.2468	0.2075	0.055
H(35C)	−0.2904	0.2946	0.1323	0.055
H(36A)	−0.1136	0.2763	0.3943	0.063
H(36B)	−0.0781	0.1693	0.3581	0.063
H(36C)	−0.2166	0.1714	0.3475	0.063
H(42)	0.4275	0.1660	0.3088	0.041
H(43A)	0.2141	0.1096	0.5483	0.113
H(43B)	0.2098	−0.0112	0.5143	0.113
H(43C)	0.1337	0.0456	0.4302	0.113
H(44A)	0.3094	−0.0749	0.3920	0.107
H(44B)	0.3943	0.0055	0.3596	0.107
H(44C)	0.2479	−0.0130	0.3070	0.107
H(45A)	0.5597	0.1379	0.4667	0.073
H(45B)	0.5975	0.2598	0.5179	0.073
H(45C)	0.6335	0.2135	0.4208	0.073
H(46A)	0.4847	0.3793	0.4130	0.067
H(46B)	0.3854	0.3289	0.2967	0.067
H(46C)	0.5282	0.3328	0.3206	0.067
H(51)	−0.2772	−0.1289	0.1388	0.072
H(52)	−0.0857	−0.0179	0.2092	0.059
H(56)	0.2696	0.1694	0.1515	0.058
H(57)	0.3644	0.2080	0.0418	0.072
H(41)	0.3949	0.0861	0.5230	0.054

