Supplementary Information for:

DFT Calculations of ^{31}P NMR Chemical Shifts in Palladium Complexes

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CALCULATIONAL DETAILS

The quantum chemical calculations have been carried out within the framework of the Kohn Sham density functional theory [1] with the Gaussian 03 [2] (Revision B.04) and the Gaussian 16 [3] (Revision A.03) software packages by using PBE0 [4] functional and a number of families of basis sets (Pople's [5-12], Ahlrichs's [13-15], Dunning's [16-17], Jensen's [18-20]). For the Pd center was used the quasi-relativistic Stuttgart-Dresden ECP28MWB with corresponding (8*s*7*p*6*d*)/[6*s*5*p*3*d*] GTO valence basis set [21] (denoted as "(SDD)"), Sappo-ro-DKH3-DZP-diffuse [deprecated] basis set [22-23] and def2-TZVPD basis set [24-25]. Wherever possible, geometry optimization was started from X-ray structure. For most of the complexes the calculations were carried out for all possible conformers/isomers and results for the lowest energy forms were used in analysis. To take into account the medium effects, calculations were also carried out in the framework of Polarizable Contin-uum Model [26] (denoted as "PCM") with chloroform as solvent. To determine the energies of triplet states geometry optimizations were performed at the spin-unrestricted formalism (UPBE0/6-31+G(d)). ^{31}P NMR CSs were calculated by the GIAO method [27]. All ^{31}P data was referenced to H_3PO_4.

The pc-2, def2-TZVP, def2-TZVPD and Sapporo-DKH3-DZP-diffuse basis sets were downloaded from the EMSL basis set library for Gaussian package [28].

The Gaussian 03 calculations were carried out on a PC with IntelCore i7-3970X CPU, 3.5 GHz. Calculations with 6-311+G(3df), pc-2, cc-pVTZ, def2-TZVP, and Sappo-ro-DKH3-DZP-diffuse [deprecated] basis sets were carried out with the Gaussian 16 on 20 CPUs, IntelXeon ES-2650 2.20 GHz.