Table S13. Anisotropic displacement parameters (Å^2) for [{PC$^\bullet$(sp^2)P}$^{t\mathrm{Bu}}$PdO($C_{14}H_8$)OPd{PC$^\bullet$(sp^2)P}$^{t\mathrm{Bu}}$]·C_6H_{12} (**5·C_6H_{14}**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ...+ 2hka^*b^*U_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	0.0228(1)	0.0209(1)	0.0152(1)	−0.0010(1)	0.0004(1)	0.0025(1)
C(24)	0.0263(13)	0.0391(14)	0.0171(12)	0.0069(10)	0.0031(10)	−0.0004(11)
P(2)	0.0240(3)	0.0228(3)	0.0222(3)	0.0028(2)	0.0007(2)	0.0021(2)
C(25)	0.0336(14)	0.0280(13)	0.0196(12)	0.0010(10)	0.0043(10)	−0.0022(10)
C(26)	0.0332(14)	0.0242(12)	0.0213(12)	0.0028(10)	0.0035(10)	0.0040(10)
C	0.0264(12)	0.0259(12)	0.0198(12)	0.0016(10)	0.0008(10)	0.0009(10)
C(11)	0.0296(13)	0.0238(12)	0.0171(11)	−0.0001(9)	0.0036(10)	0.0013(10)
C(12)	0.0265(12)	0.0234(12)	0.0175(11)	0.0002(9)	0.0038(9)	0.0019(10)
C(13)	0.0241(12)	0.0269(12)	0.0173(11)	0.0004(9)	0.0008(9)	0.0028(10)
C(15)	0.0357(14)	0.0205(12)	0.0214(12)	−0.0001(10)	0.0009(10)	−0.0006(10)
C(14)	0.0287(13)	0.0262(12)	0.0211(12)	0.0044(10)	0.0066(10)	0.0044(10)
C(16)	0.0329(14)	0.0269(13)	0.0189(12)	0.0000(10)	−0.0036(10)	0.0013(11)
C(17)	0.0363(15)	0.0345(15)	0.0347(14)	0.0129(12)	0.0055(12)	0.0013(12)
C(63)	0.103(7)	0.048(4)	0.078(5)	0.004(4)	0.045(5)	0.001(4)
C(62)	0.069(2)	0.052(2)	0.086(3)	−0.001(2)	0.027(2)	0.0183(18)
C(61)	0.050(2)	0.0369(17)	0.088(3)	−0.0032(17)	0.0251(18)	0.0069(14)
C(10)	0.0319(13)	0.0256(12)	0.0236(12)	0.0052(10)	0.0052(10)	0.0032(10)
C(18)	0.0557(18)	0.0282(14)	0.0359(15)	0.0082(12)	0.0167(13)	0.0120(12)
C(19)	0.0342(14)	0.0308(14)	0.0344(14)	0.0125(11)	0.0040(11)	0.0070(11)
C(21)	0.0260(12)	0.0224(12)	0.0190(11)	0.0027(9)	0.0011(10)	−0.0020(10)
C(20)	0.0380(10)	0.0707(16)	0.0226(9)	0.0111(8)	−0.0020(7)	0.0083(10)
C(22)	0.0238(12)	0.0263(12)	0.0185(11)	0.0047(9)	0.0030(9)	−0.0006(10)
C(23)	0.0244(12)	0.0380(14)	0.0232(12)	0.0093(11)	0.0050(10)	0.0062(10)
P(1)	0.0218(3)	0.0203(3)	0.0148(3)	−0.0004(2)	0.0012(2)	0.0015(2)
O	0.0761(15)	0.0362(11)	0.0224(9)	−0.0051(8)	−0.0063(9)	0.0300(10)
C(27)	0.0380(10)	0.0707(16)	0.0226(9)	0.0111(8)	−0.0020(7)	0.0083(10)
C(28)	0.0380(10)	0.0707(16)	0.0226(9)	0.0111(8)	−0.0020(7)	0.0083(10)
C(29)	0.0380(10)	0.0707(16)	0.0226(9)	0.0111(8)	−0.0020(7)	0.0083(10)
C(73)	0.0380(10)	0.0707(16)	0.0226(9)	0.0111(8)	−0.0020(7)	0.0083(10)
C(72)	0.0380(10)	0.0707(16)	0.0226(9)	0.0111(8)	−0.0020(7)	0.0083(10)
C(71)	0.0380(10)	0.0707(16)	0.0226(9)	0.0111(8)	−0.0020(7)	0.0083(10)
C(31)	0.0289(13)	0.0250(12)	0.0153(11)	0.0019(9)	0.0030(9)	0.0026(10)
C(32)	0.0261(12)	0.0232(12)	0.0254(12)	−0.0002(10)	0.0075(10)	−0.0004(10)
C(33)	0.0320(13)	0.0283(13)	0.0174(11)	0.0007(10)	0.0022(10)	0.0053(10)
C(34)	0.0430(16)	0.0400(15)	0.0247(13)	0.0035(11)	0.0109(12)	−0.0043(12)
C(35)	0.0276(13)	0.0350(15)	0.0428(16)	0.0014(12)	0.0117(12)	0.0040(11)
C(36)	0.0437(16)	0.0525(18)	0.0322(15)	0.0124(13)	0.0186(13)	0.0045(13)
C(42)	0.0283(13)	0.0406(15)	0.0254(13)	−0.0029(11)	0.0070(11)	0.0066(11)
C(43)	0.061(2)	0.066(2)	0.097(3)	0.054(2)	0.015(2)	−0.0051(18)

Continued on next page

Table S13. – continued from previous page

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(44)	0.077(2)	0.0236(15)	0.064(2)	−0.0016(14)	−0.0290(18)	0.0103(15)
C(45)	0.0313(15)	0.067(2)	0.0395(16)	0.0010(14)	0.0091(13)	0.0125(14)
C(46)	0.0406(16)	0.0506(18)	0.0405(16)	0.0056(13)	0.0196(13)	−0.0019(13)
C(51)	0.063(2)	0.0486(19)	0.095(3)	0.037(2)	0.045(2)	0.0317(17)
C(52)	0.072(2)	0.0421(17)	0.0459(17)	0.0168(14)	0.0236(16)	0.0373(16)
C(53)	0.0484(16)	0.0246(13)	0.0299(14)	0.0049(11)	0.0087(12)	0.0214(12)
C(54)	0.0510(17)	0.0241(13)	0.0226(13)	−0.0016(10)	−0.0011(12)	0.0216(12)
C(55)	0.0390(15)	0.0213(12)	0.0340(14)	−0.0013(11)	−0.0021(12)	0.0151(11)
C(56)	0.0427(17)	0.0331(16)	0.058(2)	0.0050(14)	0.0053(15)	0.0138(13)
C(57)	0.0471(19)	0.0399(18)	0.085(3)	0.0147(18)	0.0123(19)	0.0177(15)
C(41)	0.0437(17)	0.0259(14)	0.0455(17)	0.0148(12)	−0.0098(13)	0.0005(12)