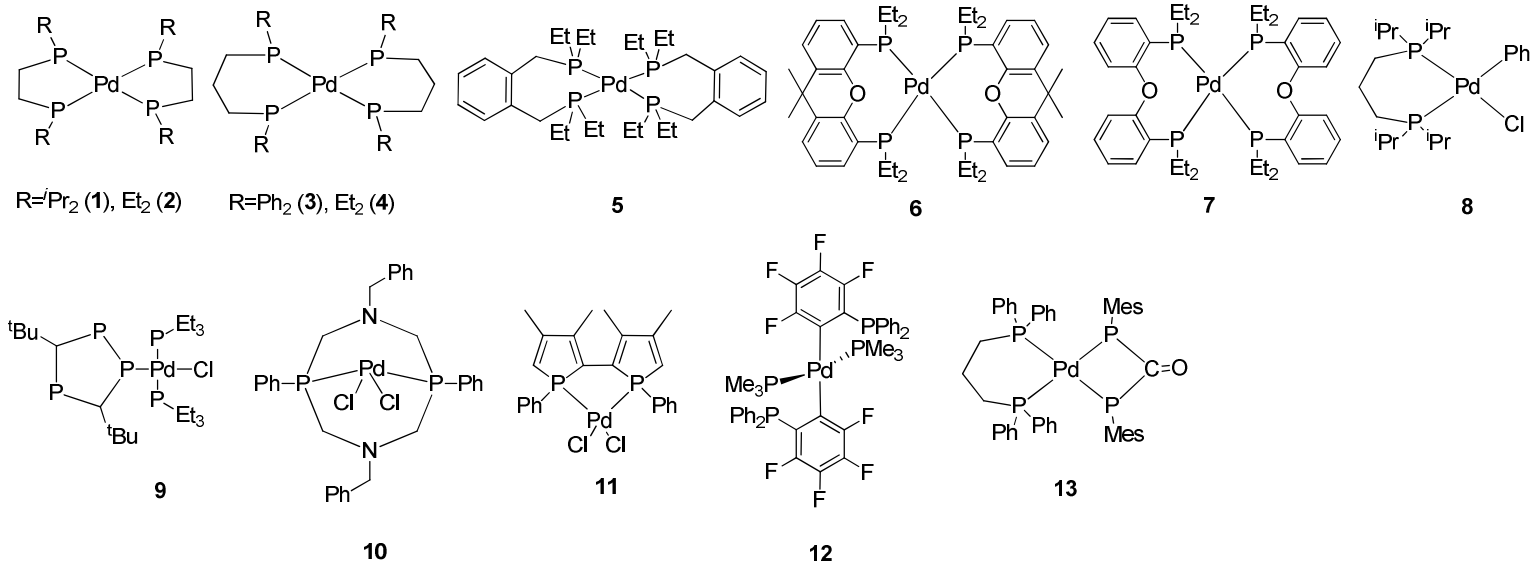

Figure S1. Complexes based on σ-donor ligands.

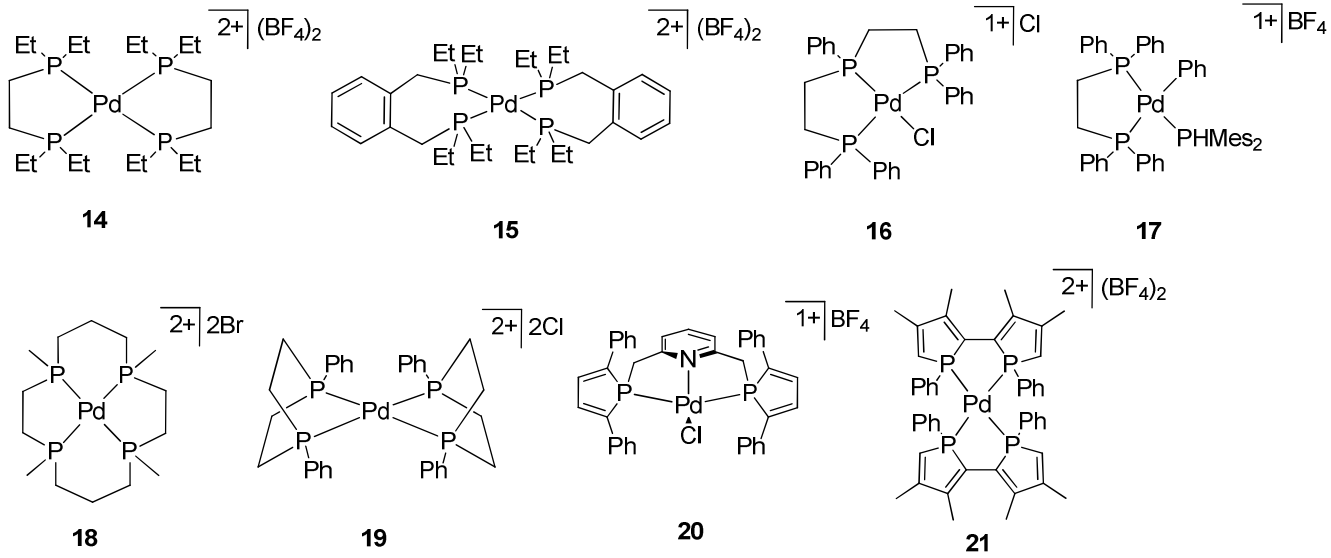

Figure S2. Charged complexes based on σ-donor ligands.