Table S14. Distances [Å] for [{PC$^{\bullet}$(sp^2)P}$^{t\mathrm{Bu}}$PdO($C_{14}H_8$)OPd{PC$^{\bullet}$(sp^2)P}$^{t\mathrm{Bu}}$]·C_6H_{12} (**5·C_6H_{14}**).

atom – atom	distance	atom – atom	distance
Pd – C	2.004(2)	Pd – O	2.0597(17)
Pd – P(2)	2.2728(6)	Pd – P(1)	2.3109(6)
C(24) – C(23)	1.388(3)	C(24) – C(25)	1.399(4)
C(24) – C(20)	1.527(3)	P(2) – C(22)	1.804(2)
P(2) – C(42)	1.835(3)	P(2) – C(41)	1.837(3)
C(25) – C(26)	1.380(3)	C(25) – H(25)	0.9500
C(26) – C(21)	1.411(3)	C(26) – H(26)	0.9500
C – C(11)	1.447(3)	C – C(21)	1.449(3)
C(11) – C(16)	1.412(3)	C(11) – C(12)	1.413(3)
C(12) – C(13)	1.391(3)	C(12) – P(1)	1.816(2)
C(13) – C(14)	1.387(3)	C(13) – H(13)	0.9500
C(15) – C(16)	1.374(3)	C(15) – C(14)	1.403(3)
C(15) – H(15)	0.9500	C(14) – C(10)	1.527(3)
C(16) – H(16)	0.9500	C(17) – C(10)	1.527(3)
C(17) – H(17A)	0.9800	C(17) – H(17B)	0.9800
C(17) – H(17C)	0.9800	C(63) – C(62)	1.302(8)
C(63) – H(63A)	0.9800	C(63) – H(63B)	0.9800
C(63) – H(63C)	0.9800	C(62) – C(61)	1.515(5)
C(62) – H(62A)	0.9900	C(62) – H(62B)	0.9900
C(61) – C(61)#1	1.498(7)	C(61) – H(61A)	0.9900
C(61) – H(61B)	0.9900	C(10) – C(18)	1.531(3)
C(10) – C(19)	1.531(3)	C(18) – H(18A)	0.9800
C(18) – H(18B)	0.9800	C(18) – H(18C)	0.9800
C(19) – H(19A)	0.9800	C(19) – H(19B)	0.9800
C(19) – H(19C)	0.9800	C(21) – C(22)	1.413(3)
C(20) – C(72)	1.417(8)	C(20) – C(28)	1.466(7)
C(20) – C(29)	1.493(6)	C(20) – C(73)	1.583(10)
C(20) – C(27)	1.623(7)	C(20) – C(71)	1.628(9)
C(22) – C(23)	1.390(3)	C(23) – H(23)	0.9500
P(1) – C(31)	1.849(2)	P(1) – C(32)	1.852(2)
O – C(54)	1.322(3)	C(27) – H(27A)	0.9800
C(27) – H(27B)	0.9800	C(27) – H(27C)	0.9800
C(28) – H(28A)	0.9800	C(28) – H(28B)	0.9800
C(28) – H(28C)	0.9800	C(29) – H(29A)	0.9800
C(29) – H(29B)	0.9800	C(29) – H(29C)	0.9800
C(73) – H(73A)	0.9800	C(73) – H(73B)	0.9800
C(73) – H(73C)	0.9800	C(72) – H(72A)	0.9800
C(72) – H(72B)	0.9800	C(72) – H(72C)	0.9800
C(71) – H(71A)	0.9800	C(71) – H(71B)	0.9800