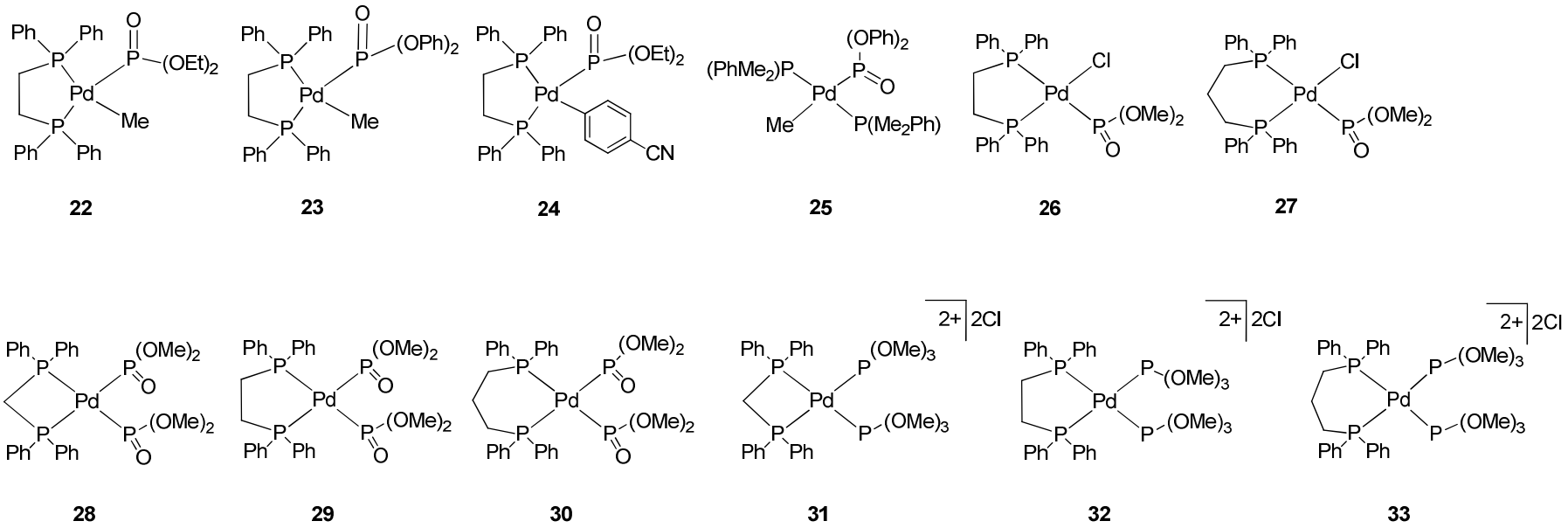

Figure S3. Complexes containing P=O groups.

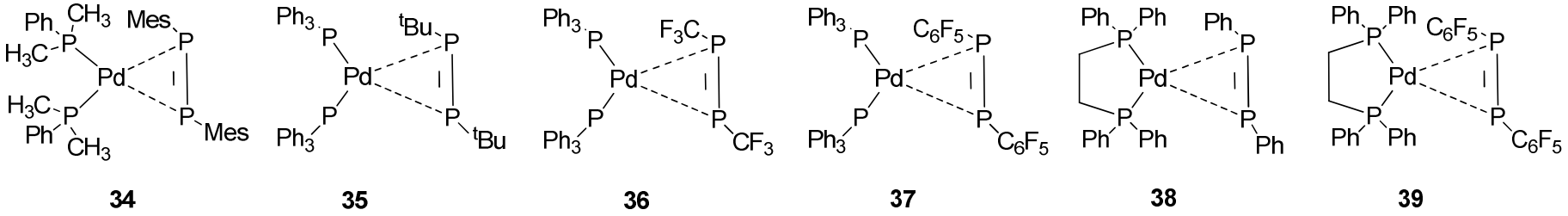

Figure S4. Complexes based on π-donating ligands.

Table S1. Experimental and calculated ^{31}P NMR shifts (ppm) for all model complexes.