Symmetry transformations used to generate equivalent atoms:

#1 −x+1,−y,−z; #2 −x,−y,−z

Continued on next page

Table S14. – continued from previous page

atom – atom	distance	atom – atom	distance
C(71) – H(71C)	0.9800	C(31) – C(33)	1.520(3)
C(31) – C(34)	1.531(3)	C(31) – H(31)	1.0000
C(32) – C(35)	1.518(3)	C(32) – C(36)	1.522(3)
C(32) – H(32)	1.0000	C(33) – H(33A)	0.9800
C(33) – H(33B)	0.9800	C(33) – H(33C)	0.9800
C(34) – H(34A)	0.9800	C(34) – H(34B)	0.9800
C(34) – H(34C)	0.9800	C(35) – H(35A)	0.9800
C(35) – H(35B)	0.9800	C(35) – H(35C)	0.9800
C(36) – H(36A)	0.9800	C(36) – H(36B)	0.9800
C(36) – H(36C)	0.9800	C(42) – C(46)	1.521(4)
C(42) – C(45)	1.526(4)	C(42) – H(42)	1.0000
C(43) – C(41)	1.504(5)	C(43) – H(43A)	0.9800
C(43) – H(43B)	0.9800	C(43) – H(43C)	0.9800
C(44) – C(41)	1.534(4)	C(44) – H(44A)	0.9800
C(44) – H(44B)	0.9800	C(44) – H(44C)	0.9800
C(45) – H(45A)	0.9800	C(45) – H(45B)	0.9800
C(45) – H(45C)	0.9800	C(46) – H(46A)	0.9800
C(46) – H(46B)	0.9800	C(46) – H(46C)	0.9800
C(51) – C(52)	1.374(5)	C(51) – C(57)#2	1.400(5)
C(51) – H(51)	0.9500	C(52) – C(53)	1.430(4)
C(52) – H(52)	0.9500	C(53) – C(54)	1.405(4)
C(53) – C(55)#2	1.437(3)	C(54) – C(55)	1.414(4)
C(55) – C(56)	1.413(4)	C(55) – C(53)#2	1.438(3)
C(56) – C(57)	1.336(5)	C(56) – H(56)	0.9500
C(57) – C(51)#2	1.400(5)	C(57) – H(57)	0.9500
C(41) – H(41)	1.0000		

Symmetry transformations used to generate equivalent atoms:

#1 −x+1,−y,−z; #2 −x,−y,−z

Table S15. Angles [°] for [{PC•(sp^2)P}$^{t\mathrm{Bu}}$PdO($C_{14}H_8$)OPd{PC•(sp^2)P}$^{t\mathrm{Bu}}$]·C_6H_{12} (**5·C_6H_{14}**).

atom – atom – atom	angle	atom – atom – atom	angle
C – Pd – O	171.43(8)	C – Pd – P(2)	83.23(7)
O – Pd – P(2)	89.07(5)	C – Pd – P(1)	83.56(7)
O – Pd – P(1)	104.11(5)	P(2) – Pd – P(1)	166.79(2)
C(23) – C(24) – C(25)	116.3(2)	C(23) – C(24) – C(20)	122.1(2)
C(25) – C(24) – C(20)	121.6(2)	C(22) – P(2) – C(42)	107.86(11)
C(22) – P(2) – C(41)	106.90(12)	C(42) – P(2) – C(41)	106.20(14)
C(22) – P(2) – Pd	102.50(8)	C(42) – P(2) – Pd	114.18(9)
C(41) – P(2) – Pd	118.52(9)	C(26) – C(25) – C(24)	122.7(2)
C(26) – C(25) – H(25)	118.7	C(24) – C(25) – H(25)	118.7
C(25) – C(26) – C(21)	121.2(2)	C(25) – C(26) – H(26)	119.4
C(21) – C(26) – H(26)	119.4	C(11) – C – C(21)	121.8(2)
C(11) – C – Pd	118.99(16)	C(21) – C – Pd	119.22(17)
C(16) – C(11) – C(12)	115.9(2)	C(16) – C(11) – C	124.8(2)
C(12) – C(11) – C	119.1(2)	C(13) – C(12) – C(11)	121.2(2)
C(13) – C(12) – P(1)	124.27(17)	C(11) – C(12) – P(1)	113.90(17)
C(14) – C(13) – C(12)	122.5(2)	C(14) – C(13) – H(13)	118.8
C(12) – C(13) – H(13)	118.8	C(16) – C(15) – C(14)	122.4(2)
C(16) – C(15) – H(15)	118.8	C(14) – C(15) – H(15)	118.8
C(13) – C(14) – C(15)	116.2(2)	C(13) – C(14) – C(10)	123.7(2)
C(15) – C(14) – C(10)	119.9(2)	C(15) – C(16) – C(11)	121.8(2)
C(15) – C(16) – H(16)	119.1	C(11) – C(16) – H(16)	119.1
C(10) – C(17) – H(17A)	109.5	C(10) – C(17) – H(17B)	109.5
H(17A) – C(17) – H(17B)	109.5	C(10) – C(17) – H(17C)	109.5
H(17A) – C(17) – H(17C)	109.5	H(17B) – C(17) – H(17C)	109.5
C(62) – C(63) – H(63A)	109.5	C(62) – C(63) – H(63B)	109.5
H(63A) – C(63) – H(63B)	109.5	C(62) – C(63) – H(63C)	109.5
H(63A) – C(63) – H(63C)	109.5	H(63B) – C(63) – H(63C)	109.5
C(63) – C(62) – C(61)	116.2(5)	C(63) – C(62) – H(62A)	108.2
C(61) – C(62) – H(62A)	108.2	C(63) – C(62) – H(62B)	108.2
C(61) – C(62) – H(62B)	108.2	H(62A) – C(62) – H(62B)	107.4
C(61)#1 – C(61) – C(62)	114.6(4)	C(61)#1 – C(61) – H(61A)	108.6
C(62) – C(61) – H(61A)	108.6	C(61)#1 – C(61) – H(61B)	108.6
C(62) – C(61) – H(61B)	108.6	H(61A) – C(61) – H(61B)	107.6
C(14) – C(10) – C(17)	108.4(2)	C(14) – C(10) – C(18)	110.8(2)
C(17) – C(10) – C(18)	109.4(2)	C(14) – C(10) – C(19)	111.4(2)
C(17) – C(10) – C(19)	108.1(2)	C(18) – C(10) – C(19)	108.7(2)
C(10) – C(18) – H(18A)	109.5	C(10) – C(18) – H(18B)	109.5
H(18A) – C(18) – H(18B)	109.5	C(10) – C(18) – H(18C)	109.5
H(18A) – C(18) – H(18C)	109.5	H(18B) – C(18) – H(18C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 −x+1,−y,−z; #2 −x,−y,−z