Compound	Experiment	Calculated								Reference
		PBE0/6-311G(2d,2p)// PBE0/6-31+G(d)	PBE0/6-311G(2d,2p)// PBE0/6-31+G(d)[a]	PBE0/6-311G(2d,2p) (PCM)// PBE0/6-31+G(d) (PCM)	PBE0/6-311G(2d,2p) (PCM)// PBE0/6-31+G(d) (PCM)[a]	PBE0/6-311G(2d,2p)// PBE0/6-311+G(2d)	PBE0/6-311G(2d,2p)// PBE0/6-311+G(2d)[a]	PBE0/def2-TZVP// PBE0/6-311+G(2d)	PBE0/ def2-TZVP // PBE0/6-311+G(2d)[a]	
1	45.5	22.5	29.6	29.7	33.9	27.1	36.1	43.7	38.1	29
2	31.5	15.0	23.2	14.2	20.8	12.0	22.8	28.1	24.2	30
3	3.7	-2.0	8.8	-3.0	6.4	-0.1	12.2	12.3	10.1	29
4	-2.6	-14.0	-1.4	-14.2	-3.1	-13.3	0.5	-2.2	-2.8	30
5	1.3	-17.6	-4.5	-14.4	-3.2	-17.5	-3.2	-1.4	-2.1	30
	-0.4	-18.1	-4.9	-21.5	-9.2	-24.5	-9.3	-9.0	-8.8	
6	-0.9	-19.1	-5.8	-18.6	-6.8	-21.9	-7.1	-5.6	-5.8	30
	-9.9	-27.6	-13.0	-27.3	-14.1	-30.7	-14.8	-13.1	-12.5	
7	-1.3	-20.1	-6.6	-19.1	-7.2	-23.3	-8.3	-8.4	-8.3	30
8	11.2	-6.3	5.1	-3.2	6.2	-4.4	8.4	6.1	4.6	29
	29.0	23.1	30.1	30.9	34.9	25.5	34.7	36.0	31.2	
9	123.0	121.3	113.5	143.0	129.2	120.2	118.2	133.9	118.4	31
	18.5	17.0	24.9	18.1	24.1	13.8	24.4	30.0	25.9	
10	-9.2	-9.4	2.5	-7.5	2.6	-6.9	6.2	3.7	2.5	32
11	33.4	30.7	36.5	36.9	39.9	29.1	37.9	42.0	36.6	33
12	-2.9	-17.1	-4.1	-18.0	-6.3	-17.4	-3.1	-8.4	-8.3	34
13	3.5	-17.7	-4.6	-14.9	-3.7	-20.9	-6.2	2.0	1.0	35
	172.3	183.3	166.2	166.7	149.2	180.7	171.5	200.0	177.2	
14	65.2	60.6	62.0	60.2	59.6	56.8	62.3	72.1	63.3	30
15	19.0	15.2	23.4	14.9	21.4	15.0	25.5	26.5	22.8	30
16	44.2	34.1	39.4	39.6	42.2	31.3	39.8	47.8	41.7	36
	109.3	99.2	94.8	109.5	101.1	96.3	97.1	114.0	100.6	