Continued on next page

Table S15. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(10) – C(19) – H(19A)	109.5	C(10) – C(19) – H(19B)	109.5
H(19A) – C(19) – H(19B)	109.5	C(10) – C(19) – H(19C)	109.5
H(19A) – C(19) – H(19C)	109.5	H(19B) – C(19) – H(19C)	109.5
C(26) – C(21) – C(22)	115.7(2)	C(26) – C(21) – C	125.0(2)
C(22) – C(21) – C	119.3(2)	C(28) – C(20) – C(29)	113.3(4)
C(72) – C(20) – C(24)	115.7(4)	C(28) – C(20) – C(24)	114.1(3)
C(29) – C(20) – C(24)	110.5(3)	C(72) – C(20) – C(73)	112.8(5)
C(24) – C(20) – C(73)	107.3(4)	C(28) – C(20) – C(27)	104.2(4)
C(29) – C(20) – C(27)	106.4(3)	C(24) – C(20) – C(27)	107.7(3)
C(72) – C(20) – C(71)	110.8(5)	C(24) – C(20) – C(71)	105.5(3)
C(73) – C(20) – C(71)	103.8(5)	C(23) – C(22) – C(21)	121.8(2)
C(23) – C(22) – P(2)	125.51(19)	C(21) – C(22) – P(2)	112.67(16)
C(24) – C(23) – C(22)	121.9(2)	C(24) – C(23) – H(23)	119.1
C(22) – C(23) – H(23)	119.1	C(12) – P(1) – C(31)	101.89(10)
C(12) – P(1) – C(32)	108.72(11)	C(31) – P(1) – C(32)	105.63(11)
C(12) – P(1) – Pd	100.60(8)	C(31) – P(1) – Pd	124.22(8)
C(32) – P(1) – Pd	114.12(8)	C(54) – O – Pd	130.52(16)
C(20) – C(27) – H(27A)	109.5	C(20) – C(27) – H(27B)	109.5
H(27A) – C(27) – H(27B)	109.5	C(20) – C(27) – H(27C)	109.5
H(27A) – C(27) – H(27C)	109.5	H(27B) – C(27) – H(27C)	109.5
C(20) – C(28) – H(28A)	109.5	C(20) – C(28) – H(28B)	109.5
H(28A) – C(28) – H(28B)	109.5	C(20) – C(28) – H(28C)	109.5
H(28A) – C(28) – H(28C)	109.5	H(28B) – C(28) – H(28C)	109.5
C(20) – C(29) – H(29A)	109.5	C(20) – C(29) – H(29B)	109.5
H(29A) – C(29) – H(29B)	109.5	C(20) – C(29) – H(29C)	109.5
H(29A) – C(29) – H(29C)	109.5	H(29B) – C(29) – H(29C)	109.5
C(20) – C(73) – H(73A)	109.5	C(20) – C(73) – H(73B)	109.5
H(73A) – C(73) – H(73B)	109.5	C(20) – C(73) – H(73C)	109.5
H(73A) – C(73) – H(73C)	109.5	H(73B) – C(73) – H(73C)	109.5
C(20) – C(72) – H(72A)	109.5	C(20) – C(72) – H(72B)	109.5
H(72A) – C(72) – H(72B)	109.5	C(20) – C(72) – H(72C)	109.5
H(72A) – C(72) – H(72C)	109.5	H(72B) – C(72) – H(72C)	109.5
C(20) – C(71) – H(71A)	109.5	C(20) – C(71) – H(71B)	109.5
H(71A) – C(71) – H(71B)	109.5	C(20) – C(71) – H(71C)	109.5
H(71A) – C(71) – H(71C)	109.5	H(71B) – C(71) – H(71C)	109.5
C(33) – C(31) – C(34)	111.8(2)	C(33) – C(31) – P(1)	113.71(16)
C(34) – C(31) – P(1)	108.65(16)	C(33) – C(31) – H(31)	107.5
C(34) – C(31) – H(31)	107.5	P(1) – C(31) – H(31)	107.5
C(35) – C(32) – C(36)	111.6(2)	C(35) – C(32) – P(1)	113.98(17)
C(36) – C(32) – P(1)	108.90(17)	C(35) – C(32) – H(32)	107.4

Symmetry transformations used to generate equivalent atoms:

#1 −x+1,−y,−z; #2 −x,−y,−z

Continued on next page

Table S15. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(36) – C(32) – H(32)	107.4	P(1) – C(32) – H(32)	107.4
C(31) – C(33) – H(33A)	109.5	C(31) – C(33) – H(33B)	109.5
H(33A) – C(33) – H(33B)	109.5	C(31) – C(33) – H(33C)	109.5
H(33A) – C(33) – H(33C)	109.5	H(33B) – C(33) – H(33C)	109.5
C(31) – C(34) – H(34A)	109.5	C(31) – C(34) – H(34B)	109.5
H(34A) – C(34) – H(34B)	109.5	C(31) – C(34) – H(34C)	109.5
H(34A) – C(34) – H(34C)	109.5	H(34B) – C(34) – H(34C)	109.5
C(32) – C(35) – H(35A)	109.5	C(32) – C(35) – H(35B)	109.5
H(35A) – C(35) – H(35B)	109.5	C(32) – C(35) – H(35C)	109.5
H(35A) – C(35) – H(35C)	109.5	H(35B) – C(35) – H(35C)	109.5
C(32) – C(36) – H(36A)	109.5	C(32) – C(36) – H(36B)	109.5
H(36A) – C(36) – H(36B)	109.5	C(32) – C(36) – H(36C)	109.5
H(36A) – C(36) – H(36C)	109.5	H(36B) – C(36) – H(36C)	109.5
C(46) – C(42) – C(45)	111.4(2)	C(46) – C(42) – P(2)	109.20(18)
C(45) – C(42) – P(2)	114.80(19)	C(46) – C(42) – H(42)	107.0
C(45) – C(42) – H(42)	107.0	P(2) – C(42) – H(42)	107.0
C(41) – C(43) – H(43A)	109.5	C(41) – C(43) – H(43B)	109.5
H(43A) – C(43) – H(43B)	109.5	C(41) – C(43) – H(43C)	109.5
H(43A) – C(43) – H(43C)	109.5	H(43B) – C(43) – H(43C)	109.5
C(41) – C(44) – H(44A)	109.5	C(41) – C(44) – H(44B)	109.5
H(44A) – C(44) – H(44B)	109.5	C(41) – C(44) – H(44C)	109.5
H(44A) – C(44) – H(44C)	109.5	H(44B) – C(44) – H(44C)	109.5
C(42) – C(45) – H(45A)	109.5	C(42) – C(45) – H(45B)	109.5
H(45A) – C(45) – H(45B)	109.5	C(42) – C(45) – H(45C)	109.5
H(45A) – C(45) – H(45C)	109.5	H(45B) – C(45) – H(45C)	109.5
C(42) – C(46) – H(46A)	109.5	C(42) – C(46) – H(46B)	109.5
H(46A) – C(46) – H(46B)	109.5	C(42) – C(46) – H(46C)	109.5
H(46A) – C(46) – H(46C)	109.5	H(46B) – C(46) – H(46C)	109.5
C(52) – C(51) – C(57)#2	119.9(3)	C(52) – C(51) – H(51)	120.1
C(57)#2 – C(51) – H(51)	120.1	C(51) – C(52) – C(53)	121.2(3)
C(51) – C(52) – H(52)	119.4	C(53) – C(52) – H(52)	119.4
C(54) – C(53) – C(52)	121.5(3)	C(54) – C(53) – C(55)#2	121.0(2)
C(52) – C(53) – C(55)#2	117.5(3)	O – C(54) – C(53)	119.7(3)
O – C(54) – C(55)	121.8(3)	C(53) – C(54) – C(55)	118.4(2)
C(56) – C(55) – C(54)	121.0(3)	C(56) – C(55) – C(53)#2	118.4(3)
C(54) – C(55) – C(53)#2	120.6(2)	C(57) – C(56) – C(55)	122.2(3)
C(57) – C(56) – H(56)	118.9	C(55) – C(56) – H(56)	118.9
C(56) – C(57) – C(51)#2	120.8(3)	C(56) – C(57) – H(57)	119.6
C(51)#2 – C(57) – H(57)	119.6	C(43) – C(41) – C(44)	111.7(3)
C(43) – C(41) – P(2)	109.4(2)	C(44) – C(41) – P(2)	110.4(2)

Symmetry transformations used to generate equivalent atoms:

#1 −x+1,−y,−z; #2 −x,−y,−z

Continued on next page

Table S15. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(43) – C(41) – H(41)	108.4	C(44) – C(41) – H(41)	108.4
P(2) – C(41) – H(41)	108.4		

Symmetry transformations used to generate equivalent atoms:

#1 −x+1,−y,−z; #2 −x,−y,−z