17	50.6	38.0	42.7	48.1	49.4	44.1	51.1	61.8	54.2	37
	44.6	26.4	32.9	30.1	34.2	26.1	35.3	41.4	36.0	
	-49.9	-58.2	-39.0	-60.2	-41.8	-61.2	-41.7	-48.6	-44.1	
18	38.5	33.6	39.0	33.5	37.1	29.5	38.2	43.8	38.2	38
19	55.6	46.2	49.7	47.8	49.1	42.8	50.0	58.2	51.0	39
20	33.2	25.1	31.8	35.5	38.8	34.6	42.7	47.0	41.0	40
21	36.6	29.4	35.4	28.1	32.5	16.6	26.9	40.0	34.8	33
22	83.1	95.2	91.4	103.2	95.8	84.5	86.7	96.0	84.6	41
	36.5	14.9	23.1	20.0	25.7	13.4	24.1	31.2	26.9	
	42.6	37.0	41.9	41.5	43.8	34.2	42.4	49.9	43.6	
23	92.9	101.9	97.1	116.4	106.9	95.8	96.7	107.0	94.4	42
	48.3	44.6	48.4	49.0	50.1	40.9	48.3	56.4	49.4	
	40.1	29.8	35.8	30.4	34.5	24.3	33.7	40.1	34.9	
24	74.7	106.5	101.0	99.6	92.7	83.4	85.8	94.5	83.3	41
	38.0	23.9	30.8	30.6	34.6	23.7	33.1	37.1	32.2	
	39.0	36.3	41.3	36.0	39.2	20.7	30.5	40.8	35.5	
25	99.5	111.5	105.2	115.4	106.0	100.1	100.5	110.1	97.2	42
	-0.2	-1.3	9.3	-0.9	8.1	-4.8	8.0	10.6	8.6	
26	39.2	13.6	22.0	24.1	29.2	9.5	20.6	24.9	21.3	43
	57.3	50.9	53.7	62.7	61.7	48.8	55.3	65.3	57.3	
	67.7	87.3	84.6	91.5	85.9	77.4	80.5	88.2	77.7	
27	-5.1	-19.9	-6.5	-12.2	-1.4	-22.7	-7.8	-7.1	-7.1	43
	16.7	16.7	24.6	23.5	28.7	14.4	24.9	30.6	26.4	
	64.8	90.4	87.3	95.5	89.3	81.3	83.9	91.8	80.9	
28	-29.7	-47.6	-30.0	-46.8	-30.5	-48.8	-30.8	-32.5	-29.8	43
	75.0	94.2	90.5	99.1	92.3	84.3	86.5	94.2	83.0	
29	43.1	22.9	29.9	38.6	41.4	25.7	34.9	43.2	37.6	43
	73.9	85.2	82.9	96.5	90.1	80.3	83.0	90.3	79.5	
30	0.5	-8.9	2.9	-4.7	4.9	-11.0	2.6	4.6	3.3	43
	70.5	89.7	86.7	94.9	88.8	80.6	83.3	91.2	80.3	
31	-32.4	-58.7	-39.4	-56.2	-38.4	-60.4	-41.0	-45.8	-41.6	43
	104.5	114.7	107.9	115.8	106.4	106.6	106.2	117.5	103.8	
32	54.9	66.9	67.3	64.9	63.5	62.7	67.5	78.4	69.0	43
	103.0	112.7	106.2	117.1	107.4	108.2	107.6	118.8	104.9	
33	4.2	10.7	19.5	11.5	18.6	8.1	19.4	24.1	20.6	43
	100.3	113.0	106.5	113.7	104.6	105.2	105.0	116.1	102.5	
34	49.7	53.1	55.6	38.2	41.0	48.3	54.8	62.2	54.5	44

	-12.8	-26.1	-11.7	-23.6	-11.0	-28.7	-13.0	-13.6	-12.9	
35	123.7	121.0	113.3	106.8	98.8	115.8	114.3	128.4	113.5	45
	21.4	9.0	18.1	9.8	17.1	7.3	18.7	22.9	19.6	
36	50.5	49.0	52.1	35.6	38.9	45.1	52.0	57.4	50.3	46
	22.7	12.4	21.0	13.6	20.3	10.7	21.7	25.1	21.5	
37	32.0	22.1	29.2	9.3	16.7	17.3	27.5	30.7	26.5	47
	24.8	15.2	23.4	15.9	22.3	13.7	24.3	29.3	25.3	
38	34.3	20.5	27.9	31.5	35.4	20.4	30.2	34.6	30.0	47
	41.0	25.9	32.5	27.3	31.9	23.1	32.6	39.2	34.1	
39	1.7	-4.0	7.1	-24.5	-11.7	1.5	13.6	14.4	12.0	47
	52.1	33.4	38.8	36.6	39.7	32.1	40.5	47.9	41.8	
R^2		**0.9535**	**0.9535**	**0.9447**	**0.9447**	**0.9627**	**0.9627**	**0.9720**	**0.9720**	
RMSE		**13.8**	**8.9**	**14.2**	**9.8**	**13.6**	**8.0**	**10.8**	**6.9**	

[a] corrected by using the factors for empirical linear scaling obtained by the linear regression procedure for the title Pd-complexes.

Table S2. Empirical scaling factors obtained by the linear regression analysis of calculated and experimental $\delta^{31}P$ for the title Pd-complexes.

Level of theory	R^2	Slope	Intercept	*RMSE*
PBE0/6-311G(2d,2p)//PBE0/6-31+G(d)	0.954	1.1766	-12.297	8.9
PBE0/6-311G(2d,2p) (PCM)//PBE0/6-31+G(d) (PCM)	0.945	1.1881	-10.561	9.8
PBE0/6-311G(2d,2p)//PBE0/6-311+G(2d)	0.963	1.1346	-13.8962	8.0
PBE0/def2-TZVP//PBE0/6-311+G(2d)	0.972	0.9297	1.1235	6.9

Table S3. Triplet-singlet states energy gap (UPBE0/6-31+G(d)) for the "training" set of Pd complexes (**2, 9, 17, 22-23, 26, 28-30, 32, 38**).

Compound	E, kcal/mol
38	38.9
9	38.9
17	46.6
2	51.7
22	46.1
23	44.9
26	40.9
28	-[a]
29	35.8
30	35.6
32	67.6

[a] triplet state does not correspond to energy minima.

Table S4. Experimental and calculated (by different combinations) ^{31}P NMR shifts (ppm) for the "training" set of Pd complexes (**2, 9, 17, 22-23, 26, 28-30, 32, 38**).

		Calculated																				
		Combination																				
Compound	Experimental	6-311G(2d,2p)//6-31+G(d)	6-311G(2d,2p)//6-31+G(2d)	6-311G(2d,2p)//6-311+G(d)	6-311G(2d,2p)//6-311+G(2d)	6-311+G(2d,2p)//6-311+G(2d)	6-311G(2d,2p)//6-311+G(3df)	6-311G(2d,2p)//6-311+G(2d) Pd - def2-TZVPD//def2-TZVPD	6-311G(2d,2p)//6-311+G(2d) Pd - SDD//DKH3-DZP	6-311G(2d,2p)//6-311+G(2d) Pd - DKH3-DZP//DKH3-DZP	cc-pVTZ//6-311+G(3df)	pc-2//6-311+G(3df)	def2-TZVP//6-311+G(3df)	def2-TZVP//6-311+G(2d)	TZV//6-311+G(3df)	def2-TZVP//def2-TZVP	6-311G(2d,2p)//cc-pVDZ	6-311G(2d,2p)//cc-pVTZ	6-311G(2d,2p)//pc-2	6-311G(2d,2p)//def2-TZVP	TZV//TZV	cc-pVTZ//6-31+G(d)	cc-pVTZ//cc-pVDZ
2	31.5	15.0	22.3	25.8	12.0	21.8	25.3	14.8	1.3	-4.0	13.7	27.2	31.3	28.1	-37.8	30.3	12.4	22.2	25.0	24.2	-58.2	3.2	-3.9
9	123.0	121.3	129.4	133.5	120.2	131.8	132.0	124.6	111.7	112.3	123.1	131.9	135.2	133.9	75.4	133.8	119.2	128.9	138.0	130.5	68.9	112.5	109.0
	18.5	17.0	24.3	27.8	13.8	24.0	25.8	17.6	22.8	21.7	7.4	33.4	31.9	30.0	-46.8	31.0	14.4	23.5	25.4	24.9	-66.4	-1.5	-6.9
17	50.6	38.0	53.4	57.8	44.1	56.2	56.4	47.9	49.1	47.2	37.3	64.2	64.2	61.8	-8.9	62.9	44.7	54.2	55.8	55.2	-32.8	28.5	22.6
	44.6	26.4	35.4	39.8	26.1	36.7	38.4	29.3	28.2	27.9	27.5	41.3	43.7	41.4	-33.9	42.6	25.7	35.8	37.7	37.3	-58.0	17.6	10.8
	-49.9	-58.2	-52.0	-47.3	-61.2	-51.7	-49.0	-57.6	-62.8	-68.3	-52.2	-44.7	-46.6	-48.6	-122.8	-48.6	-63.6	-53.6	-50.1	-51.0	-150.8	-64.2	-71.3
38	34.3	20.5	31.5	34.4	20.4	33.0	24.8	25.2	49.0	92.4	23.0	28.0	28.5	34.6	-33.4	28.7	22.6	25.9	27.0	24.6	52.4	11.4	15.7
	41.0	25.9	32.0	36.6	23.1	34.8	35.9	26.3	17.8	13.4	26.0	39.1	41.9	39.2	-0.8	40.9	23.3	33.5	35.2	34.6	-55.4	38.7	8.5
22	83.1[a]	95.2	96.7	104.4	84.5	94.4	93.7	88.9	90.0	93.2	85.4	92.2	95.0	96.0	76.7	94.6	104.7	95.9	94.3	93.4	119.8	85.6	89.1
	36.5	14.9	23.0	26.2	13.4	25.6	26.3	16.8	12.0	9.5	13.4	28.1	34.1	31.2	-39.5	32.8	12.3	23.3	25.3	24.9	-40.2	2.5	-3.9
	42.6	37.0	43.6	48.4	34.2	46.0	46.6	37.9	34.3	32.0	34.3	49.4	52.3	49.9	-19.9	51.3	36.1	44.5	46.0	45.5	-66.0	25.1	19.9
23	92.9	101.9	106.3	117.4	95.8	106.9	104.5	99.5	100.6	105.6	96.8	120.5	105.9	107.0	94.7	104.4	119.4	106.6	100.9	102.9	150.3	98.1	104.9
	48.3	44.6	50.6	55.2	40.9	52.9	53.2	44.4	38.5	21.9	41.9	72.9	58.7	56.4	-16.5	58.3	42.1	51.3	50.0	52.3	-37.7	33.3	29.1
	40.1	29.8	32.4	38.0	24.3	34.1	36.4	27.6	23.0	35.6	24.6	55.6	42.1	40.1	-32.7	40.6	23.4	33.7	32.5	34.7	-52.6	14.6	6.4
26	39.2	13.6	20.2	23.6	9.5	21.3	21.1	13.1	11.8	12.2	10.8	21.5	26.4	24.9	-45.8	26.3	13.4	20.7	21.7	20.6	-53.9	1.4	-5.0
	57.3	50.9	58.2	63.0	48.8	59.9	60.9	53.1	51.0	47.1	47.2	62.3	67.3	65.3	-14.4	66.3	47.8	58.4	60.2	59.8	-36.3	38.2	31.3
	67.7	87.3	89.6	95.6	77.4	87.0	86.1	81.4	83.0	85.4	78.1	85.5	87.1	88.2	77.1	87.4	96.2	89.1	87.5	86.4	115.0	79.1	82.6
28	-29.7	-47.6	-38.5	-35.9	-48.8	-36.6	-36.7	-45.1	-41.6	-50.4	-45.8	-34.2	-30.7	-32.5	-101.8	-31.6	-54.3	-40.2	-37.7	-37.9	-133.1	-55.1	-64.8
	75.0	94.2	95.3	103.2	84.3	93.5	93.2	88.7	88.5	90.6	84.9	91.9	93.7	94.2	80.8	93.6	106.0	95.5	93.9	93.0	117.4	85.2	92.1
29	43.1	22.9	35.3	39.4	25.7	38.4	37.9	29.0	20.5	11.5	21.8	43.0	45.6	43.2	-25.1	39.8	25.3	34.7	36.4	34.1	-48.7	15.6	8.1

	73.9	85.2	91.8	99.0	80.3	89.8	89.4	84.5	85.9	87.5	81.1	87.5	89.6	90.3	75.6	90.3	103.9	91.5	90.1	89.9	120.6	80.8	87.8
30	0.5	-8.9	-1.9	2.3	-11.0	-0.1	0.4	-7.8	-7.6	-11.5	-13.6	5.6	6.5	4.6	-67.3	5.5	-12.1	-2.3	0.0	-0.8	-94.8	-22.8	-30.0
	70.5	89.7	92.1	99.8	80.6	91.8	89.9	85.2	86.8	87.1	81.5	88.7	90.3	91.2	80.6	90.3	98.9	92.2	90.7	89.9	120.3	81.1	84.4
32	54.9	66.9	72.1	77.1	62.7	72.9	73.9	66.5	74.0	78.3	58.8	77.7	79.6	78.4	8.3	78.7	65.6	73.0	73.9	73.0	-4.7	51.8	47.0
	103.0	112.7	119.1	124.5	108.2	118.9	116.4	112.1	115.0	116.3	103.9	113.6	117.0	118.8	89.4	116.5	124.0	117.7	116.6	115.9	112.4	102.7	105.4
	R^2	**0.9359**	**0.9512**	**0.9439**	**0.9547**	**0.9593**	**0.9586**	**0.9530**	**0.9042**	**0.8287**	**0.9498**	**0.9428**	**0.9654**	**0.9644**	**0.8333**	**0.9638**	**0.9113**	**0.9529**	**0.9582**	**0.9564**	**0.6889**	**0.9271**	**0.901**
	$\Delta\delta^b$	24	19	22	18	18	14	19	20	28 (65)[c]	15	19	9	13	68	11	36	17	11	15	118 (101)[d]	22	37

[a] ^{31}P NMR shifts of P=O phosphorus atoms colored in red; [b] average deviation (ppm) from the general correlation line for P=O phosphorus atoms; [c] in brackets average deviation from the general correlation line for P=P phosphorus atoms.

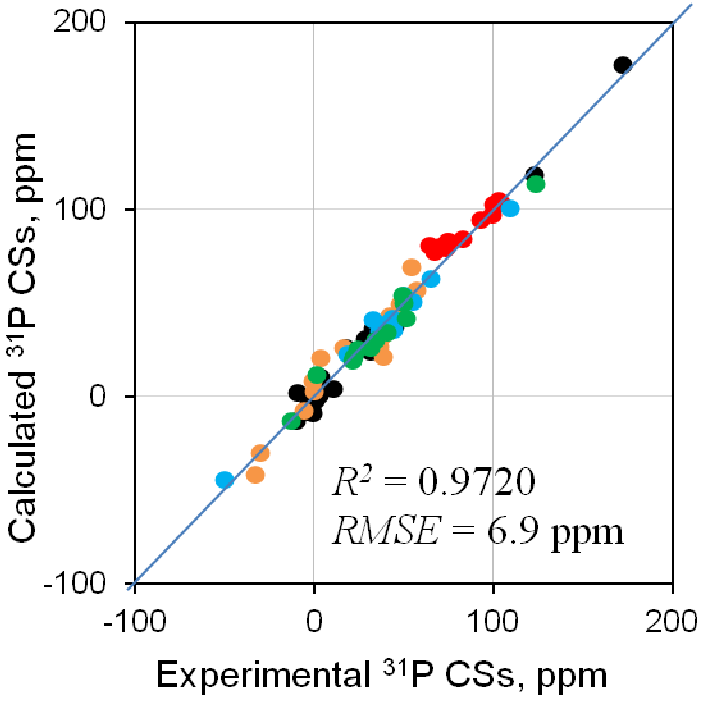

Figure S5. Correlation of calculated (PBE0/{def2-TZVP; Pd(SDD)}//PBE0/{6-311+G(2d); Pd(SDD)}, scaled) *vs* experimental ^{31}P CSs for palladium complexes **1-39**. Complexes based on σ-donor ligands (●), charged palladium complexes based on σ-donor ligands (●), complexes containing P=O groups (● are the P = O phosphorus, ● are other phosphorus atoms in this type of complexes) and complexes based on π-donor ligands (●).

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